# Chapter 4 Processing: What Improvements for What Products?

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**Abstract** This chapter describes the current activities of a multi-stakeholder project known as the "Processing Node of Global TraPs" which focuses on the sustainable management of the global phosphorus cycle. The node team will outline the current state on phosphorus processing (rock phosphate concentrate and phosphorus-rich secondary materials to fertilizers, feed phosphates, and non-agricultural products), identify knowledge gaps as well as critical questions and sketch areas for potential transdisciplinary case studies. The node's critical questions refer to efficiencies, losses, and the environmental footprint of the various manufacturing processes as well as the effects of applying products in terms of fertilizing value, spreading/accumulation of pollutants, and eutrophication as a result of excessive application. Further issues involve the future of local, not fully integrated processing and identification of potential knowledge gaps. The guiding question is, *How to improve the energy, water and material flow balances during the production of fertilizers and other P-based products?* Currently, phosphate processing primarily concerns chemical processing (91 % of concentrates) with acids. Only 5 % of rocks

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are thermally processed to elemental phosphorus. If the latest technologies are employed, P losses during chemical processing generally do not exceed 5 %. The widely used phosphoric acid route (72–78 % of concentrates) transfers impurities to the product or to phosphogypsum, a massive by-product/waste flow amounting to five tonnes per tonne of P<sub>2</sub>O<sub>5</sub> in phosphoric acid. About 82 % of rock phosphates are processed to fertilizers, 6-8 % to feed phosphates and the rest to non-agricultural products for a wide variety of applications. Rock processing is usually located near a phosphate mine in highly integrated manufacturing plants designed to process low-impurity rocks to water-soluble phosphate fertilizers with high nutrient concentrations. However, changing natural, societal, and environmental framework conditions challenge the prevailing paradigms. Benefits and drawbacks of high nutrient concentrations and water solubility will be investigated in transdisciplinary case studies, preferably in cooperation with an integrated global phosphate industry. Even though 82 % of rock phosphates are eventually used as fertilizers, they represent only 36 % of P inputs to European soils, by far outnumbered by the P inputs from secondary resources, such as manure, which account for 63 %. Excessive P application in regions with high livestock density and nutrient mining in regions with neither relevant animal husbandry nor access to mineral fertilizers represent a global environmental and food security problem.

**Keywords** Innovation in phosphate processing • Wet chemical processing of phosphate • Thermal processing of phosphate

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# 1 Current Status of Knowledge on P Processing

The processing node of the Global TraPs (global transdisciplinary processes for sustainable phosphorus management) project covers the industrial conversion of phosphate rock and phosphorus-rich secondary materials by wet or thermochemical processes to a variety of liquid and solid concentrates that are used as fertilizers or as intermediates for P-based industrial products. Wet chemical processes encompass (a) reaction of rock phosphate with sulfuric acid to partly acidulated rock phosphate or single superphosphate as solid fertilizers and to phosphoric acid as an intermediate for high-analysis phosphate fertilizers and industrial products; (b) reaction of rock phosphate with nitric acid to produce nitrophosphate fertilizers. Thermo-chemical processes are used to produce (a) elementary P as an intermediate for food, detergent, clean room as well as other high-purity products and (b) different solid P concentrates, largely by melting the feed material.

The processing node is a supply chain node with the *body of knowledge largely* found in fertilizer companies, consulting companies and independent consultants specializing in intelligence and studies for the phosphate industry. Other organizations which may have an in-depth understanding of the issues associated with processing include a limited number of international organizations such as International Fertilizer Development Center (IFDC), International Fertilizer Industry Association (IFA), Center for Excellence in Fertilizers, Brazil (CFErt), Fertilizers Europe (the former European Fertilizer Manufacturers Association, EFMA), Florida Industrial and Phosphate Research Institute formerly Florida Institute of Phosphate Research (FIPR), the AleffGroup, London, and International Atomic Energy Agency, Vienna (IAEA). Other stakeholders include national, regional, and local governments as well as the public at large. Details about fertilizerprocessing technologies are published in various books and papers, e.g., in the Fertilizer Manual, edited by IFDC/UNIDO (UNIDO/IFDC 1998) and in a series of eight Best Available Technology (BAT) booklets [edited by the former European Fertilizer Manufacturers Association (EFMA 2000)].

Process optimization can be viewed from various perspectives. One issue to consider is the efficiency and environmental impact of the production lines. The separation/recovery of heavy metals, uranium, and members of the uranium family is a known challenge as is the processing/disposal of by-products and waste. A second issue involves adjusting the products to the real needs of soils in different geographical and climatic zones. A third issue focuses on transport and logistics. Whereas large centralized processing plants are usually located near the source of raw materials, secondary phosphate sources (recovered from sewage, animal wastes, biomass, and industry) will be processed in much smaller, local manufacturing plants, providing an opportunity for continuing or revitalizing local processing in absence of primary resources.

The scope of the processing node's activities encompasses mechanical, chemical, and thermal processing of *rock phosphate concentrate* as received from mining and beneficiation and *mineral, phosphate (and potash and magnesium) containing material* as received from conversion of biomass to energy or precipitation of P from liquids via the struvite route.

The normative reference point of the transdisciplinary approach is *sustainable development* largely following the interpretation of the Brundtland Report "Our Common Future (World Commission on Environment and Development; Brundtland 1987).

The goal of phosphate processing to fertilizers is to achieve a safe, environment-friendly material with a high plant nutrition value directly applicable to soils and plants. Fertilizers are primarily addressed because of their dominant position in the phosphate market.

