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COMPARATIVE EVALUATION OF CALCIUM FEED PHOSPHATE PRODUCTION METHODS USING LIFE CYCLE ASSESSMENT

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PORÓWNAWCZA OCENA RÓŻNYCH METOD PRODUKCJI PASZOWYCH FOSFORANÓW WAPNIA Z ZASTOSOWANIEM TECHNIKI LCA

W niniejszej pracy porównano, jaki wpływ na środowisko mają procesy wytwarzania fosforanów paszowych. Porównano trzy metody: termiczną zmodyfikowaną oraz dwie niskotemperaturowe endotermiczne (instalacja pracująca w KZPN „Bonarka" oraz instalacja w GZNF „Fosfory"). Ocenę wpływu na środowisko przeprowadzono techniką LCA w układzie *„gate to gate"* przy wykorzystaniu metodyki Ekowskaźnika 99. Stwierdzono, bazując na wynikach LCA, iż najkorzystniejszą technologią jest instalacja produkcji fosforanów paszowych metodą niskotemperaturową endotermiczną zlokalizowaną w GZNF „Fosfory". Ponadto wykazano, iż technika LCA może być skutecznych narzędziem oceny aspektów środowiskowych szczególnie, gdy jest konfrontowana z innymi metodami oceny wpływu procesów na środowisko naturalne.

Summary

This paper presents a comparative analysis of feed phosphates production processes using the Life Cycle Assessment (LCA) methodology and process analysis in the quantification of cumulated calculation. Three feed phosphates production processes were compared: a modified thermal process and two different low temperature endothermic units (one working in the "Bonarka" Inorganic Works (BIW) in Cracow and the other in the Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk). The LCA results indicated that the most advantageous technology is the feed phosphates production unit in "Fosfory". It was shown that LCA can be an efficient instrument for evaluating environmental impact, though it should be compared with other estimation methods.

INTRODUCTION

Phosphorus is an essential component of every living organism. It is the main component of the bone (together with calcium it is a component of hydroxyapatite). Phosphorus compounds have an important role in the development of teeth, biochemical conversions of blood, or acid/base regulation in the organism [5, 19]. It is the most deficient component in natural animal feeds and therefore it is essential to supplement it by adding calcium phosphate to animal feed to correct functioning and growth [5, 19].

In the past feed phosphates were produced in Poland using different technologies. The oldest method, thermal defluorination of apatite (the classic thermal method of the DFP production process) was used with different modifications until 1993 [3, 9, 15]. This technology, in spite of numerous modernizations introduced in the period 1991–1993, was still extremely energy-intensive and harmful to the natural environment [7–9, 13, 15]. Production of feed phosphates using new technology (low-temperature endothermic) was implemented in 1993 in the "Bonarka" Inorganic Works (BIW) in Cracow in a unit previously used for DFP production [9, 13]. However, due to the outdated equipment, the unit was still harmful to the environment. A design for a new feed phosphates unit for the Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk was developed according to the same technology [15]. The latest low-temperature endothermic technology was implemented in the "Silikaty" Works in Klucze in 1995 [11].

The aim of our research was to compare the influence on the natural environment of different feed phosphates production technologies. Feed phosphates processes using a thermal method and low-temperature endothermic methods (two different units) were compared, and two methods of environmental evaluation of production processes were applied:

LCA – Life Cycle Assessment, allowing for the analysis of a process or product throughout its "life cycle" (from mining of raw materials, production of semi-finished products, production of main products and product use, to final utilization of the product and its disposal) [1, 16].

FEED CALCIUM PHOSPHATES PRODUCTION TECHNOLOGIES

Feed phosphate is a source of mineral components in animal feed (phosphorus, calcium sodium, magnesium) [20]. Important parameters affected by phosphorus availability in feed are, besides its content, a proper calcium to phosphorus ratio (which differs depending on the animal species), and the type and degree of hydration of the compound in which phosphorus occurs [12, 19]. The presence of vitamin D is also important for reabsorption and transport of phosphorus proportionally to accepted calcium ions, and for settling calcium and magnesium ions and phosphates in bone tissues [5]. The chemical measure of phosphorus availability in animal organisms is accepted as being its solubility in 0.4% HCl. This corresponds approximately to hydrochloric acid concentration in digestive juices [12, 19, 22].

