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LIFE CYCLE ASSESSMENT FOR INDUSTRIAL PROCESSES ON THE EXAMPLE OF PARTIALLY ACIDULATED PHOSPHATE ROCKS

ANALIZA CYKLU ŻYCIA DLA PROCESÓW PRZEMYSŁOWYCH NA PRZYKŁADZIE PRODUKCJI FOSFORYTÓW CZĘŚCIOWO ROZŁOŻONYCH

Abstract: The aim of work was life cycle assessment (LCA) of simple inorganic PAPR (partially acidulated phosphate rock) type fertilizer. PAPR type fertilizers are specified as products of partial dissolution of grinded phosphate rock with usage of sulfuric or phosphoric acid, containing as a main components monocalcium phosphate, tricalcium phosphate and calcium sulfate. LCA was made by using the model of PAPR type fertilizer production process produced under the laboratory conditions. Model was based on the research provided for assessment of product physical properties, phosphorus content expressed as a P_2O_5 soluble in mineral acids and water, mass balance and emissions from the process. Results, supplemented with reference data were used as a input data for GaBi 4 software which constitutes the computer support to perform LCA.

Keywords: partially acidulated phosphate rocks (PAPR), Life Cycle Assessment (LCA), phosphate fertilizers

Intensified efforts to evaluate the impact of industrial plants and enterprises on the environment are observed as a response to increasing degree of environmental awareness. Currently, public concern regarding the phenomenon of global depletion of natural resources results in the search for effective strategies and systems that limit the human adverse impact on the environment. Many companies, to counteract the global environmental threats, introduced to the market “greener” products, defined by the manufacturer as environmentally friendly, which are produced using “greener” technology. Environmental characteristics of products and manufacturing processes has become a major contributor to the development of enterprises in the field of investigation of methods for minimizing their adverse impact on the environment. Recently, various businesses use the advantages of applying pollution prevention

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strategies and environmental management systems in order to gain a marketing supremacy over competitors. *Life Cycle Assessment* – LCA is one of tools used for these purposes. This method presents a comprehensive approach to the environmental aspects of a product life cycle “cradle-to-grave”. It begins with the process of natural resources extraction in order to manufacture the product and ends at the point where all materials are re-utilized [1–3].

LCA evaluates all stages of product life cycle from the perspective of their total interdependence, thereby understanding that every successive operation leads to the next. LCA enables the estimation of the total environmental impact resulting from all stages of product life cycle, often including impacts not considered in more traditional studies (*eg* raw material extraction, material transportation, final disposal of the product, *etc.*). Taking into account the impact on the environment, therefore raw materials and energy consumption, wastes, effluents and emissions, which is connected with the production, usage and ultimately the management of waste product (recycling, storage, scrapping), LCA provides a comprehensive view of the environmental aspects of the product or process and more accurate product selection and its manufacturing process. In addition to the materials and energy flows, also information on financial flows are often collected. This process is referred to LCC – *Life Cycle Cost* [4, 5]. LCA has its origin in an ISO standards of 14000 – Environmental Management series. Life cycle assessment is presented in detail in the standards starting from 14040 to 14043. Both definitions specific to the subject and discussion on the particular stages of the environmental life cycle assessment were included within these reference documents [6–8].

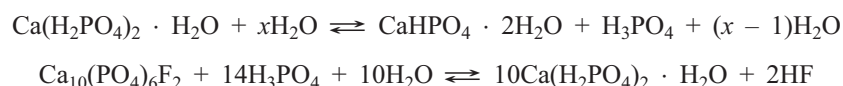
Implementation of environmental life cycle assessment is time-consuming process and often requires large amounts of data about the processes and materials included in the manufacturing system. Performing the LCIA stage and the final report involves conducting the arduous and complicated calculations and specifications. One of the commercially available software tools may be used to simplify performing LCA. Computer programs such as GEMSIS, SimaPro, GaBi are the most popular. The use of computer support also allows making quick alterations in created project (sensitivity analysis) and keeping standardized, comparable results.