### 1.1 Wet Chemical Processing of Phosphate to Fertilizer

With the exception of a few rocks classified as reactive, phosphate minerals as they exist in the ground are not soluble and are difficult for the plant to access. To provide the plant with the phosphate it needs, in a form it can take up through its roots, about 96 % of mined phosphate rocks are processed. More than 90 % are acidulated by the wet chemical route: converted with sulfuric acid to phosphoric acid (72–78 %), treated with sulfuric acid to single superphosphate and partially acidulated rock phosphate (10–14 %), or converted with nitric acid to nitrophosphates (2–4 %). A few small plants treat rock with hydrochloric acid with the largest one in Europe scheduled for shutdown by 2014. Less than 5 % is converted to elemental phosphorus by a thermal process which is further transformed into chlorides, oxides, and sulfides acting as the entry point to produce a multitude of (organo-)phosphorus compounds as well as to food and clean room-grade phosphoric acid.

More than 82 % of the phosphoric acid produced by the wet chemical route is used to make fertilizers, about 6–8 % to produce animal feed supplements and a small percent goes to detergents. The remainder is employed in a wide variety of products and applications (Prud'homme 2010; Jung 2012; Shinh 2012). There is phosphate in fire extinguishers, camera film, and indoor light bulbs. It also helps make steel harder and water softer. It plays a part in making and dyeing cloth as well as in washing dishes. Phosphate is in the fluids used to drill for oil and gas and in cementing the drilling holes. It helps to polish aluminum and to protect steel from corrosion. Most high-purity acids (produced by the thermal route or by liquid/liquid extraction) are used in the food, beverage, and electronics industries.

Wet phosphoric acid is usually produced in a fertilizer manufacturing facility (sometimes called a chemical processing plant) which is not necessarily connected to the mining operations, though new plants are conceived as integrated systems where mining, beneficiation, and processing are in one location. If mining operations follow the geographic extension of commercially viable deposits, such as in Florida's mining district, processing plants will not relocate. It is less costly to ship the rock back to existing plants for processing than to move the processing operations and the phosphogypsum stacks associated with the process.

Once the phosphate rock has been separated from the sand and clay at the beneficiation plant, it goes to the processing plant. At this point, the phosphate concentrate contains  $25-40 \% P_2O_5$ . The average grades have been slowly declining over the last 20 years (Prud'homme 2010).

In the processing plant, the phosphate concentrate is reacted with sulfuric acid to produce the phosphoric acid needed to make the most widely used high-analysis phosphate fertilizers diammonium phosphate (DAP) with a market share of 38 % and monoammonium phosphate (MAP) with a market share of 27 %. Both products are made by reacting ammonia with phosphoric acid. The third high-analysis phosphate fertilizer made from phosphoric acid is triple superphosphate (TSP) with a market share of 7 % (IFA 2012). DAP, MAP, and TSP fertilizers are water soluble and available for plants to absorb through their roots.

The sulfuric acid needed to convert the phosphate rock into phosphoric acid is frequently produced at the chemical processing plant using liquid (molten) sulfur or pyrite (a sulfur-containing ore), most of which is shipped to a port and then trucked to processing plants. Since the 1970s' energy crisis, most phosphate companies capture the heat released during sulfur burning and sulfuric acid production and use it to produce steam. The steam is used to produce the heat required to concentrate the phosphoric acid and to generate electricity to run the plant. Because of the exothermic process when converting sulfur to sulfuric acid, integrated plants produce most of the energy they need and some sell excess energy to a commercial provider.

When sulfuric acid is reacted with phosphate rock to produce phosphoric acid, the by-product *calcium sulfate known as phosphogypsum* is also produced. There are approximately five tonnes of phosphogypsum produced for every tonne of  $P_2O_5$  in phosphoric acid. Phosphogypsum, like natural gypsum, is calcium sulfate, but it frequently contains a relevant amount of radioactivity due to the radium that naturally occurs in most phosphate rocks (IAEA 2006). Because of this radioactivity, a 1992 US Environmental Protection Agency (EPA) rule bans most uses of phosphogypsum in the country (Lloyd 2004).

Numerous applications for phosphogypsum, such as in agriculture as a soil conditioner, or in construction as plasterboards, have been developed in all phosphate-producing countries. However, estimates suggest that currently some 3–4 billion tonnes of phosphogypsum are disposed of in stacks in more than 50 countries. These stacks are growing by 150–200 million tonnes each year (Hilton 2010). Moreover, a small number of phosphoric acid plants still discharge phosphogypsum to the sea, entailing environmental hazards and eutrophication, particularly in the absence of strong currents, such as in the Baltic Sea (Wissa 2003).

Apart from the by-product phosphogypsum, the chemical process produces gaseous emissions in the form of hydrofluoric acid (HF) and silicon tetrafluoride (SiF<sub>4</sub>), released during the digestion of phosphate rock, which typically contains 2–4 % fluorine. In case the energy generated from the exothermic reactions in the process is not effectively recovered (IFC 2007), modest amounts of CO<sub>2</sub> are released to the air. Large amounts of CO<sub>2</sub> are released, however, from carbonates as part of the crystal structure of sedimentary apatite (francolite) or as impurities in the form of calcite or dolomite, the latter being a challenge to remove even with the latest beneficiation technologies available.

Whereas most NP fertilizers are processed from phosphoric acid, roughly 15 % of acidulated phosphate fertilizers do not use phosphoric acid as a starting product.

Phosphate rock can be partly or fully acidulated with sulfuric acid, the latter marketed as single superphosphate with 16–22 %  $P_2O_5$ . If phosphate rock is reacted with nitric acid, nitrophosphates are produced, which cover a wide range of NP and NPK grades. The presence of ammonium nitrate and the hygroscopic nature of the product impose special manufacturing, handling, and storing conditions for nitrophosphates.

### 1.2 Thermal Processing of Phosphate Rock

In principle, there are two thermal routes for mineral phosphate processing: (1) production of elemental phosphorus at 1,500 °C in an electric arc furnace as an intermediary for technical phosphate compounds and phosphoric acid for applications requiring high-purity acid and (2) reacting mineral phosphates at temperatures at or above 1,000 °C with alkaline compounds to relatively low-grade calcined or fused phosphates.

