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# EXPANSION OF THE RICHARDS BAY DIHYDRATE PHOSPHORIC ACID PRODUCTION COMPLEX (a)

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## 1. Résumé

En 1999, Indian Ocean Fertilizers (IOF, appelé maintenant Foskor Limited) et Sulphos ont signé un contrat EPCM pour tous les services relatifs à la construction et l'extension du complexe de production d'acide phosphorique à Richards Bay, Afrique du Sud.

Sulphos est une Joint Venture constituée de S.A. SNC-Lavalin Europe N.V., SNC-Lavalin International Inc, Monsanto South Africa (Pty) Ltd, Engineering Management Services (Pty) Ltd (appelé maintenant Murray & Roberts Engineering Solutions), et B.E. Morgan Associates (Pty) Ltd. Ce projet, achevé au troisième trimestre 2002, apportera au propriétaire une production annuelle additionnelle de 330,000 tonnes P<sub>2</sub>O<sub>5</sub> d'acide phosphorique d'une qualité marchand supérieure.

Le projet inclut :

- une nouvelle usine d'acide phosphorique avec une capacité journalière de 1,100 tonnes de P<sub>2</sub>O<sub>5</sub> basée sur le procédé Prayon Mark IV.
- une nouvelle usine d'acide sulfurique avec une capacité journalière de 3,000 tonnes H<sub>2</sub>SO<sub>4</sub> basée sur le procédé Monsanto Enviro-Chem de double absorption avec HRS.
- L'extension des stockages de l'acide marchand
- Production d'électricité et de toutes les utilités nécessaires.

L'intégration de toutes les nouvelles installations dans un complexe existant a constitué un réel défi. En plus de devoir rencontrer les hautes exigences du client sur l'acide marchand 54% P<sub>2</sub>O<sub>5</sub>, basse température (max 45° C) et faible teneur en matières solides (max 0.6 w%), le projet a dû être réalisé dans un espace disponible restreint et dispersé.

Ce projet a été réalisé en respectant des standards très stricts en matière d'environnement et de sécurité. Une étude d'impact sur l'environnement a permis de vérifier que le projet respectait les normes en matière d'environnement et plus particulièrement les normes EFMA sur les émissions de fluor.

Une étude HAZOP a été effectuée pour respecter l'OSHA et les "bonnes règles en matière de sécurité et d'opérabilité."

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## **1. Abstract**

In 1999, Indian Ocean Fertilizer (IOF), now called Foskor Limited, and Sulphos signed an EPCM contract for all the services related to the construction and expansion of their phosphoric acid production complex at Richards Bay, South Africa.

Sulphos is a joint venture formed between S.A. SNC-Lavalin Europe N.V., SNC-Lavalin International Inc., Monsanto South Africa (Pty) Ltd., Engineering Management Services (Pty) Ltd, now called Murray & Roberts Engineering Solutions, and B.E. Morgan Associates (Pty) Ltd.

This project, commissioned during Q3 2002, will bring to the owner an additional production capacity of 330,000 tons  $P_2O_5$  per annum of phosphoric acid of high merchant grade quality. It includes:

- A new dihydrate phosphoric acid plant with a daily capacity of 1,100 tons  $P_2O_5$  based on the Prayon Mark IV process.
- A new sulphuric acid plant with a daily capacity of 3,000 tons  $H_2SO_4$  based on the double absorption Monsanto Enviro-Chem process with HRS.
- Increased export acid storage facilities.
- Power generation and all required utilities.

Integrating all the new facilities into an existing complex was a real challenge. In addition to meeting the owners requirements of high quality merchant grade acid at 54%  $P_2O_5$ , low temperature (max 45°C) and a low solids content (max 0.6 w%), the project had to be executed and constructed within very restricted space constraints.

The project had to comply with and be executed within strict environmental and safety standards. An Environmental Impact Assessment (EIA) formed the base to which environmental compliance would be measured especially with EFMA regulations regarding fluorine emissions. To comply with OSHA and “acceptable operational and safety practices” a HAZOP study has been performed.

## **2. Existing Facilities**

Constructed in the late seventies, the existing facilities of Foskor Limited at Richards Bay comprise:

- A 1,200 (upgraded to 1,500) MTD  $P_2O_5$  merchant grade phosphoric acid plant based on the Mark III dihydrate Prayon process, constructed on a turn-key basis by SNC-Lavalin Europe (formerly Coppée-Rust)
- A 2 x 1,650 (upgraded to 2 x 1,800) MTD sulphuric acid plant based on the double absorption Monsanto Enviro-Chem process
- A 400,000 MTY DAP granulation plant based on the Weatherly process.

The existing phosphoric acid plant consists of an 8-compartment reactor with 2 parallel high level flash coolers, 3 digestion tanks, 2 parallel Prayon tilting pan filters and 7 concentration units.

During the mid-nineties, the tilting pan filters were upgraded <sup>(1)</sup> and equipped with fast draining cells, increasing the filtration capacity by more than 15%.

In order to increase its share in the merchant grade phosphoric acid worldwide market, Foskor Limited decided to expand their phosphoric acid production complex by adding on new facilities.

The project will give Foskor Limited an additional yearly production of 330,000 tons of P<sub>2</sub>O<sub>5</sub> with high merchant grade quality.

### **3. The Sulphos Joint Venture Activities**

#### **3.1 The Sulphos partners**

In 1999, Indian Ocean Fertilizer (IOF) now owned by and called Foskor Limited, and Sulphos signed an EPCM contract for all the services related to the construction and expansion of the phosphoric acid production complex in Richards Bay in the province of Kwa-Zulu Natal, Republic of South Africa.

Sulphos is a joint venture formed between:

- S.A. SNC-Lavalin Europe N.V. Brussels, Belgium
- SNC-Lavalin International Inc, Johannesburg, South Africa
- Monsanto South Africa (Pty) Ltd, in collaboration with Monsanto Enviro-Chem, Missouri, USA
- B.E. Morgan Associates (Pty) Ltd (BEMA), Johannesburg, South Africa
- Engineering Management Services (Pty) Ltd, now called Murray & Roberts Engineering Solutions (Pty) Ltd, Johannesburg, South Africa

Prior to the signature of this contract, SNC-Lavalin Europe and Prayon performed the process engineering package in order to determine, together with BEMA, a detailed budget estimate for the project.

Sulphos supplied Foskor Limited with the necessary process licences, basic and detailed Engineering, Procurement and Construction Management services related to the design, construction, commissioning and start-up of both the sulphuric and the phosphoric acid plant.

The entire project, from engineering stage up to start-up is realised according to the ISO 9001 standards as per the policy of the Joint Venture members.

The overall capital investment is estimated to be 1100 million ZAR (about 110 million Euro).