PAPR-type (*partially acidulated phosphate rocks*) fertilizers are produced in contrast to conventional superphosphate fertilizers as a result of the partial acidulation of ground phosphate rock with sulfuric or phosphoric acid [9]. They contain monocalcium phosphate, tricalcium phosphate and calcium sulfate as a main components. The parameter, which classifies the PAPR-type fertilizer formulations is the degree of PAPR stoichiometric norm (η_{PAPR}) expressed by the following formula:

$$\eta_{\text{PAPR}} = \frac{\eta_{\text{min. ac}}^{\text{a}}}{\eta_{\text{min. ac}}^{\text{s}}}$$

where: η_{PAPR} – degree of PAPR stoichiometric norm;
 $\eta_{\text{min. ac}}^{\text{a}}$ – actual amount of mineral acid used for acidulation [kg];
 $\eta_{\text{min. ac}}^{\text{s}}$ – amount of mineral acid resulting from stoichiometry of phosphate rock acidulation reaction [kg] [10].

Values of η_{PAPR} in the range 0.1–0.5 are commonly used in industry. The idea of the PAPR fertilizer manufacturing is mainly attributable to economic reasons. Lower acid consumption reduces the unit price of the total content of phosphorus compounds in the product in relation to the fertilizer produced by the complete acidulation of raw material (*single superphosphate* – SSP or *triple* – TSP). Another advantage is the tolerance of the manufacturing process for low-grade raw phosphate rocks, which are not suitable for use in the manufacture of superphosphate. In addition, a number of experiments on various crops showed that fertilizers produced by this method represent the same, and under certain conditions, higher efficiency than superphosphates, in particular the SSP [11,12]. As an explanation for this phenomenon the following chemical reactions occurring in the soil have been proposed [13]:



As a result of hydrolysis of monocalcium phosphate molecule free phosphoric acid is formed, which subsequently reacts with the prior unreacted part of phosphate rock, forming of dicalcium phosphate and further less soluble compounds [14]. The rate of each reaction is different. The first one is faster, a second slower. The rate of the second reaction is limited by the phosphorus uptake by plants, which successively increases the amount of soluble compounds. Therefore, phosphorus contained in the structure of the PAPR has a prolonged release profile in the soil environment.

Emissions are important aspect in terms of life cycle assessment of PAPR fertilizers. As the production of SSP and PAPR is based on the same raw materials and the same reaction, both processes are characterized by emission of the same type of pollutants into the environment. The first type are dusts released into the atmosphere during the reloading, milling and transportation of phosphate rocks. Their amount depends on the fineness of the raw material. Another type of emission are volatile fluorine and silicon compounds. They are formed as a by-product of phosphate rock acidulation with sulfuric acid. The last type of emissions are dusts generated by the crushing and transportation of a final product.

Materials and methods

The investigated PAPR-type fertilizer preparations were obtained under laboratory scale, applying for calculations of the amount of sulfuric acid resulting from the stoichiometry of the acidulation reaction of phosphate rock ($\eta_{\text{min. ac.}}^{\text{s}}$) procedure recommended by the U.S. Department of Agriculture (1964) expressed by the following formula [15]:

$$\begin{aligned} \frac{\text{kg H}_2\text{SO}_4 \text{ 100\%}}{100 \text{ kg phosphate rock}} &= 1.749(\% \text{ CaO}) + 0.962(\% \text{ Al}_2\text{O}_3) + \\ &+ 0.614(\% \text{ Fe}_2\text{O}_3) + 2.433(\% \text{ MgO}) + 1.582(\% \text{ Na}_2\text{O}) + \end{aligned}$$

$$+ 1.041(\% \text{ K}_2\text{O}) - 0.691(\% \text{ P}_2\text{O}_5) - 1.225(\% \text{ SO}_3)$$

The investigations were conducted for the degree of PAPR stoichiometric norm values of 0.3, 0.4, 0.5 and 1.0 – as a control batch of single superphosphate (SSP). Morocco phosphate rock 68 BPL samples with a declared content of P_2O_5 min. 31 % w/w and 95 % w/w sulfuric acid supplied by POCH manufacturer were used for the experiments. Fertilizer products of assumed degree of PAPR stoichiometric norm values were prepared in a model-type apparatus produced by Atlas Syrris Ltd which was equipped with automatic control of process parameters such as temperature, stirring rate and time. The applied apparatus allowed manufacturing of fertilizers by batch processing, while the conditions have been adjusted to imitate the continuous process for PAPR and SSP fertilizers production.