In 2001 a global feed phosphates production was estimated at 3.5 million Mg/year, while production capacity was estimated at over 4.5 million Mg/year [18]. Industrial methods of feed phosphates production can be divided into three groups [21]:

- thermal methods – based on decomposition of phosphorus raw material by phosphorus acid in high temperature;
- precipitation methods – based on precipitation of phosphates from phosphorus acid by calcium oxide or by calcium carbonate;
- chemical methods – based on the direct reaction of phosphorus acid with calcium oxide, hydroxide or carbonate.

Table 1 presents basic types of feed phosphates produced in the world and their production methods [6, 12, 17].

Table 1. Types of calcium feed phosphates used

Phosphates type	Content [%]		Weight ratio Ca : P	Production method
	P	Ca		
MCP – monocalcium phosphate	21–22	5	≤ 0.8 : 1	precipitation, chemical
DCP – dicalcium phosphate	18–20	≥ 21	≤ 1.15 : 1	precipitation, chemical
TCP – tricalcium phosphate	≤ 18	≥ 35	1.9 : 1	chemical
DFP – defluorinated phosphate	≤ 14	≤ 22	~1.5 : 1	thermal
DFP, CaNaP – tricalcium phosphate with sodium content	18–18.3	32–33 and 4–5 Na	1.9 : 1	thermal

Until 1993 only CaNaP phosphate was produced in Poland [7–9, 15, 19], using a thermal method involving calcining of an apatite, soda and phosphorus acid mixture in rotary kilns at a temperature of ~1800K. The greatest hazard for the environment were emissions of dust, acidic fumes and also hydrogen fluoride [7] which were absorbed in lime milk to form a calcium fluoride slurry. This was released into a sedimentary pond, in which over 200,000 Mg of sludge accumulated [3, 9, 15]. In 1990–1992 the method of thermal feed phosphates production was modernized. The modifications implemented were as follows [7–9, 13]:

- introduction of phosphorus salt instead of phosphorus acid and soda ash, which allowed for the elimination of the soda, apatite and phosphoric acid mixing stage (elimination of acid fumes and dust forming during mixing); the use of phosphorus salts also resulted in a 15% decrease of natural gas consumption;
- introduction of recycling of oversize particles (containing > 0.5% F), which increased the efficiency of the process;
- substitution of pneumatic transport with mechanical transport, which limited dust emissions.

In spite of modernization, annual production of 20,000 Mg of CaNaP caused emission of 6 Mg of fluorine into the atmosphere, and annual storage of 2,800 Mg of calcium fluoride [7–9, 13].

Production of feed phosphates using low-temperature endothermic technology was implemented in 1993 in Cracow inorganic Works "Bonarka" on the old DFP unit (in order to keep investment costs to a minimum) [9, 13]. Thermal defluorination substituted with drying in 400K resulted in a decrease of natural gas consumption exceeding 95%. The technology was waste-free and emission of fluorine compound was eliminated. However, there were problems with product quality due to the old equipment used (especially in the dedusting and charge preparation stages). For these reasons the process had a production yield of 90% [20].

An entirely new, waste-free unit of DCP feed phosphate production was designed on the basis of this method for the Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk [15]. In 1995, a low-temperature, endothermic method was implemented in the "Silikaty" Works in Klucze. This method is based on a strongly exothermic reaction of calcium oxide and phosphoric acid. The heat of the reaction was used to evaporate water that contained phosphoric acid and water formed in the process reactions [11]. The unit was designed to use cleaner production methods, especially "waste reduction at source" [11, 19].