### 3.2 Realisation of the Project

Within the Sulphos Joint Venture, the services related to the realisation of the project were executed as follows:

- SNC-Lavalin, being a permanent licensee of Prayon, supplied:
  - the phosphoric acid license (Prayon Mark IV process) and the related basic engineering
  - leadership of the overall management of the joint venture
  - supervision of project management, detailed engineering and procurement services related to the phosphoric acid plant
  - the commissioning and performance testing of the phosphoric acid plant
- Monsanto South Africa in collaboration with Monsanto Enviro-Chem USA supplied:
  - the sulphuric acid license (Monsanto Enviro-Chem process) and the related basic engineering
  - supervision of project management, detailed engineering and procurement services related to the sulphuric acid plant
  - the commissioning and performance testing of the sulphuric acid plant
- BEMA supplied:
  - off-sites project management
  - basic and detailed engineering for the sulphur and phosphate rock storage and handling facilities, the final merchant grade phosphoric acid export tanks, the utilities and off-sites piping and the electrical reticulation
  - commissioning and performance testing assistance
- Murray & Roberts Engineering Solutions supplied:
  - the project office facilities and project management system
  - detailed engineering, procurement and site services related to the sulphuric and phosphoric acid plants
  - commissioning and performance testing assistance

Teams of specialists of SNC-Lavalin Europe and Monsanto Enviro-Chem (USA) were shifted to Johannesburg where the engineering activities took place.

Finally, the Sulphos team moved to Richards Bay at the Foskor Limited facilities for:

- the construction management
- training of operators
- precommissioning and commissioning activities
- supervision of start-up and performance guarantee run

Precommissioning and commissioning activities were executed in close collaboration with the quality assurance team of the owner, as per the quality procedures agreed by Sulphos and Foskor Limited.

The EPCM contract included the project budget management on an “ open book “ basis with the owner, which was a particular and successful feature.

#### 4. The Phosphoric Acid Plant

The phosphoric acid plant, producing 54%  $P_2O_5$  merchant grade acid, consists of the following units that had to be integrated into the existing infrastructure.

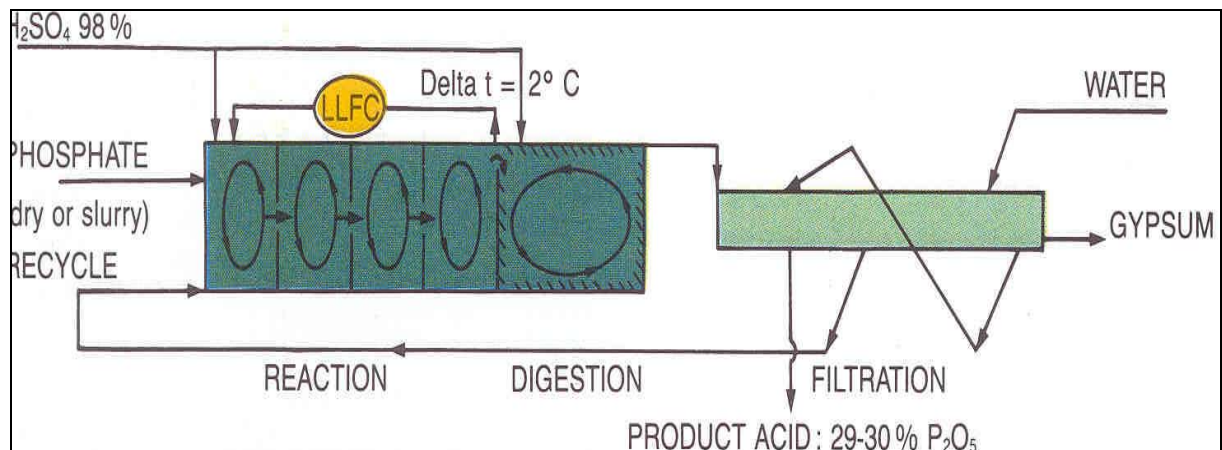
- Phosphate rock handling
- Reaction, as per the Prayon Mark IV multi compartment dihydrate process
- Filtration with 3 parallel Gaudfrin-Phosfil belt filters
- Gypsum slurry transfer
- Gas scrubbing
- Weak acid clarification and storage
- Phosphoric acid concentration and fluosilicic acid production
- Concentrated acid cooling, clarification and storages
- Cooling tower

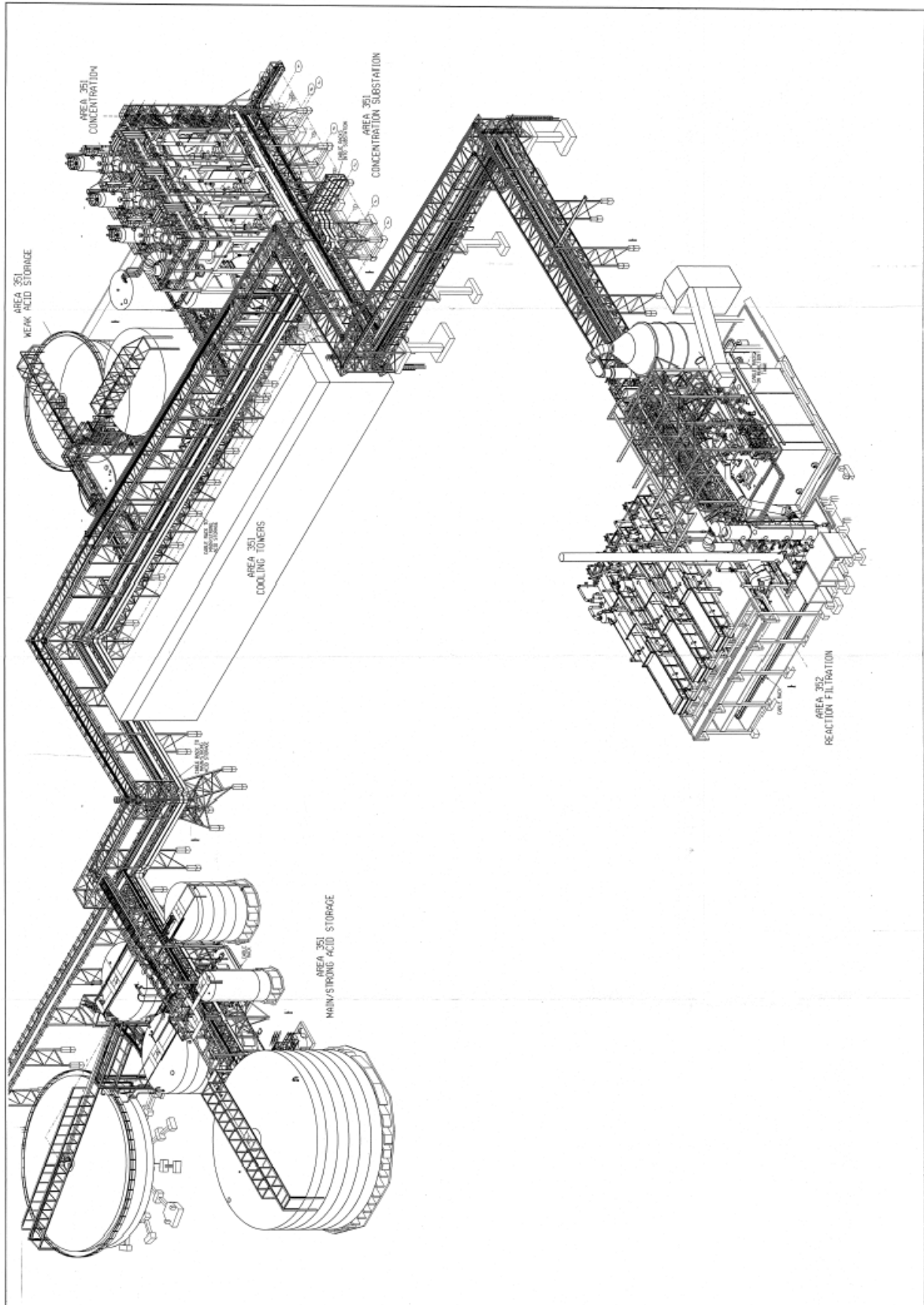
Integrating all these units into an existing complex was a real challenge and had to be executed without interrupting or disrupting production on the old plant. The project required an impressive double deck sloped piperack (as shown on the 3-D image of the phosphoric acid plant layout hereafter) which connects:

- the necessary tie-ins for raw materials, utilities and final product with the existing facilities
- the separated operating units, as they were located dispersed where space was available.
- the new sulphuric acid plant with the new phosphoric acid plant

General arrangement of the Prayon Mark IV reaction-filtration section is as follows:

General reaction-filtration arrangement





3D - image of the phosphoric acid plant layout

#### 4.1 Phosphate rock handling

The existing rock conveying system bringing phosphate rock from the store to the phosphoric acid plants has been adapted and additional dosing hoppers have been installed, in order to deal with the increased (almost doubled) rock feed towards the two parallel (old and new) phosphoric acid plants. Phosphate rock is fed by conveyors to the attack tanks without the requirement for additional crushing or milling.

## 4.2 Reaction

The reaction comprises the following main items (in order of flow):

- One anti-acid protected concrete attack tank divided into 6 equal compartments:  
 All the compartments are provided with powerful agitators (Profile design), which homogenise the reaction slurry in each compartment by vigorous stirring, prevent solids from settling and actively participate to a better reaction efficiency thanks to a high shear rate.  
 Due to the high MgO content of the Palphos rock, which increases the viscosity, the reaction slurry is kept at 27% P<sub>2</sub>O<sub>5</sub> phosphoric acid and 30 w% gypsum solids. Free sulphate level is maintained at 1.85 w% SO<sub>3</sub>.  
 Phosphate rock, together with recycled effluent and gypsum sludge from the clarifiers are fed into the first compartment. Sulphuric acid mixed with recycled acid from the 3 parallel belt filters is fed into the second and third compartment.
- One flash cooling system:  
 The major part of the heat generated by the attack reaction, dilution of concentrated sulphuric acid and agitation is removed by evaporation of water in a low level flash cooler (LLFC).  
 A large flow (11,000 m<sup>3</sup>/h) of reaction slurry is pumped by a circulation axial flow pump from compartment 6, via the flash cooler, which is kept under vacuum, to compartment 1. Thanks to this large flow, the temperature difference between the inlet and the outlet of the flash cooler is kept small (max 3 °C) which limits the scaling inside the ducts. The temperature in the reactor is kept at 73-76 °C. The vapours from the flash cooler are condensed:  
 - First and partly in a precondensor by the blowdown of the cooling tower, this preheated blowdown is used as filter cloth and gypsum cake washing water.  
 - Downstream, the remaining vapours are condensed in a direct contact condenser with cold cooling water.  
 The non-condensed gases are taken by a vacuum pump of which the rejected liquid ring seal water is used as part of the gas scrubber make-up liquid, in order to reuse as much as possible of the process water and so minimise the total water consumption (about 7 m<sup>3</sup>/ton P<sub>2</sub>O<sub>5</sub>).
- Three digestion tanks:  
 Before filtration, the reaction slurry matures inside gently agitated digestion tanks, leading to the enlargement and homogenisation of the gypsum crystals and desaturation of the solution. The standard split for the Prayon reaction volume is 66% for attack and 34% for digestion. Three vertical pumps bring the matured slurry to the three parallel belt filters.



### 4.3 Filtration

For process operation flexibility, it was decided to install three 90 m<sup>2</sup> parallel Gaudfrin-Phosfil belt filters <sup>(2)</sup> of which one can be considered as a full spare. In this way, one complete filtration circuit can be washed while the two others are in operation.

The plant is designed to run on a filtration rate of 6.11 MTD P<sub>2</sub>O<sub>5</sub>/m<sup>2</sup> but can also be used on a 4.07 MTD P<sub>2</sub>O<sub>5</sub>/m<sup>2</sup> ratio, if required.

On the filters, the reaction slurry is separated as weak acid (filtrate) and solids (dihydrate phosphogypsum). The solids are submitted to two successive countercurrent washings and one final drying in order to reduce its acid content to a minimum.

Some special features of this Gaudfrin-Phosfil belt filter <sup>(3)</sup>, provided by Profile, when compared to usual belt filters, are the following:

- The large diameter vacuum box is provided with several separated liquid and air outlets of which the cross sections are large enough to ensure a low air velocity and consequently a low amount of entrained liquid.
- A single centred water-lubricated wear belt is installed between the static vacuum box and the moving rubber belt. Transversal grooves in the wear belt allow some transversal displacements of the main filtering belt without impeding the natural acid discharge through the draining holes of the filtering belt.
- Transportation of the main carrier belt is unique, minimizing friction and therefore increasing belt life.
- A special cloth tension device is provided in order to maintain the optimum filter cloth tension.

The gypsum cake from all the filters is discharged on a common belt conveyor, which brings the gypsum to a reslurrying tank. The 27% weak acid from the three filters is sent to a homogenisation tank.

### 4.4 Gypsum slurry transfer

Gypsum from the three filters is discharged from the belt conveyor and mixed with the gypsum slurry (20 w% solids) from the old plant and sent to a slurry de-gasifying vessel. Gases are taken by the gas scrubbing fan and brought to the stack.

The final gypsum slurry (31 w% solids) overflows to an adjacent, agitated vessel from where a set of three pumps, installed in series, bring the final gypsum slurry of both the old and new plants, via the adapted and existing long pipeline, towards the Indian Ocean. This feature was also analysed during the Environmental Impact Assessment (EIA) study.