The first is the short contact time of reactants (2–3 min). Under operating conditions of the process it was achieved through intensive mixing of the reactants together – stirring rate was 600 rpm. Taking into consideration small volume of the reaction mixture pre-heating of the reactor before adding the reactants to about 90–100 °C was implemented. Diluted sulfuric acid at a concentration of 70 % w/w and temperature of about 70 °C was introduced into the reactor, while the temperature of the process, measured inside the reactor was $110 \text{ °C} \pm 5 \text{ °C}$. Exhaust gases were absorbed in distilled water in a scrubber, and subsequently analyzed for the fluoride ions content using Orion ion-selective electrode. The extraction of phosphate in the form of total P_2O_5 (soluble in mineral acids) and water-soluble P_2O_5 was performed in accordance with the procedures enclosed in Regulation (EC) No. 2003/2003 of the European Parliament and of the council of 13 October 2003 relating to fertilizers at 0, 4, 7, 14 and 28 day after production [9]. Extracted forms of phosphorus were determined using a spectrophotometric method according to the recommendations contained in PN-88/C-87015 based on creation of yellow complexes between metavanadate-molybdate and an orthophosphate ion [16].

The assessment of environmental impact of the PAPR industrial manufacturing process was performed using GaBi 4 from PE International GmbH as a software supporting LCA. The process of industrial production of such fertilizer formulation includes the following unit operations: phosphate rock unloading, dilution and cooling the sulfuric acid, fertilizer acidulation (reaction with sulfuric acid), crushing the product, absorption of gases and dusts, product storage. Unloading raw materials, product storage and outputs from the absorption process were considered as system boundaries. One ton of the final product was assumed as a functional unit and a mixture of raw materials and mineral acid was as a reference stream.

Results and discussion

In comparison with conventional superphosphate fertilizers, the PAPR products obtained under laboratory conditions are characterized by shorter solidification time. In connection with the observed lack of significant changes in contents of various forms of phosphates during curing process, further processing of the PAPR fertilizer formula-

tions with elimination of this process is possible, which in the case of SSP and TSP constitutes crucial requirement to achieve a product with demanded physical properties and content of available phosphorus.

The Life Cycle Assessment was performed for PAPR fertilizer $\eta_{\text{PAPR}} = 0.5$, which meets the requirements imposed to partially acidulated phosphate rocks by European legislation regarding the percentage of phosphorus (20 % P_2O_5 Phosphorus expressed as P_2O_5 soluble in mineral acids, at least 40 % of the declared content of P_2O_5 being water soluble) [1].

1. LCI

The analysis of a set of inputs and outputs were based on data collected from all unit operations included in the product manufacturing system. The streams of Inputs/Outputs of substances, emissions and energy were assigned. Streams values calculated on the basis of assumptions that were concluded from experimental part or discovered from bibliographic resources were depicted in Table 1.

Table 1

Balance sheet of calculated streams values.