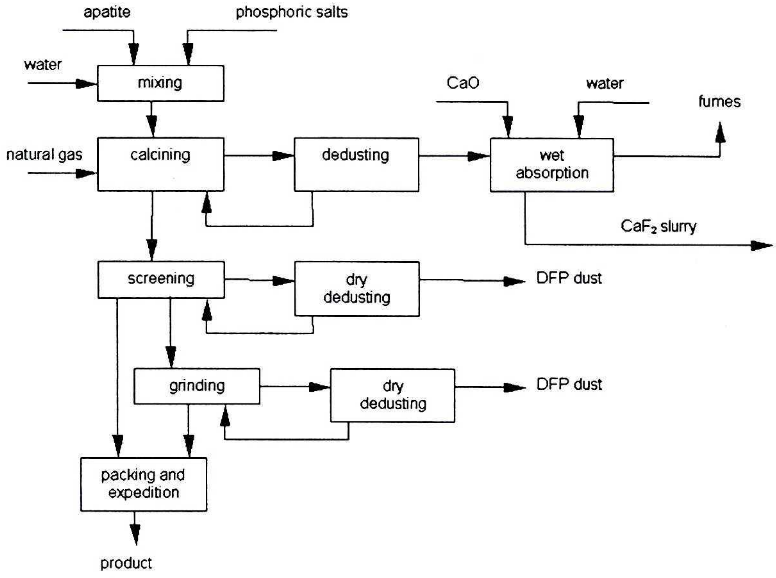

Fig. 1. Flow-sheet of DFP production by a modernized thermal method [1, 18]

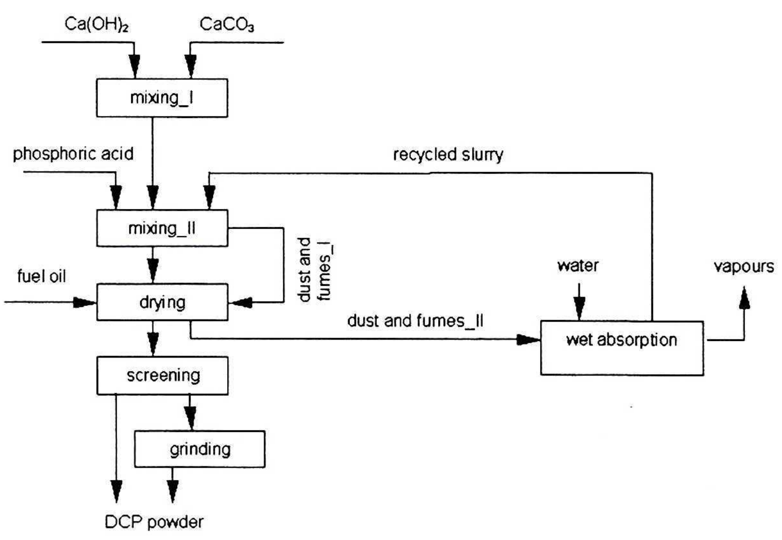

Fig. 2. Flow-sheet of DCP production by a low-temperature endothermic method in Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk [13]

Table 2 and 3 present a summary of process figures and quantities of produced waste, for different methods and different units of feed phosphates production. The data was calculated per 1000 kg of P_2O_5 in the product, due to the differences in the composition of the product depending on the technology and unit used.

Table 2. Comparison of process figures for different methods of feed phosphates production (in 1000 kg P_2O_5 in product) [4, 7–9, 14, 15]

Raw materials	Technological method / installation / product [kg]				
	Thermic classical "Bonarka", DFP	Thermic modified "Bonarka", DFP, DNaP	Low-temperature endothermic "Bonarka", DCP	Low-temperature endothermic "Fosfory", DCP	Low-temperature exothermic "Silicaty" MCP, DCP
Apatite	2221	2184.5	–	–	–
Phosphoric acid 100%	473	–	1446	1344	2017
CaO	180	180	–	–	805
$Ca(OH)_2$	–	–	361.5	463	–
Sodium salts (as Na_2O)	256[1]	235[2]	–	–	–
Water	500	500	200	590	250
Natural gas [m^3]	364	328	36	–	–
Electric energy [kWh]	206	182	181	116	152.5
Fuel oil	–	–	–	87	–