## 4.5 Gas Scrubbing

Main equipment from which gases could escape are kept under slight depression by means of a ventilation/scrubbing system provided on:

- The 6 attack tank compartments
- The 3 digestion tanks
- The 3 belt filter hoods
- The gypsum de-gasifying tank

Downstream from the scrubber, a fan provides the circulation of the gases through the scrubber and delivers them, after intense washing, to the stack. The top part of the scrubber is fitted with a cyclonic droplet separation in order to catch entrained droplets.

Great care has been taken to keep the fluorine emissions below  $5 \text{ mg/m}^3$ , as per the EFMA standards.

The make-up water to the scrubber and spraying of the ducts comes mainly from process water leaving the reaction and filtration vacuum pumps. The blow down of the scrubber together with the cooling tower blow down is used as cake and filter cloth washing water.

## 4.6 Weak Acid clarification and storage

Homogenised 27%  $\text{P}_2\text{O}_5$  weak acid in the homogenisation tank overflows to the weak acid clarifier.

This homogenisation tank also receives the sludge collected at the bottom of the concentrated acid clarifier filled with 54%  $\text{P}_2\text{O}_5$ . In this way, hemihydrate solids, formed during concentration, can rehydrate to dihydrate crystals before being recycled to the attack tank.

Gypsum sludge leaving the weak acid clarifier is mixed with effluent water (collected from weekly washing waters and various spillages collected in the sumps) and is sent back to the attack tank.

Thanks the above described scheme, only one instead of three flows (i.e. the two gypsum sludge flows from the two clarifiers and the recycled effluent) is returned to the attack tank, which is an important feature taking into account the particular layout.

Clarified weak acid leaving the weak acid clarifier is pumped to a buffer tank from which it is fed to the concentration unit.

## 4.7 Phosphoric acid concentration and fluosilicic acid production

The plant includes three identical concentration lines of the forced circulation type and is designed for parallel operation.

One concentration line includes the following:

- The circulation loop is equipped with an axial circulation pump, a lump screen downstream from the vertical carbon tubes heat exchanger and an evaporator where water flashing takes place.
- Concentrated 54% phosphoric acid is directly taken, via an overflow outlet at the evaporator, by a self-regulating pump bringing the acid to the first maturing/cooling tank.

- A fluosilicic acid recovery system (Prayon design) with a P<sub>2</sub>O<sub>5</sub> droplet separator, a fluorine absorber and a H<sub>2</sub>SiF<sub>6</sub> (fluosilicic acid) droplet separator, a fluosilicic acid circulation loop with seal tank and circulation pump absorb as much as possible of the fluorine from the evaporated matters before they enter the main condenser. Fluosilicic acid (18-20 w% H<sub>2</sub>SiF<sub>6</sub>) is sent to a storage tank.
- In the condenser, remaining water vapours are condensed by spraying cold cooling water. Finally the non-condensed gases are taken by a vacuum pump. Sealing water leaving the latter, serving as a part of the cooling tower make-up water, is introduced into the hot cooling water collector.
- Hot water is sent back by gravity towards the nearby cooling tower feeding and distributing manifold.

#### 4.8 Concentrated acid cooling, clarification and storage

- In order to meet the client merchant grade acid specifications, the 54% P<sub>2</sub>O<sub>5</sub> concentrated acid receives the following post treatment:
- Concentrated acid is cooled down in two steps, while using two maturing/cooling tanks, each equipped with a wide-gap type plate heat exchanger and a cooled acid circulation loop. Partly cooled acid overflows via a launder from the first towards the second maturing/cooling tank where it is finally cooled down to 45°C.
- Via a second launder, the cooled acid overflows to the concentrated acid clarifier. Solids slurry collected at the bottom is sent to the weak acid clarifier.
- Clarified acid is pumped to the concentrated maturing export settler, which is equipped with a rake. Sludge originating from post precipitation (which is a typical behaviour for the applied Palphos rock), collected at the bottom of this vessel are sent to a buffer vessel from which they will be pumped to the existing granular fertilizer plant.
- Finally, export merchant grade acid, with a solids content of maximum 0.6 w%, is pumped to the export tanks for ship loading. If required, this acid can be cooled down to 35°C before being pumped to the two new 10,000 tons P<sub>2</sub>O<sub>5</sub> export shipping tanks. Each tank is equipped with agitators to keep the remaining solids in suspension.

#### 4.9 Cooling Tower

The cooling tower consists of ten plus one spare parallel forced draft concrete cells, which cool down all the hot water coming from the condensers and the merchant grade acid coolers.

In order to avoid the use of a ground floor hot cooling water channel, it was decided, taking into account the complicated layout, to:

- Pump back the hot cooling water from the flash cooler and belt filter condensers to the main hot cooling water header feeding the top of the cooling tower.
- Install the concentration condenser seal tanks at higher level so that hot cooling water can flow to the main header by gravity.
- Feed the merchant grade acid coolers with cold cooling water via a loop, which finally brings the hot cooling water back to the main header.

Four vertical pumps bring the cold cooling water via separate circuits to the 3 concentration condensers and the reaction/filtration/merchant grade acid coolers respectively. The thermal capacity of the cooling towers is 80,000,000 kcal/h delivering cold water at 32 °C.

Complying with the strict environmental rules, fluorine emissions are kept extremely low by limiting:

- the fluorine level of the cooling water at maximum 0.5 w%
- the cooling tower drift losses at maximum 0.002 %.

## 5. Operating Parameters

### 5.1 Raw Materials

#### 5.1.1 Phosphate rock

The phosphate rock used in the plant is the local Palphos 80M phosphate rock. This igneous rock delivered to the plant does not need additional crushing and is introduced as such in the attack tank.

Table 1: Analysis of Palphos 80M Phosphate Rock  
Chemical analysis: % weight on dry basis

	Fluctuation Range
P <sub>2</sub> O <sub>5</sub>	Min 36.1
CaO	52 – 53
CO <sub>2</sub>	4 - 4.5
SO <sub>4</sub>	0.1
SiO <sub>2</sub>	0.8 - 1.4
Al <sub>2</sub> O <sub>3</sub>	0.04 - 0.12
F	2.1 - 2.6
Fe <sub>2</sub> O <sub>3</sub>	0.4 - 0.5
MgO	1.3 - 1.8
Na <sub>2</sub> O	0.23
K <sub>2</sub> O	Up to 0.15
Cl	0.05 – 0.17
Water content	Up to 2.5

Table 2: Rock sieve analysis range

	mm	Mass %
Retained on	1	0
Retained on	0.5	Max 1.0
Retained on	0.150	Max 35.5
Passing	0.075	Min 25

#### 5.1.2 Sulphuric acid

Sulphuric acid (98,5% H<sub>2</sub>SO<sub>4</sub>) is delivered from the new adjacent 3000 MTD sulphuric acid plant, via a buffer storage tank.

### 5.2 Production data

The phosphoric acid plant was mechanically completed during Q3 2002. Full weak acid production was progressively started on one belt filter until all three were operating smoothly in parallel.