Name of unit process	Inputs		Outputs	
	Name of stream	Value	Name of stream	Value
Phosphate rock unloading	Phosphate rock (32 % w/w P_2O_5)	658.66 kg	Phosphate rock (32 % w/w P_2O_5)	658.6 kg
			Phosphate dusts	0.06 kg
Sulfuric acid dilution and cooling	Sulfuric acid (VI) 96 % w/w	227.6 kg	Sulfuric acid (VI) 64 % w/w	455.2 kg
	Water	113.80 kg	Cooling water	373.9 kg
	Cooling water	373.9 kg	Residual heat	78.3 MJ
	Electric power consumption	0.21 kWh		
Phosphate rock acidulation	Sulfuric acid (VI) 64 % w/w	341.4 kg	PAPR 0.5	998.64 kg
	Phosphate rock (32 % w/w P_2O_5)	658.6 kg	Fluorides	0.11 kg
	Electric power consumption	9.14 kWh	Phosphate dusts	1.25 kg
PAPR crushing	PAPR 0.5	998.64 kg	PAPR 0.5	997.8 kg
	Electric power consumption	2.35 kWh	Fluorides	0.07 kg
			Phosphate dusts	0.77 kg
Absorption	Fluorides	0.18 kg	Water after absorption	100 kg
	Phosphate dusts	2.02 kg	Fluorides	0.0018 kg
	Water for absorption	100 kg	Phosphate dusts	0.0202 kg
	Electric power consumption	20 kWh	Fluorides (sewages)	0.1782 kg
			Phosphate dusts (sewages)	1.9998 kg
Storage	PAPR 0.5	997.8 kg	PAPR 0.5	997.8 kg
	Land area	1500 m ²		

The data collected during LCI stage were entered into the program. The data constituted the basis for preparation of a plan for PAPR $\eta_{\text{PAPR}} = 0.5$ fertilizer manufacturing system. Screenshot of the GaBi Software was demonstrated on Fig. 1.

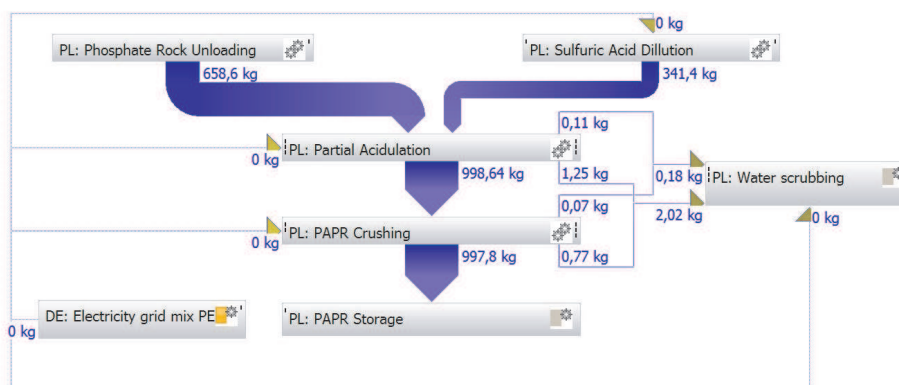


Fig. 1. Plan of the PAPR $\eta_{\text{PAPR}} = 0.5$ product manufacturing system carried out in GaBi 4 software

Names and values of input and output streams were supplemented, allocated and appropriate streams were labeled as tracked ones. This allowed their connection with the subsequent processes included within the plan composition. Creating a stream required the pre-qualification. For example, in this case, among streams called “phosphates” a group “air emissions” rather than “non-renewable resources” were selected. Energy demand was 396.3 MJ.

2. LCIA

After constructing the plan of manufacturing system based on data collected from the LCI stage and connecting the respective streams between processes the balances were created. These operations allowed the calculation of impact of the PAPR manufacturing process on the environment. All streams within the manufacturing system were assigned to the appropriate category of raw materials and energy resources (renewable, non-renewable), emissions (organic, inorganic; into water, soil, air). Classification and selection of the category indicator were executed automatically after selection of model of impact category, and indirectly by defining streams at the LCI stage. For the purposes of described case the following categories were selected from multiple models of the impact categories included in the GaBi 4 program:

- Mass balance;
- Energy balance;
- CML2001, Eutrophication Potential (EP);
- CML 2001, Global Warming Potential (GWP100 Years);
- EDIP 1997, Human toxicity air;

- EDIP 1997, Human toxicity soil;
- EDIP 1997, Human toxicity water;
- EI 99, EA, Ecosystem quality, Land conversion.

Successive LCA analysis was based on selection of the appropriate option of outputs presentation. The influence of manufacturing system on greenhouse effect was evaluated. For this purpose according to the path “Quantity” => “CML 2001, Global Warming Potential 100 Years” option was selected. In the balance window only those flows and processes that contribute to the greenhouse effect were displayed. In this case, with given values, it was only electric power introduced into the process. Normalization method was chosen each time to the appropriate category of influence. Normalization did not include material and energy balances of the process.