The traditional electric arc process, which is used in the Netherlands, the USA, China, Vietnam, and Kazakhstan, consists of two steps. The first step is an agglomeration of the rock at 1,500 °C producing chunks up to 10 cm in size or a wet granulation with a clay binder, followed by a heating step at 800° which produces pellets of 1–2 cm in diameter. This step also serves to remove carbonates and sulfates that are detrimental to energy use in the subsequent arc furnace process. The rock pellets are mixed with cokes as a reducing agent and-as an option depending on the rock's silica content—pebbles (SiO<sub>2</sub>) for slag formation. The mix is fed to a furnace heated to 1,500 °C by means of electric resistance. Under these conditions, phosphate is reduced to  $P_4$  which leaves the furnace as a gas, together with the by-product CO and some dust. The dust is removed in an electrostatic precipitator and-after calcination-landfilled or recycled into the process. The P<sub>4</sub> is condensed to a liquid. This is further processed (oxidized) to phosphorus chlorides, sulfides, and oxides which serve as building blocks for a multitude of bulk and fine chemicals, often in the form of organophosphorus compounds. Typical examples include flame retardants, herbicides, lubricant additives, or lithium-ion battery electrolytes. Part of P<sub>4</sub> is converted to high-purity phosphoric acid (25 % of  $P_4$  production) which is used in the food and electronic industries. The resulting CO gas stream is used as fuel for sintering plants and other on-site processes. The calcium oxide, which is left in the furnace after the phosphate has reacted, combines with the SiO<sub>2</sub> to form a liquid slag, which is tapped and either quenched directly with water or cooled and then crushed. It may be landfilled or used for road construction.

Iron, present as an impurity in the rock, is also reduced in the furnace. It forms a separate, ferrophosphorus slag which contains roughly 75 % Fe and 25 % P, with small amounts of other metals. It is used as a steel additive (Schipper et al. 2001).

Advantages of the furnace process are the ability to use low-grade phosphate rock, the production of a relatively high-value building block with a diverse and attractive application spectrum, as well as a higher tolerance to a number of impurities such as silica, magnesium, and aluminum. Disadvantages are the high energy consumption and investment cost.

The emissions typically associated with the electric arc process for elemental phosphorus and thermal phosphoric acid include phosphate, fluoride, dust, cadmium (Cd), lead (Pb), zinc (Zn), and radionuclides (Po-210 and Pb-210; see IFC 2007).

The Tennessee Valley Authority (TVA) has developed a thermal process where a mixture of phosphate rock and magnesium silicates (olivine or serpentine) is fused in an electric or fuel-fired furnace. Several hundred thousand tonnes of the resulting calcium–magnesium–phosphate glass are produced in Japan, Korea, Taiwan, China, Brazil, and South Africa. It contains about 20 %  $P_2O_5$  soluble to over 90 % in citric acid and plant-available MgO in the order of 15 %. The product reportedly produces better yields than acid-based fertilizers on acidic soils (UNIDO/IFDC 1998).

Other products from thermo-chemical processes such as Thomas Slag or Rhenania Phosphate have disappeared from the—predominantly European market because they were by-products of outdated steel production processes (Thomas converter) or because of the increased energy cost following the first global oil crisis, when the last Rhenania phosphate plant in Germany was shut down in 1982.

# 1.3 Phosphate Processing to Feed Supplements and Detergents

About 3.1 million tonnes of  $P_2O_5$  per year or 6–8 % of processed phosphates is supplied to the (livestock) feed supplement industry, chiefly in the form of monoor dicalcium phosphates (MCP/DCP). Despite significantly increased livestock production, this market has been growing slowly because of the addition of phytase to animal feed, an enzyme improving the digestibility of naturally occurring phosphates in plant-based feeds (phytate) by monogastric animals (Jung 2012), thus decreasing the need to add digestible feed phosphates.

About 800,000 tonnes of  $P_2O_5$  per year or close to 2 % of processed phosphates are used in the detergent industry, largely as sodium tripolyphosphate (STPP). The demand for STPP has fallen by about 1,000,000 tonnes of  $P_2O_5$  since 2007, and the outlook is a potentially stabilizing production capacity at 1,200,000 tonnes of product per year with about 58 %  $P_2O_5$  (Shinh 2012).

Detergent phosphates perform various relevant functions, in particular as builders and disinfectants in dishwasher detergents. Eutrophication, potentially the result of phosphorus-rich wastewaters, can be effectively prevented by phosphate elimination in sewage treatment plants. Even if phosphates were replaced by other chemicals, phosphorus elimination from wastewater would still be mandatory to avoid eutrophication, as human excretions typically contribute at least 75 % or more to the sewage system's P inflow.

### 1.4 Current Status Summary

More than 90 % of the globally mined phosphates are processed using the wet chemical route. The best phosphoric acid processes (hemi-dihydrate process) achieve a  $P_2O_5$  transfer efficiency of 98.5 %, which does not leave much room for further improvement (BAT No. 4, EFMA 2000). In addition, BAT processes for the production of the most common phosphate fertilizers (DAP/MAP and single superphosphate/triple superphosphate) release excess energy due to the huge surplus energy formation in modern sulfuric acid processes, making the wet chemical fertilizer process very energy efficient (Jenssen and Kongshaug 2003).

In contrast,  $P_4$  production has a lower phosphate recovery rate of about 94 % and a significant energy consumption of 13–14 MWh/t of product (Schrödter 2008). The product has little, if any, overlap with the fertilizer market. The only real competition is found in the purified wet phosphoric acid sector and the equivalent pure phosphoric acid produced via the oxidation of  $P_4$ . If high-purity products are required for applications in the food and beverage industries and even more so in the electronics industries, the need for downstream purification of fertilizer-grade phosphoric acid by multi-step solvent extraction and—where necessary—re-crystallization put the electric arc process on equal footing.