The concentration unit and the merchant acid production were put into service shortly after weak acid production started.

Table 3: Production capacity

	Obtained capacity	Guaranteed capacity
Weak acid	(**)	1100 MTD P <sub>2</sub> O <sub>5</sub>
Concentration units	(**) MTD	2195 MTD (*)
	Evaporated matter	Evaporated matter

(\*) Due to recirculation of phosphoric acid slurry from the concentrated clarifier, the average concentration of weak acid, fed to the concentration unit, is increased from 27 up to about 29,4% P<sub>2</sub>O<sub>5</sub>. However, the design capacity is based on the quantity of matters to be evaporated based on the nominal capacity of 1,100 MTD starting from 26% P<sub>2</sub>O<sub>5</sub>.

Table 4: Analysis of Phosphoric Acid  
Expected chemical analysis: % weight on solids free basis

	Weak Acid ex-filters	Merchant grade acid ex final settler
P <sub>2</sub> O <sub>5</sub>	(**)	(**)
CaO	(**)	(**)
SO <sub>4</sub>	(**)	(**)
F	(**)	(**)
Al <sub>2</sub> O <sub>3</sub>	(**)	(**)
MgO	(**)	(**)
Cl	(**)	(**)
Solids	(**)	(**)
Temperature	(**) °C	(**) °C

(\*\*) To be completed after start-up of the phosphoric acid plant

The concentrated acid leaving the export tanks is per the merchant acid quality standards imposed by Foskor limited:

- Min 54% P<sub>2</sub>O<sub>5</sub>
- Max 0.6% solids
- Max 45°C (or max 35°C depending on shipping requirements)

## **6. Conclusion**

The realisation of the project on an EPCM basis, between Foskor Limited and a joint venture consisting of American, European and South African partners, asked for a close collaboration and an open team spirit. Considering the tight project schedule and the “open book” project budget management, the project can be considered a success.

This expansion project being realised, Foskor Limited owns a unique combination of two dihydrate Prayon process phosphoric acid plants, producing high quality merchant grade acid:

- A 1,200 MTD (upgraded to 1,500 MTD) Prayon Mark III unit with 2 parallel Profile tilting pan filters.
- A 1,100 MTD Prayon Mark IV unit with 3 parallel Gaudfrin-Phosfil belt filters and production of fluosilicic acid at the concentration section.

This expansion makes Foskor Limited the largest producer of merchant grade phosphoric acid in the Southern Hemisphere.

## **7. References**

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- (2) Sinden J. “1997 Clearwater Meetings attract record attendance”. Phosphorus & Potassium Nr 210 (July-August 1997)
- (3) Leyshon D. “Horizontal belt filtration – Phosphoric acid slurry filtration – Part 2”. Phosphorus & Potassium (March-April 1995)

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**K. Kirsten, Foskor Limited, Republic of South Africa**  
**J. Tytgat\*, SNC-Lavalin Europe, Belgium**  
**T. Theys, Prayon, Belgium**

### 5.2 Production data

The phosphoric acid plant was mechanically completed during Q3 2002. Full weak acid production was progressively started on one belt filter at a time until all three were operating smoothly in parallel. The concentration unit and the merchant acid production were put into service shortly after weak acid production started.

The Performance Test (PT) was successfully finalized early November 2002.

**Table 3: Production capacity**

	<b>Average obtained capacity during PT</b>	<b>Guaranteed capacity</b>
Weak acid	1166 MTD P <sub>2</sub> O <sub>5</sub>	1100 MTD P <sub>2</sub> O <sub>5</sub>
Concentration units	2350 MTD Evaporated matter	2195 MTD (*) Evaporated matter

(\*) Due to recirculation of phosphoric acid slurry from the concentrated clarifier, the average concentration of weak acid, fed to the concentration unit, is increased from 27 up to about 29,4% P<sub>2</sub>O<sub>5</sub>. However, the design capacity is based on the quantity of matters to be evaporated based on the nominal capacity of 1,100 MTD starting from 26% P<sub>2</sub>O<sub>5</sub>.

**Table 4: Analysis of Phosphoric Acid**

Average Chemical Analysis during the Performance Test: % weight on solids free basis

	<b>Weak Acid ex-filters</b>	<b>Merchant grade acid ex final settler</b>
P <sub>2</sub> O <sub>5</sub>	27.05	54.47
CaO	0.30	-
SO <sub>3</sub>	1.75	2.22
F	1.65	0.27
Solids	-	0.25 (1)
Temperature	About 65 °C	43.8 °C

(1) While using flocculant in the clarifiers

The concentrated acid leaving the export tanks is per the merchant acid quality standards imposed by Foskor limited:

- Min 54% P<sub>2</sub>O<sub>5</sub>
- Max 0.6% solids
- Max 45 °C (or max 35 °C depending on shipping requirements)

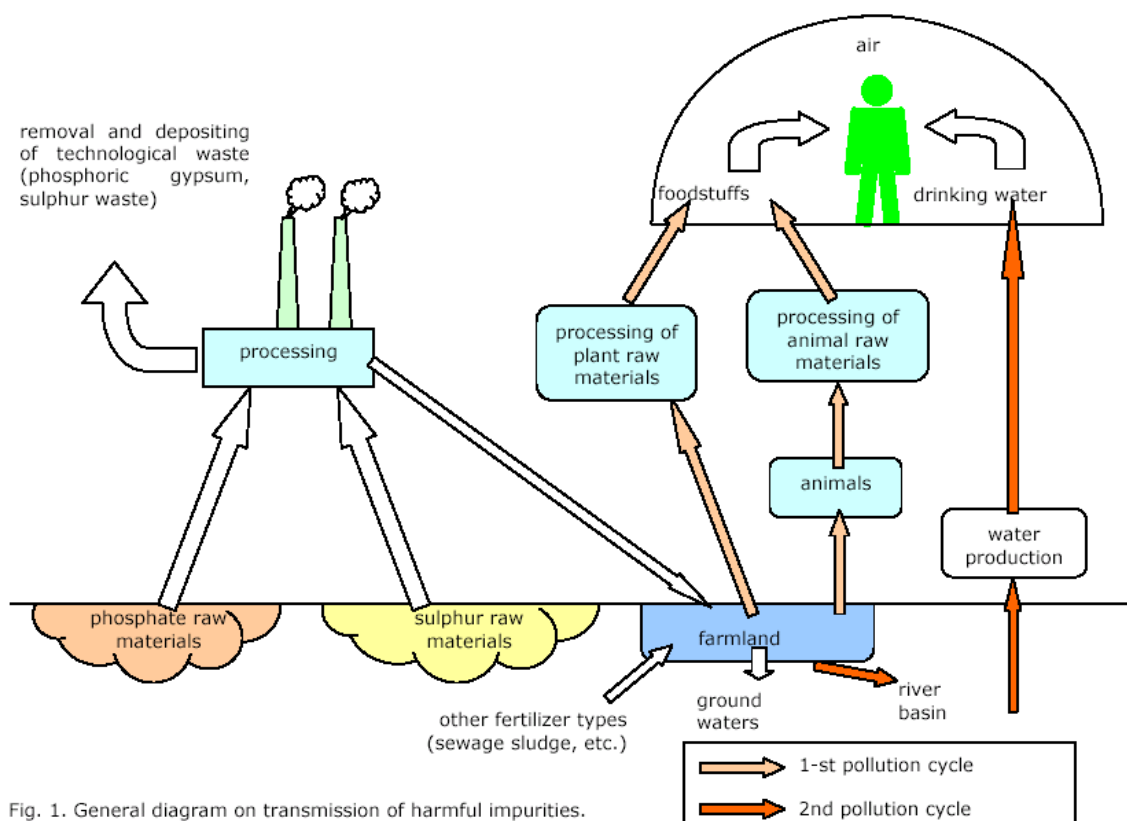
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# DEVELOPMENT OF A METHOD OF A COMPLEX ESTIMATION AND CLASSIFICATION OF BIOLOGICAL AND ECOLOGICAL HAZARDS ASSOCIATED WITH PHOSPHATE ROCK AND FERTILIZERS.