Conclusions

Manufacturing process of PAPR $\eta_{\text{PAPR}} = 0.5$, defined according to presented paper, have impact on the environment in range of electric power consumption and operations involving phosphate rock processing. The results of analyzes enabled the evaluation of process operations, which have the most adverse impact on the environment, and suggested that product system have impact on the environment on different levels:

- Global Warming Potential – manufacture of functional unit is connected with electricity consumption taking effect in emission of 22.976 kg CO₂ equivalent;
- Eutrophication Potential – manufacture of functional unit is connected with emission of 2.084 kg phosphate equivalent, in particular from absorption installation, phosphate rock unloading and electricity consumption;
- Human toxicity water – 82.545 m³ of water, in particular due to electric power consumption;
- Human toxicity air – $9.74 \cdot 10^5$ m³ of air, in particular due to electric power consumption;
- EDIP 1997, Human toxicity soil – 1.944 m³ of soil, in particular due to absorption process of volatile fluorine compounds and phosphate dusts;
- Ecosystem quality, Land conversion – consumption of storage area is connected with 37740 PDF · m².

The results of LCA analysis demonstrated number of environmental aspects that require consideration during designing or optimization of the PAPRs manufacturing process. It is necessary to eliminate “weak points” of the product system such as reduction of phosphate dusts emissions, preferably by the recirculation, utilizing fluorine and silicon compounds from the process (production of fluorosilicic acid) and water recirculation during absorption process. GaBi built-in options enabled automatically detection of so called “weak points” of product manufacturing system. The indication was proceeded by highlighting those streams that have the greatest share in appropriate category of influence. The evaluated process demonstrates the following environmental threads:

– Electric power consumption – high energy demand results in a significant impact on global warming, despite none of the unit processes in itself does not cause greenhouse gases emissions;

– Absorption of volatile fluorine compounds and phosphate dusts;

– Dilution of sulfuric acid – emission of the residual heat into environment.

To solve the problems the following procedure should be taken into account:

a) Reduction of electric power consumption by the apparatus and equipment used in the manufacturing process.

b) Recirculation of water stream in the absorption unit and rerouting the recovered fluorine compounds for the production of fluorosilicic acid. Such a solution is suggested by the reference documents as the *Best Available Technology* for the phosphate fertilizers industry [17].

c) Recycling of phosphate dusts in the process, which are emitted during the operation of acidulation, transportation and crushing of the product.

Residual heat management by its utilization *eg* heating water for sanitary purposes on the premises. It may be necessary to redesign the sulfuric acid dilution unit to obtain a higher temperature gradient between the water which cools heat exchanger and heated water for its further application.

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Abstrakt: Celem niniejszej pracy była analiza cyklu życia nawozu nieorganicznego prostego typu PAPR (*Partially Acidulated Phosphate Rock* – fosforyty częściowo rozłożone). Nawozy typu PAPR definiowane są jako produkty otrzymywane w wyniku częściowego rozłożenia zmielonego fosforytu kwasem siarkowym lub fosforowym, zawierające jako składniki główne fosforan jednowapniowy, fosforan trójwapniowy oraz siarczan wapnia. Ocenę cyklu życia wykonano na podstawie modelu procesu produkcji preparatów nawozowych typu PAPR uzyskanego w warunkach laboratoryjnych. Opracowany model bazował na badaniach uwzględniających ocenę właściwości fizycznych produktu, zawartość fosforu w przeliczeniu na P_2O_5 rozpuszczalny w kwasach mineralnych oraz w wodzie, a ponadto bilans masowy i emisje z procesu. Uzyskane wyniki, uzupełnione danymi literaturowymi posłużyły jako dane wejściowe dla programu GaBi 4, który stanowi komputerowe wspomaganie wykonywania analizy LCA.

Słowa kluczowe: fosforyty częściowo rozłożone (PAPR), ocena cyklu życia (LCA), nawozy fosforowe