[1] – soda, [2] – penthsodium triphosphate (TPFS)

Table 3. Comparison of quantities of waste materials produced in different methods of feed phosphates production (in 1000 kg P_2O_5 in product) [4, 7–9, 14, 15]

Waste material	Technological method / installation / product [kg]		
	Thermic modified "Bonarka", DFP, DNaP	Low-temperature endothermic "Bonarka", DCP	Low-temperature endothermic "Fosfory", DCP
F_2	0.1735	0.055	0.00037
NO_x	0.0061	–	0.11416
SO_2	0.00012	–	0.1239
P_2O_5	37.044 volatile 10.2 liquid	22.5	0.1576
CaO	41.372	14.8	0.1327
Na	4.49 volatile 7.2 liquid	–	–
Soda	0.061	–	–
SiO_2	0.0021	–	–
Fe_2O_3	0.0027	–	–
Al_2O_3	0.0029	–	–
H_2O	135.9	36.14	–
CaF_2	153.9	–	–
$CaCO_3$	32.6	–	–
Mg	–	–	–
Pb	–	–	0.00001
As	–	–	0.000004
CO_2	–	–	0.01239

COMPARISON OF FEED PHOSPHATE PRODUCTION METHODS USING THE LCA

Life Cycle Assessment (LCA) is an environmental management technique. The main advantage of LCA is that it takes into consideration all the factors, which can potentially affect the environment. This allows for the identification of stages of the production process that are most damaging to the environment. Use of LCA produces quantifiable results as it allows for both global appraisal of production process as well as assessment of particular phases. The basis for LCA is the analysis of real input and output data of an industrial process. It is useful for producers who wish to introduce cleaner production processes and achieve a competitive environmental position on the international market [16].

This technique can be applied in different scopes, which depend on established system boundaries [7, 15, 16, 19] (Fig. 3):

- cradle to grave – from mining of raw materials, through production of semi-finished products, products, use of product, its final utilization;
- cradle to gate – from mining of raw materials to product obtaining;
- gate to gate – only in production process phase;
- gate to grave – from product obtaining, through their usage, until final disposal.

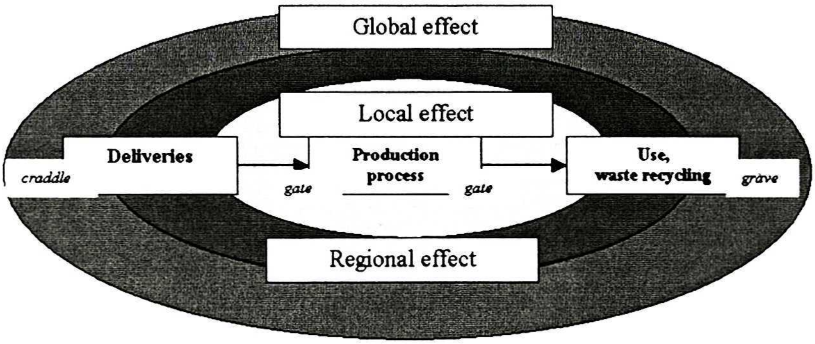

Fig. 3. Visual presentation of the scope of LCA [9]

Main phases of LCA techniques and procedure of their realization are presented in Figure 4.

LCA was performed with Sima Pro 5.0 software produced by PRe Consultants [17], using Eco-indicator 99 method [10], that proposed three areas of impacts (damages) on natural environment [7]:

- damage to human health (unit is *DALY – Disability Adjusted Life Years*) they enable to define relative decrease of human life time caused by harmful interactions; it was an elaborated model for effects of carcinogenic interactions, climatic changes, ozone layer depletion, ionising radiation;
- damages to ecosystem quality (expressed as percent of species decaying on the analyzed area as a result of impact on environment (i.e. % vasc. plant species*km^2*yr);
- damage to mineral and fossil fuels resources evaluated with quality of remainder for mining mineral raw material, included mineral fuels; it is defined as energy consumption in MJ/Mg of these exploited resources, i.e. MJ surplus energy.