Gaseous emissions from both process routes are minimized by the latest air pollution control systems.

In conclusion, a wide variety of mature BAT techniques, which are highly efficient in terms of energy and material use, are available at large scale on all five continents. Technology innovation is not a priority issue for the industry, at least if high-grade/low-impurity concentrates can be made available by mining and beneficiation operations.

However, there are an unknown number of older processing plants which are not retrofitted with BAT techniques and which continue to use unsustainable practices, some of them giving rise to serious concern about their environmental impact. A number of phosphoric acid plants continue to discharge phosphogypsum to the sea, adding point loads of thousands of tons of P to the diffuse inflows from runoff and erosion, regardless of the sensitivity and eutrophication state of the specific aquatic environment. These practices usually do not draw much public attention and foil widespread efforts to prevent P losses to aquatic bodies. In these cases, technology innovation is not the solution to protect aquatic environments; instead, transdisciplinary actions by regulators, shareholders, managers, engineers, and the public-at-large are all that is required to gradually retrofit or close polluting facilities.

As a result of the continuously employed efficiency improvement strategies, a sensitive balance between feedstock qualities and process parameters has been established. Lower-grade/higher-impurity phosphate ores and secondary materials entail lower efficiencies or require additional beneficiation steps. At this end, technology innovation may help to avoid higher losses and/or higher energy consumption. In a more system-oriented approach, the first step is a review of real

nutrient requirements for regional crops and soils as well as an assessment of the common practices for their compliance with a changing environment.

Increasing efficiency has also been a driver for high water solubility and concentration of phosphates in fertilizers because it reduces the volumes of material as well as transport and handling costs. The high water solubility requirement will be called into question with the possible consequence of more local and smaller-scale processing.

A reason for environmental concern and economic burden is the large amount of phosphogypsum left behind as a by-product, and, to a large extent, as a waste needing long-term management. Phosphogypsum, its characteristics and potential uses have been the subject of research for over 30 years and stacks are still growing.

A certain pressure on heavy metal concentrations in phosphate fertilizers, in particular on cadmium, is expected from the European Commission which is currently working on a new fertilizer regulation to replace Regulation (EC) 2003/ 2003, the document currently in force.

Though desirable from an environmental perspective and feasible from a technical standpoint (20,000 tonnes of  $U_3O_8$  were recovered between 1978 and 1998, for instance at Prayon in Belgium) and possibly profitable from an economic point of view (the current price of >USD 100/Kg should allow a payback time of <10 years for a plant producing >200,000 kg  $U_3O_8$  per year), uranium recovery from phosphoric acid no longer happens (Stana 2009). Potentially revisiting the entire phosphorus process chain with one of the leading phosphoric acid suppliers could give a stimulus to restart uranium recovery.

Another stimulus could come from reviewing the potential benefits of extracting rare earth elements, often associated with phosphate deposits. Rare earth recovery from phosphoric acid has been a subject of research for years (Koopman 1999) with little practical impact.

## 2 Work in Global TraPs

## 2.1 Knowledge Gaps and Critical Questions

In a perfect world, phosphate ores are abundant and universally accessible, pollutants removed by technologies available at pilot or industrial scale, uranium recovered by industrially proven technologies, phosphogypsum safely used, and the phosphate cycles closed. However, in real life, most of these issues are controversially discussed and do not happen. In addition, an increasing number of phosphate mine operators have to cope with lower-grade ores and higher impurities—at least in the long run—resulting in inferior process efficiency (Burnside 2012). Moreover, due to plants and processes which are not being sustainably managed—still an issue at certain manufacturing locations—large amounts of

phosphates are lost to aquatic bodies, leading to eutrophication and loss of biodiversity. Even if the phosphate industry is only marginally accountable for the eutrophication problem, occasional disregard of widely accepted practices is affecting its activities and reputation.

For several decades, efficiency and pollution prevention were the drivers for research (Scholz 2011) within the phosphate industry. The decrease in phosphate grades has become a rather recent issue (Prud'homme 2010), and efforts have been made to cope with the situation by improving traditional technologies. In response to environmental pressures, the phosphate industry assumed its responsibility by recommending fertilizing rates corresponding to good agricultural practice, largely limiting fertilizer application to phosphate uptake by crops.

Pollutant transfer from phosphate fertilizers to cropland is still an issue, though technologies for their removal have been developed, however, not on a large-scale level and not yet for universal application.

Removing cadmium, for instance, could be implemented during the calcination of rock or phosphoric acid processing by transferring existing technologies to the phosphate industries. However, industrial-scale implementation may still need some research work. Relevant barriers to overcome include commercial considerations and the current lack of legal limits values.

Long-term security of food and energy supplies may motivate uranium recovery from phosphoric acid where processes have been successfully performed in largescale industrial plants for over ten years. By the end of the twentieth century, plants were closed for economic reasons after uranium prices had significantly dropped. There are some knowledge gaps related to the capital and operational costs of a second-generation plant built after lessons were learned and applied from first-generation plants (Stana 2009). Process and plant design optimization will be the technical tasks within a potential transdisciplinary case study which focuses on a concerted plan to manage critical resources in a strategic and sustainable manner.

An initial review of current phosphate processing indicates that technologies have been developed for separating and recovering uranium, heavy metals, and fluorosilicic acid as well as for different uses of phosphogypsum and for efficient production of phosphate fertilizers with high plant availability (Zhang et al. 2009). With a few exceptions in China, all but the last technology are not in operation, allegedly due to economic factors.

To address the knowledge gaps, the processing node team in Global TraPs has agreed on the following guiding question: How can the *energy balance*, *water balance*, and *material flows* of P processing be improved when producing fertilizer and other P-based products? More specifically detailed, critical questions for the processing node include the following:

• What are the actual P *recovery rates* by process and by other factors? What is the impact of lower-grade/higher-impurity rocks on *P*-losses in BAT processes? What *innovations and/or technologies* may help to support high processing efficiency in response to changing rock and concentrate elemental composition?