**Boris Levin, Research Institute for Fertilizers, PhosAgro, Moscow, Russia (a)**

The method of estimating biological and ecological risks associated with phosphate rock is based upon the components transmitted through the circuits up to the foodstuffs. The method allows classification of the hazards associated with the commercial grades of phosphate rock and their products. The method takes into account the complex ecological hazards of phosphate rock and its products on the basis of two cycles of pollution: in agricultural soils (1) and surface and ground waters (2) (Fig.1). In this respect, the danger of the second cycle of pollution is incomparably higher, than that of the first cycle due to stricter sanitary requirements. The offered method is based on fundamental data of toxicity of chemical elements accumulated by biochemistry, agrochemistry and medicine, and is open for new inquiry.



There are two basic reasons for the urgency to derive a complex and accurate estimation of ecological and biodanger of phosphate rock and its products:

1. The leading manufacturers in the advanced countries are orientating towards a high standard in the field of environment and safety for the human health.



2. An enormous database on toxicity of chemical elements and compounds has been accumulated that allows the creation of a complex method of relative classification of products, intermediates and raw materials by criteria of ecological and biodanger.

Additionally, there is extensive practical experience in the field of processing phosphate rock by acid methods developed by the foremost engineering companies (Prayon, Rhone Poulenc / Krebs / Speichim, IMI, Norsk Hydro, etc.). Transmission of the basic and impurity components during sulphuric acid decomposition of the phosphate rock has been investigated in detail (table 1). The share of such acid decomposition is more than 85 % of the world production of phosphorus fertilizers. The lack of data concerning impurity distribution for nitric and hydrochloric acid decomposition can be easily compensated by analytical researches.

The method of the estimation of the ecological and biodanger of phosphate rock should correspond to the below requirements:

1. To integrate approach and to take into account the influence of all toxic elements;
2. To be based on the authentic and representative data on chemical structure of phosphate rock, toxicity of elements, extreme allowable concentration in ground, water, foodstuffs, and parameters of distribution of elements during processing;
3. To have heuristic properties, that can be revamped and be adaptive to new data and knowledge;
4. To be simple and verifiable, i.e. available for checking the relative biodanger of phosphorus fertilizers by accessible methods.

Recently there is too much attention concentrated on the problem with cadmium. Certainly, this problem have an objective basis, but it results in an unjustified increase of risk from other toxic elements and put out of focus other elements, which are not less dangerous.

The analysis of the special literature, devoted to questions of human resistance against influence of hazardous elements, allows allocation of groups of chemical elements on the degree of toxicity upon man. Practically all specified toxically elements are present in commercial grades of phosphate rock and appropriately in the products after their processing.

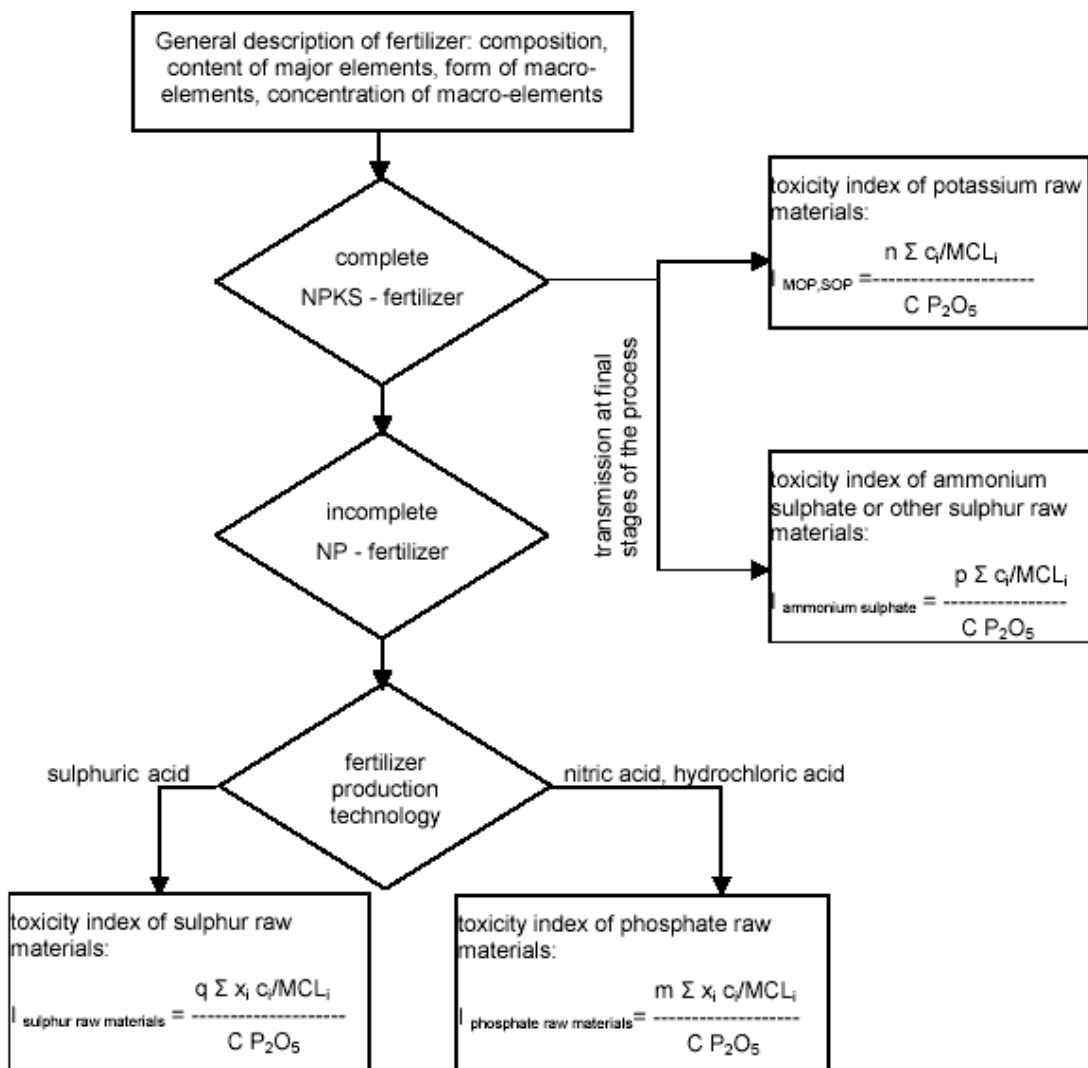
Table 1. Distribution indexes for impurities in by-products and finished products at sulphuric acid decomposition.