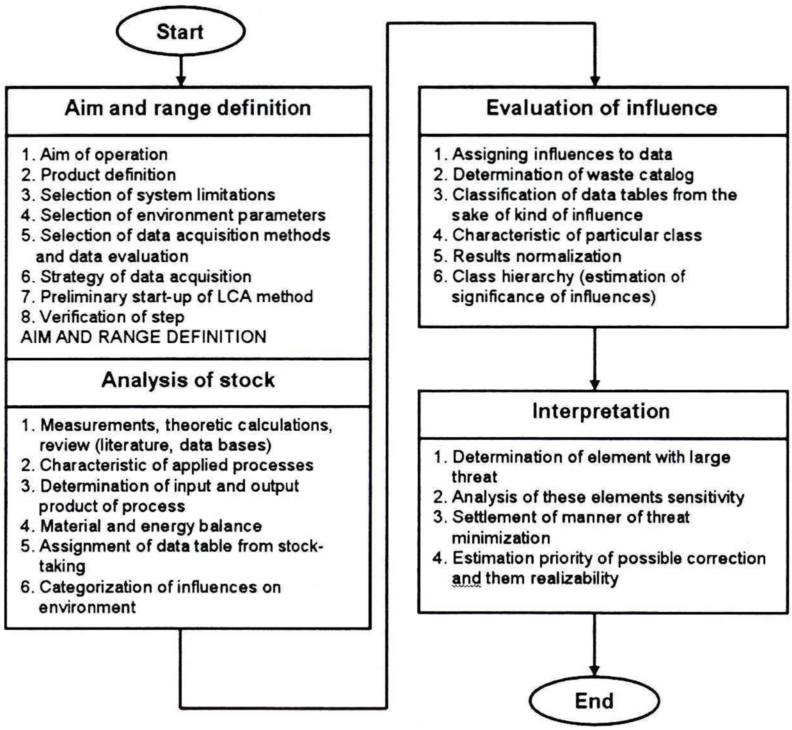

Fig. 4. Procedure of realization of LCA [18]

The model of environmental impact can be evaluated on the basis of the longest time scale (the egalitarian version – E), the short term perspective (the individual version – I), and the long term perspective (hierarchical version – H). These evaluation versions are part of evaluation systems of importance degree [10]. The differences of each version are presented in Table 4. In this research LCA was carried out using Ecoindicator 99 for version (I) due to the short functioning time of the processes being evaluated.

Table 4. Percentage share of impact areas for weighing models H, E and I [10]

Influence areas	Relative participation of influence categories [%]		
	E	H	I
Human health	30	30	55
Ecosystem quality	50	40	25
Resources	20	30	20

The Sima Pro 5.0 software presents the results of LCA in the form of histograms and "trees" of raw material and processes. Histograms are diagrams in column form, which show dependencies between impact categories and individual processes and materials.

A "tree" of raw materials and processes has a block form. A pillar is placed in each block, which shows the share of raw materials and processes in the process or life cycle being analyzed. The structure of the "tree" enables a detailed review of raw materials and their share in the processes. Performing LCA with the Sima Pro 5.0 software involves loading process figures characteristic of the materials produced (material and energy consumption balances) and waste into databases of programs, and selection of an analysis method (Ecoindicator 95, Ecoindicator 99 – egalitarian, individual or hierarchic, Outpoints 97 or others). The databases initially introduced in the Sima Pro 5.0 software were: *BUWAL250*, *Data Archive*, *ETH-ESU 96*, *IDEMAT 2001*, *Industry Data* and *Methods*. The user is able to create a personal database or work with existing data. One can, however, experience difficulties in the introductory period caused by the age of the database (2001) and the fact that it was prepared for the Dutch market.