- 4 Processing: What Improvements for What Products?
- How is *phosphogypsum* currently being disposed of, used, or stored? What are the current estimated quantities of phosphogypsum in storage around the world? What is the state of utilization globally, and, in particular, what barriers limit the use of phosphogypsum?
- What technological means and strategies are meaningful to cope with the *heavy metal*, *uranium*, and *other radionuclide* problems and what may be the costs and ramifications of removing/recovering these elements? What are the risk management options and their advantages and disadvantages?
- What may be the upside of separating (removing) elements of concern in terms of market value and sustainable management? Which elements potentially have a value that could sustain removal/separation technologies?
- What *non-apparent knowledge gaps* can be identified with respect to fertilizer processing?
- Is there a *future for* local processing *primary and recovered (secondary) phosphates*, or is the trend to large, centralized, and vertically integrated rock processing inevitable?
- How can we support the creation of *regulatory frameworks* for processing different P resources to marketable products?
- How can we promote the quality and acceptance by farmers of locally produced, potentially lower-analysis, and not water-soluble fertilizers?

# 2.2 Role, Function and Type of Transdisciplinary Process

Role, function, and the type of transdisciplinary process strongly depend on the issue at hand, such as case studies and the respective guiding question (Stauffacher et al. 2008).

With regard to processing, we can identify three types of potential case studies (see Sect. 3) which demand different transdisciplinary processes. While "re-thinking and innovating the overall processing of P to fertilizers" focus on technical issues, the "valorization of phosphogypsum" begins with a situation where technical questions have been almost completely answered, yet no agreement seems to be achievable among the key players due to differing risk assessment and risk management positions. The third type of case study, "enable the local processing of primary and secondary resources," includes both technical–scientific aspects and non-technical questions.

The *first type* of case study (see Table 1) involves optimizing phosphate production processing. The predominant function of the transdisciplinary process is *capacity building*, such as production of new knowledge. Depending on the topical focus, a number of scientific disciplines and expertise from various practices must be included. As new knowledge might directly affect a fertilizer manufacturer's performance, a clear commitment on how to use and share new knowledge between potential partners from science and industry will be necessary. The case facets might be about chemical and physical properties of fertilizers, the removal

| Type of case study (focus)                                                                                                      | Primary function/role<br>of transdisciplinary<br>process | Potential guiding question                                                                                                                                                               |
|---------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Rethinking and innovating<br>the overall processing of<br>P to fertilizers<br>(technical focus)                                 | Capacity building                                        | How can phosphate production in terms of<br>sustainability be optimized while<br>meeting requirements of regional<br>characteristics such as crop type, soil<br>conditions, and climate? |
| Valorization of<br>phosphogypsum (non-<br>technical focus)                                                                      | Mediation, consensus<br>building                         | Are there options and ways of using<br>phosphogypsum which can meet all<br>stakeholder group needs?                                                                                      |
| Enable the local processing<br>of primary and<br>secondary resources<br>( <i>technical and non-</i><br><i>technical focus</i> ) | Capacity building,<br>consensus building                 | What are the requirements to match<br>secondary resources with processing<br>facilities in terms of stakeholder<br>interests, material properties, logistics,<br>and process parameters? |

 Table 1
 Illustrating type of case study, function/role of transdisciplinary process and potential guiding question

of impurities/contaminants from products, and different aspects of process optimization with regard to crop preferences and soil conditions in target regions.

The *second type* of case study involves the potential further use of phosphogypsum and the related environmental concerns and regulatory obstacles. A potential case study might bring together key stakeholder groups to further analyze and evaluate options for phosphogypsum use. A neutral institution such as ETH Zürich co-leading with the respective industry and regulators might initiate and establish a transdisciplinary process focusing on *mediation* and *consensus building* among stakeholder groups. Stakeholders from a number of fields such as the industry, potential users, administration/regulatory bodies, and NGOs together with leaders from the science community would participate in every step of the process.

The *third case study type* deals with locally processing primary and secondary P resources. In a first step, node team members must identify hot spot areas with high livestock density. Then, they need to invite potential co-leaders among manure producers and potential users of products from manure processing. In addition, relevant scientific disciplines and industrial expertise as well as key stakeholders need to be involved in the study. Dominant functions of the transdisciplinary process include *capacity building* and *consensus building*. Faceting can be done along the supply chain including *manure production, processing, distribution, use, and regulation*.

# 2.3 Suggested Case Studies

In response to the controversial topics of phosphogypsum management, the gradually degrading natural feedstock, the need for closing the phosphate loop, and preventing eutrophication of aquatic bodies, the node team identified three relevant areas for transdisciplinary case studies.

### 2.3.1 Innovating P Processing: Rethinking and Innovating the Overall Processing of P to Fertilizers

Primary resources are frequently located far away from regions of high phosphorus use, requiring high nutrient concentrations in fertilizers to avoid disproportionately high logistics costs. Thus, fertilizer types such as DAP, MAP, and TSP with nutrient concentrations ranging from 45 to 64 % were developed and have been dominating the phosphate fertilizer market ever since.

If large secondary raw material flows and decentralized processing plants were available in regions with high phosphorus consumption, lower nutrient concentrations might be acceptable due to the reduced transport distances. In addition, plant uptake from soils with medium and high phosphate concentrations could be replenished with fertilizers of lower nutrient concentrations and with no instant (water) solubility yet with a predictable release pattern as guaranteed by EU fertilizer types.

Changing framework conditions advocate reviewing the overall process chain.