<i>Elements</i>	<i>Apatite</i>	<i>Phosphorite</i>
Cd	~60	50-80
Hg	~20	~10
As	~80	70-90
Pb	20-30	10-20
Sr	~3	-
Cu	~40	~60
Ni	~75	~50
Zn	30-35	50-86
Co	~60	-
Cr	~80	~90
V	~30	-
Mn	~90	-
F	~55	40-60

Further these elements together with useful nutritious components (N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O) pass into the soil solutions and are distributed on a circuit: partially acquired by plants, partially immobilized by organic part of the soil, partially in ground and superficial waters. Thus, it is necessary to a complex estimation of the biodanger phosphate raw material to reflect real depots - stores that are in contact with alive organisms. For the most widespread types of fertilizers (MAP, DAP, NPK) the key feature is the presence of toxic elements in their active form as against chemically or mechanically immobilized in phosphate rock.

The algorithm of an estimation of various types of phosphorus fertilizers toxicity (from ordinary up to complex), after taking into account the entry of toxic elements not only from phosphate rock is given in Fig. 2.

Fig. 2. The algorithm of the estimation of various type phosphorus fertilizers toxicity.



To summarize the source of pollution of fertilizers it is necessary to include sulphur raw material (pyrites, the natural sulphur), potassium raw material (potassium chloride, potassium sulphate), and nitric raw material and intermediate products (ammonium sulphate, ammonia, nitric acid). Thus the integrated index of the phosphorus fertilizers toxicity is as follows:

$$I_{\Sigma} = (I_{\text{sulphur}} + I_{\text{phosphate}} + I_{\text{MOP, SOP}} + I_{\text{N}})_{\text{raw material}}$$

In this work a limiting case is considered, when the integrated factor is determined by an extreme index of phosphate rock toxicity. The legitimacy of such approach is proven by that in the general case  $I_{\Sigma} \geq I_{\text{phosphate raw material}}$  in which both requirements: cleanliness and the safety of the phosphate raw material, should be set by rigid, limiting criterion.

Applying the general approach to an estimate for the biodanger of raw material, in the case of phosphate raw material the following criteria are used:

1. Pollution cycle: soil – agricultural products – foodstuffs.

$$I_{\text{p.r.m.}} = \frac{m \sum x_i C_i / MCL_{i \text{ soil}}}{C_{\text{P}_2\text{O}_5}}$$

**m** – input indices of phosphate raw material for fertilizer production, t/t;

**C<sub>i</sub>** – concentration of i-element in phosphate rock, mg/kg;

**x<sub>i</sub>** – distribution index for impurities in by-products and finished products (table 1);

**$\tilde{N}_{\text{P}_2\text{O}_5}$**  – concentration of the P<sub>2</sub>O<sub>5</sub> component in phosphate rock;

**MCL<sub>i soil</sub>** – maximum concentration level of i-element in soil, mg/kg;

2. Pollution cycle: soil – ground water – surface water – drinking water.

$$I_{\text{p.r.m.}} = \frac{m \sum x_i C_i / MCL_{i \text{ water}}}{C_{\text{P}_2\text{O}_5}}$$

**MCL<sub>i water</sub>** – maximum concentration level of i-element in water, mg/kg.

The data used are given in the Table 2, or are taken from the open publications and certificates of the companies - producers of the commercial grades of phosphate raw material. The overall results are shown in Fig. 3.

The calculation of the integral index of biological toxicity helps make up 3 groups of phosphate rocks:

1. Phosphate rocks with a low level of toxicity. They include apatite concentrates from Russia (JSC Apatit, Kovdor beneficiation plant), South Africa (Phalaborwa). This group is regarded as the elite. To process these rocks various well-known technologies and equipment can be used without any restrictions or additional removal technologies for harmful impurities. The value of the rocks is increasing today as a result of tighter environmental control.
2. Phosphate rocks with a moderate toxicity level. They include phosphorites of medium grade from Jordan, Morocco and USA. To meet environmental requirements in countries with strict regulations these rocks should be treated additionally to reduce the concentration of contaminants. Application of removal technologies involves a rise in operating costs.
3. Phosphate rocks with a high level of toxicity. These are low-grade phosphates from Tunisia, Algeria and high-grade rocks from Togo, Senegal, and Morocco. Fertilizers traditionally produced fall short of the safety requirements in economically advanced countries. To meet these environmental standards the purification of finished products is needed with expensive technologies employed (ion exchange, ion flotation, etc.)

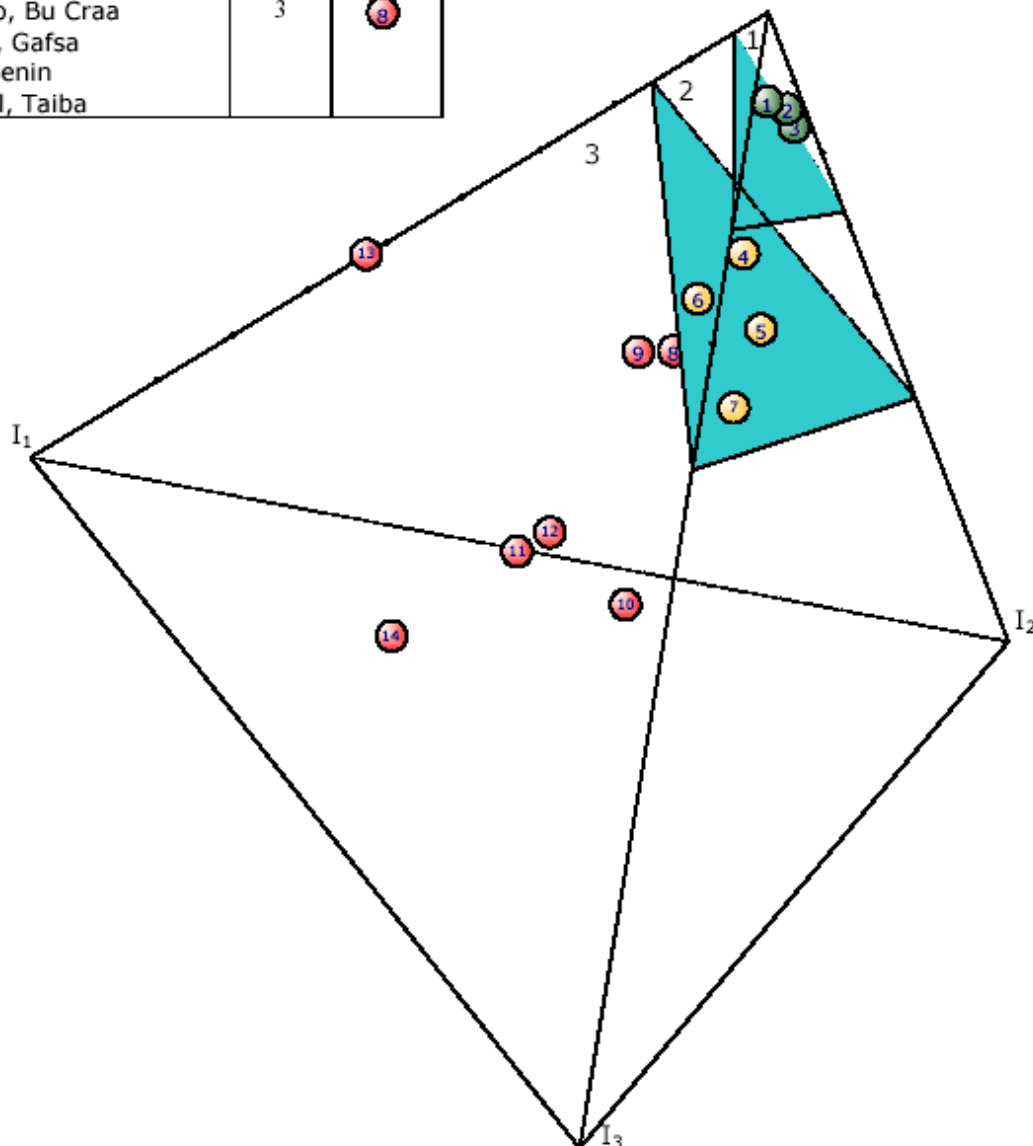
Table 2. Concentrations of hazardous elements in phosphate rocks taken into account, ppm

No	Element	Morocco		Toogo	Senegal	Jordan		Tunisia	Algeria	USA	Israel	Syria	Russia		South Africa
		Bu Craa	Khouribga	Benin	Taiba	Eshidia	El Hassa	Gafsa	Djebel Onk	Florida	Nahal Zin	Kneifiss	Kola	Kovdor	Phalaborva
1	<b>Cd</b>	34,1	12,8	85,8	73,0	5,5	5,4	34,1	15,3	9,4	23,0	13,0	0,1	0,8	1,8
2	<b>Hg</b>	0,1	0,1	-	0,3	0,0	0,2	0,1	2,2	0,1	0,5	0,1	0,0	0,1	0,2
3	<b>As</b>	5,8	8,8	-	3,0	6,0	12,2	16,7	12,5	8,7	4,0	20,0	0,6	2,7	9,3
4	<b>Pb</b>	1,0	2,4	-	4,8	3,4	6,5	7,7	11,0	18,0	4,0	6,5	1,3	6,1	11,8
5	<b>Cr</b>	130,0	300,0	30,0	70,0	75,0	80,0	81,0	200,0	91,0	60,0	-	2,5	30,0	8,0
6	<b>Sb</b>	-	-	-	-	-	-	-	12,0	-	-	-	1,5	2,7	-
7	<b>Ba</b>	-	-	-	100,0	-	-	-	-	-	-	-	850,0	300,0	-
8	<b>F*</b>	4,2	4,0	3,8	3,7	3,8	3,8	4,0	3,5	3,8	3,5	3,5	3,1	1,0	7,4
9	<b>Cu</b>	14,0	43,0	-	60,0	21,0	20,0	23,5	19,8	9,0	30,0	20,0	46,0	20,0	120,0
10	<b>Ni</b>	40,0	41,0	-	40,0	11,0	35,3	28,0	18,6	30,0	35,0	59,0	7,9	21,0	27,3
11	<b>Zn</b>	90,0	230,0	-	-	150,0	230,0	260,0	185,0	95,0	400,0	330,0	26,0	50,0	14,0
12	<b>Co</b>	-	-	-	1,0	6,0	15,5	18,0	17,0	-	-	8,0	4,0	5,0	-
13	<b>Mn</b>	200,0	-	200,0	20,0	11,6	60,0	36,0	25,0	290,0	6,0	6,5	340,0	600,0	200,0
14	<b>Sr</b>	-	150,0	30,0	460,0	-	2000,0	1925,0	2022,0	-	2500,0	1900,0	28000,0	2400,0	5000,0
15	<b>V</b>	122,0	21,0	-	140,0	60,0	55,7	62,0	45,0	70,0	130,0	-	100,0	36,0	12,7

\* concentration in %

Fig. 3. 3D - Diagram of relational classification of biological and ecological hazard of phosphate rock. 2nd pollutions cycle.

N <sup>o</sup>	Phosphate rock	Groups or phosphate rock	
1	South Africa, Phalaborva	1	①
2	Russia, Kovdor		
3	Russia, Kola		
4	Jordan, Eshidia	2	④
5	USA, Florida		
6	Jordan, El Hassa		
7	Syria, Kneifiss	3	⑧
8	Morocco, Khouribga		
9	Israel, Nahal Zin		
10	Algeria, Djebel Onk		
11	Morocco, Bu Craa		
12	Tunisia, Gafsa		
13	Togo, Benin		
14	Senegal, Taiba		



Radioactivity is an additional factor, which helps to distinguish the 1st group from the other two. All types of apatite concentrates have a low radioactivity level, by far lower than the levels required by radiological safety standards. By contrast, phosphorite concentrates are enriched with radioactive isotopes and have a high radioactivity level. Russia has enough reserves of high-quality contaminant-free apatite concentrates to provide regions under high environmental requirements with eco-friendly

phosphate rocks and apatite concentrate-based finished products. Apatite concentrates from Russia and South Africa have the lowest integral toxicity and radioactivity levels of all phosphate raw materials. Phosphate fertilizers produced meet the strictest environmental and sanitary demands without any additional purification phases and operating costs involved. The value of apatite concentrates and their fertilizer derivatives becomes far more evident despite their small share in world production and trade – about 13%. Another option for the use of apatite concentrates and environmentally clean phosphate fertilizer is an increase in capital costs to equip operating plants with additional phases for contaminant removal and a consequent rise in operating costs.

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