- Low-grade primary and secondary phosphates are not easily processed to highanalysis fertilizers—many products from secondary resources come with  $P_2O_5$ concentrations in the order of 15–25 %, largely comparable to single superphosphate and other low-analysis but high-fertilizing value products. They generally contain additional nutrients such as sulfur, calcium, magnesium, potash, manganese, and others.
- The growing awareness of dependency on limited resources and the increasing acceptance of political regulation may open a window of opportunity for reviewing and re-evaluating the potential for uranium recovery from phosphoric acid. If this opportunity is missed, the expertise gained during the engineering and operating of U recovery plants in the 1960s, 1970s, and 1980s may be irrecoverably lost with experts slowly retiring from the business.
- Legitimate decision makers such as the European Commission are currently reviewing fertilizer regulations aiming at a par market access of primary and secondary resources while limiting pollutant concentrations in fertilizers, regardless of their raw material basis. If the currently proposed limits are enforced, many feedstock materials will need to be processed by thermo- or wet chemical metal separation processes.
- Some phosphate rocks contain relevant mass fractions of rare earth elements that may be commercially extracted during rock processing. Extracting rare earth elements may improve the economic viability of processing low-grade rocks and removing undesirable elements from the fertilizers.

This is not a complete list of arguments for revisiting the phosphate production processes and trying to accommodate the needs of different stakeholders. Whereas most critical questions are raised from a global perspective, different answers may be developed from a regional or local perspective. Thus, similar transdisciplinary case studies should be performed in selected regions with different economic, societal, and agricultural framework conditions. These critical questions need to be addressed:

- What is the most efficient and sustainable way to supply nutrients to crops in a designated target region? What are the characteristics (chemical and physical properties) of phosphate fertilizers that best comply with the criteria set by answering the first question? How could these criteria be translated into process and product specifications?
- What is the required nutrient solubility on various soils and under different climatic conditions to achieve a high fertilizing value and how is the determined solubility reproduced by chemical (solubility) tests to enable manufacturers to control the quality of their products online?
- How can the removal of impurities and pollutants, in particular cadmium and uranium, be integrated into phosphate processing without creating unacceptable cost hikes? Can the removal of impurities/pollutants be financed by the exploitation of additional high-value products such as rare earth elements? Which commercial, technical, political, and legal framework conditions are needed to facilitate the sustainable management of impurities and pollutants?

Case studies reviewing the fertilizer manufacturing process require fertilizer producers as practice stakeholders. Partnerships are sought with integrated phosphate fertilizer manufacturers who have the resources to actively participate and transfer the beneficial results to the daily processes. Scientific stakeholders can be selected from the Global TraPs team and from NGOs who have conducted a comprehensive amount of research work during the last half century.

#### 2.3.2 P Gypsum: Valorization of Phosphogypsum

Phosphogypsum has been a major research subject for many decades. The FIPR has conducted targeted projects since 1979 and partnered in 2005 with the Aleff Group in the project "Stack Free by 53" (www.stackfree.com). The FIPR and Aleff Group have published a large amount of evidence on phosphogypsum, both on research and applications, much of it in the public domain. A phosphogypsum working group has been set up with members from industry, academia, and regulatory bodies. After the research phase was completed in 2009, the current action plan (2011–2014) aims at using the entire current and future production of phosphogypsum, and this target must be supported by both countries and international agencies.

After preliminary considerations, the goal seems to be feasible (Wissa 2003) with a focus on agricultural uses (fertilizer, soil conditioner, soil remediation, and increased water efficiency) and construction, including materials for the construction of wallboards and roads. The IAEA has drawn up "The Phosphate Industry Safety Report," to be published in the near future.

However, phosphogypsum stacks continue to grow by the order of 150–200 million tonnes per year (Hilton 2010), apparently due to the controversial perception of risks related to the various use options. A relevant percentage is still discharged to the sea, even in sensitive maritime environments.

With regard to the management of phosphogypsum, these critical questions have been raised:

- What are the barriers preventing more sustainable phosphogypsum management practices?
- What impact do reviewed and potentially modified processes have on the risks related to phosphogypsum use?
- How can we attain a less controversial risk assessment and develop a risk management which is acceptable to a majority of stakeholders?

A transdisciplinary approach to these questions will primarily focus on consensus building upon risk assessment and management. Technical issues will be addressed within the field of revisiting phosphate processing.

The problem strongly begs for knowledge sharing between science and society. If a case study is performed, scientific stakeholders who have been developing options for phosphogypsum reuse in the past need to play an important role. However, without a profound methodological change, no breakthrough can be expected as long as stacks are accepted as a management option. Among the studies proposed in this chapter, this case may be the best example of how technology-oriented science fails to abate environmental problems if stakeholders cannot come to a consensus. Thus, a truly transdisciplinary process involving scientists, risk assessors and managers as well as stakeholders from environmental activist groups, legitimate decision makers (political bodies), and industry should be involved.

Two scenarios are conceivable: (1) the review of general phosphate processing leads to disruptive progress in terms of eliminating radionuclides from fertilizers and phosphogypsum. In this case, the evidence of a pollutant-free material may clear up any concerns and open the pathway to the use of phosphogypsum without further dedicated action. (2) In the absence of technical process improvements, only the transdisciplinary approach may bring about a new and different assessment of risks and benefits concerning phosphogypsum reuse options.

### 2.3.3 Local Processing: Enable the Local Processing of Primary and Secondary Resources

The prevailing paradigm in fertilizer production is to concentrate every processing step in the vicinity of raw material resources. If this trend continues, local processing would gradually disappear, cutting jobs, idling production facilities, and increasing dependency on a limited number of vertically integrated suppliers.

Secondary resources largely derived from human or animal excreta could compensate for the limited supply of rock phosphate. They are mainly produced in densely populated areas or in regions with high livestock density. In contrast to phosphate rock mines covering an area of a few square kilometers, secondary resources must be collected from a number of widespread livestock farms and wastewater treatment facilities to achieve relevant volumes. Thus, processing secondary resources preferably takes place in decentralized, regional, and comparatively small facilities. Existing local phosphate and fertilizer-processing plants may be appropriate and could replace imported phosphate rocks by utilizing locally available secondary resources, offering new business opportunities for industries which have either no or limited access to phosphate rock. However, having industrial processing plants in operation is not a precondition for a region to qualify for a transdisciplinary case study dealing with local processing. Relevant factors are as follows:

- Collectable regional resources which are currently not being sustainably utilized,
- suppliers and stakeholders willing to cooperate,
- industry or distributors to use or sell the product from the processing facilities,
- end-users who believe in the commercial value of the product,
- the implementation of legislation to stimulate or enforce the sustainable use of nutrients which are currently lost to sea, diluted beyond recovery, or landfilled, and
- the public at large which accepts industrial processing plants in their neighborhoods.

A preliminary investigation has produced evidence that livestock manure is the largest secondary phosphate resource requiring alternative management (Ott and Rechberger 2012). At present, manure is spread on cropland in the vicinity of livestock farms, largely contributing to phosphate losses to aquatic bodies and eutrophication. Regulatory bodies of some European countries, such as the Netherlands, Denmark, and Belgium, are starting to impose restrictions on current management practices.

The efficient exploitation of manure as a secondary phosphate resource is hampered by its (a) high water content and (b) pathogens and pollutants. In highly industrialized countries, incineration or gasification of biomass destroys pathogens and concentrates nutrients in the residues, thus providing an inorganic phosphate feedstock as required by the industry. However, there are only a handful of manure incinerators actually in operation, mainly because spreading manure on cropland is easier and cheaper than implementing sophisticated energy and nutrient recovery process chains. The current practice will only change if regulatory bodies enforce and control nutrient load limits on cropland. In less developed or less densely populated countries, incineration may not be the first choice and other processing methods could be preferred, provided that they produce a safe and plant-available product.

The task is to match secondary resources with processing facilities in terms of stakeholder interests, material properties, logistics, and process parameters. Apparently, this is a new research topic which was not addressed prior to the recent phosphate recovery initiatives. The knowledge gap is evident.

A project dealing with these issues faces several major challenges:

- Identifying regions with large phosphorus-containing waste flows with the potential to be transferred to a relevant feedstock for processing facilities;
- getting access to resources controlled by various stakeholders who are either in favor of or against the intended use;
- getting industrial processes politically supported, implemented, and licensed by regulatory bodies;
- achieving (relatively) high phosphorus concentrations at low cost in industrial processes upstream of the fertilizer and phosphorus manufacturing, necessitating close collaboration of the various stakeholders.

Thus, conflicting interests meet with uncertainty regarding the availability of appropriate upstream process technologies and require a transdisciplinary approach.

The case study begins with an initial screening to assess relevant P flows from agriculture in a spatially explicit manner. Based on this knowledge, up to three case study areas are selected to identify the hot spot regions with massive livestock waste flows where processing plants make sense. Following the initial phase, the methodology of "Area Development Negotiation" (Scholz and Tietje 2002; Scholz et al. 2006; Loukopoulos and Scholz 2004) will be performed.

Additional insight into complex management practices and waste flows can be gained by performing the case studies on different continents, preferably in countries with different agricultural practices in accordance with their state of development and development targets. Hot spots are determined by their importance within the geographical context. Preliminary investigations have produced evidence that northwestern Europe—the Netherlands, Belgium, Germany, and Denmark, the Russian province Leningrad, as well as the central and southern provinces of Brazil may host such hot spots.

Practice stakeholders are livestock farmers, agricultural cooperatives, the fertilizer and phosphorus industry, investors, and the public at large. Scientific stakeholders are members of the Global TraPs team who perform the case studies and selected experts with a specific local or specialist knowledge. Processing technologies (mechanical, wet chemical, and thermochemical) are selected in cooperation with the processing industry.

Assessment criteria (value trees) are determined along with the identified stakeholders, and the various technologies are evaluated using two approaches: (1) referring to data from existing industrial practice and research and by employing scientific research methods assessing aspects such as investment and operational costs, environmental impacts ( $CO_2$  emissions), the overall environmental footprint of different process approaches, the impact on regional GDP; and (2) assessing preferences from various stakeholder groups ("Exploration Parcours").

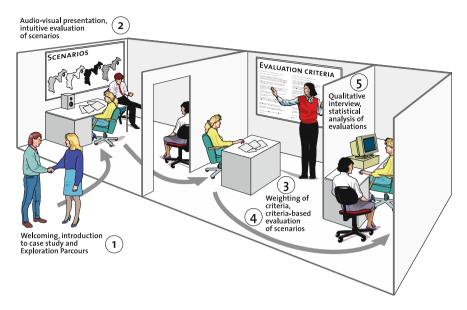


Fig. 1 Five stations of an exploration parcours (according to Scholz and Tietje 2002, p. 214)

### **Box** Exploration Parcours

The five-step procedure (see Fig. 1) aiming at the evaluation of stakeholder interests is called exploration parcours (EP). An EP generally starts from a set of scenarios identified in preceding steps and it facilitates gathering quantitative and qualitative data.

Step 1: The study team welcomes the participants and informs them about the goals of the study, the EP procedure and the rules. Step 2: The team presents the scenarios for thorough evaluation by the participants in a ranking procedure (first assessment). Step 3: Participants weigh evaluation criteria presented by the study team. Step 4: Participants evaluate the scenarios on the basis of the criteria (second assessment). Step 5: A qualitative interview supporting the interpretation of the stakeholders' evaluation patterns concludes the procedure (Scholz and Tietje 2002).

The EP setting is very flexible and can be performed in many ways. The study team may conduct single interviews, parallel sessions and group sessions with the various stakeholder groups. Group sessions facilitate conclusive group discussions which may initiate a reflection process to be followed by a negotiation process among the stakeholder groups. Universities or other institutions can collect the data. EP procedures are not limited to scenario assessments. Study teams have successfully performed in-depth interviews on stakeholder preferences with regard to key aspects of a repository site selection process for nuclear waste and safety issues (Krütli et al. 2010a, b).

Based on these steps, robust orientations can be developed; if and how the P resources in the selected hot spots can be processed with an acceptable environmental footprint and general lessons can be derived both on substantive and process level for similar hot spots.

### 2.4 Expected Outcome

The expected outcome follows the specific function of the transdisciplinary process in each area of its application.

In the area of revisiting phosphate processing, capacity building and incremental technical improvements in terms of the energy, water, and material balances are expected. The case studies should produce evidence that the environmental footprint of fertilizer production may be reduced without excessive cost hikes if all aspects of the benefits from potential by-products are taken into consideration.

With regard to the valorization of phosphogypsum, the immediate outcome of a transdisciplinary case study could be a risk management strategy in compliance with the needs of all stakeholders. Down the road, phosphogypsum may be used in a variety of safe applications.

As for the local processing of primary and secondary resources, the waste nutrient accumulation hot spots will be identified and secondary phosphorus resources processed to feedstock for safe and effective fertilizers and other products. The case study demonstrates the most appropriate techniques to accommodate local societal and environmental needs.

There is reason enough to believe that the market alone will not provide enough incentives to overcome the current barriers to more sustainable practices. Consequently, case studies must provide a decision support tool for an appropriate regulatory framework for the sustainable use of primary and secondary phosphate resources.

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# **Appendix: Spotlight 5**

# **Options in Processing Manure from a Phosphorus Use Perspective**

#### **Diane F. Malley**

Of the livestock manures, hog manure is one of the most challenging for the management and recycling of nutrients. It is generally liquid, being a mixture of faeces, urine, feed residues, and wash water from the barns. Manitoba is one of the largest producers of hogs among Canadian provinces with a population of 8 to 10 million head in recent years (Honey 2011). The manure from these hogs is collected in open lagoons, or less commonly, in concrete storage tanks. The digestion of feed by the hogs is not complete, resulting in a considerable range of solids among samples of manure. Although the feeds may contain sufficient total P for nutritional purposes, the incomplete digestion leads to the need for supplemental P to be added to the diet. This adds to the P concentration in the manure. In recent years, the addition of the enzyme phytase to feed enhances digestion and somewhat reduces the use of supplemental P. The solids in the manure settle upon standing, such that manure stores are typically mechanically agitated, though incompletely, whenever manure is to be handled.

In Manitoba, periodically the manure is pumped from the manure stores through hoses up to 4 or 5 km distance and injected into the soil. This both disposes of the manure and provides nutrients for future crops. Despite the agitation, manure withdrawn from the stores is highly variable at the time of injection, varying over the pump-out from 0.4 to nearly 15 % solids, 0.5–6.5 g/L total N, and 0.03–5.7 g/L total P. Thus, solids may vary more than 37-fold, N 13-fold, and P 190-fold. The N/P ratios vary widely and on the average differ widely from the 15:1 needed to support agricultural productivity. Consequently, the application of manure to agricultural fields is more a form of disposal of the manure than an effective application of the nutrients as the valuable fertilizer that they are. Fertilizers are generally applied to these fields in addition to the manure to ensure the agronomic needs for N and P are met since the contribution of nutrients by the manure is unknown.

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Beginning in 1999, a global technology used commercially first 30 years ago for the measurement of protein in wheat, now analyzing 85 % of marketed wheat globally, was applied to the analysis of nutrients in liquid manure. This technology, near-infrared spectroscopy (NIRS), analyzes samples on the spot in real time without the use of chemicals, when the instrument has been appropriately calibrated. Early results showed that NIRS accurately predicted total solids, total N, and total P in hog manure (Malley et al. 2002). This technology has been demonstrated in the laboratory with flowing manure. It has the potential to measure hog manure being applied to fields and to permit GPS mapping of the nutrients applied. In this way, a second pass with commercial fertilizers can result in the accurate application of nutrients for agronomic needs. Moreover, the nutrients in the hog manure can return financial value to the hog producers and manure applicators. The P and N can be accurately managed to avoid unintended losses to the surrounding environment.

# The Netherlands

In the Netherlands, with a population of 12.2 million hogs in 2012, there is insufficient land base upon which to apply untreated liquid manure. Nutrients are highly managed under the economic instrument of MINAS (OECD 2005). Incoming nutrients onto farms are highly tracked and accounted for against nutrients outgoing from farms as products or manure. This reduces accumulation of nutrients on the land and loss of nutrients from the land to air and water. This is a shift in manure policy from regulations to economic incentives for managing nutrients. Yet, the oversupply of P in manure may amount to 60 million kg by 2015 (Schoumans et al. 2010). Manure processing is being seriously considered. Among the techniques are anaerobic digestion, manure separation into solid and liquid fractions, followed by composting or incineration of the solid fraction, reverse osmosis anaerobic treatment of the liquid fraction, and acidification (EC 2010). Not all manure treatments contribute to a better utilization of the N and P resources, nor are all focused on recycling P to agricultural soil. One option for reducing/ recycling P is manure separation on livestock farms producing a liquid fraction containing N to be recycled back to their land along with a portion of the solids fraction containing the majority of the P. The second option is the recovery of P from manure as P fertilizer, biochar, or elementary P for export (Schoumans et al. 2010). These options require significant financial investments and institutional arrangements. Operational costs can be significantly reduced by employing near-infrared spectroscopy strategically in the processing stream for continuous, real-time monitoring of the process, the incoming raw materials, and the final products by batch. Furthermore, the technology has been demonstrated to measure the P in sediments of lakes and can be used as an indicator of unintended runoff of P from surrounding land.

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