In the analysis, phosphoric acid from Sima Pro 5.0 libraries (under the name of "phosphoric acid ETH T") was used. There was no data in these libraries for "*technological water*" so it was substituted with "*water demineralised ETH T*" (the last letters of names denote the name of the database). In the databases for raw materials there was no term "*apatite*", so data for "*apatite*" according to [6] were introduced. Due to the absence in the databases of "*calcium fluoride*" it was substituted with "*calcium*" and "*fluoride ions*". "Trees" of feed phosphates production processes for the three methods of production analyzed are presented in Figs 5–7.

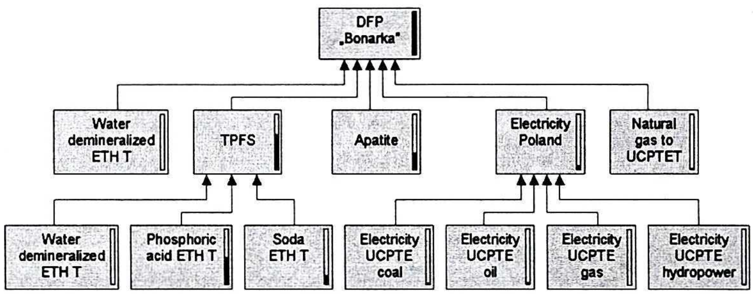

Fig. 5. Material "tree" for a DFP production process using a modernized thermal method in Cracow Inorganic Work "Bonarka" – data for 1 kg P_2O_5

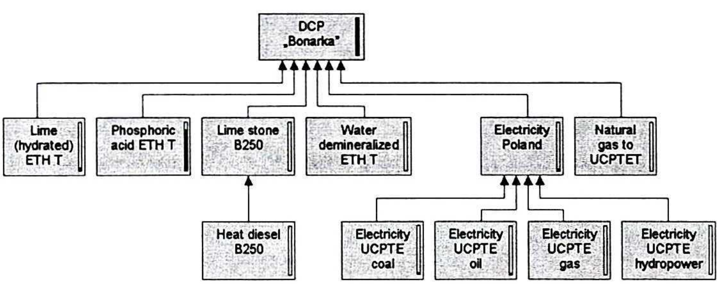

Fig. 6. Material "tree" for a DCP production process based on a low-temperature endothermic method in Cracow Inorganic Work "Bonarka" – data for 1 kg P_2O_5

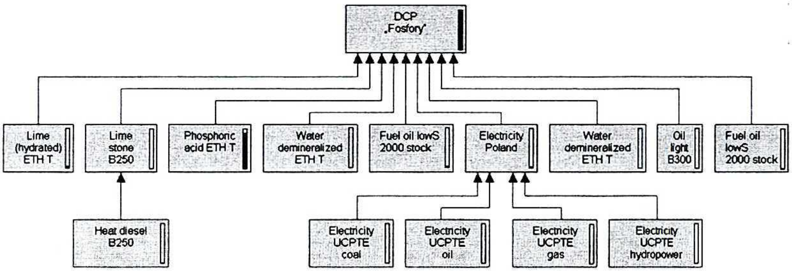

Fig. 7. Material "tree" for a DCP production process using a low-temperature endothermic method in Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk – data for 1 kg P_2O_5

Figs 5–7 show that the main factor affecting the results of LCA was phosphoric acid (the column near the name of compounds represents its share in the process – in Figs 5–7 the largest one is next to phosphoric acid ETH T). Electric power had marginal significance in the processes analyzed.

Based on inventory results, the environmental impact was calculated on three damage categories (endpoints), i.e. human health, ecosystem quality, and resources (Fig. 8). The result is presented in the form of histograms of comparable processes. The highest calculated effect score is scaled to 100%. This means the materials can only be compared on the basis of their environmental impact.

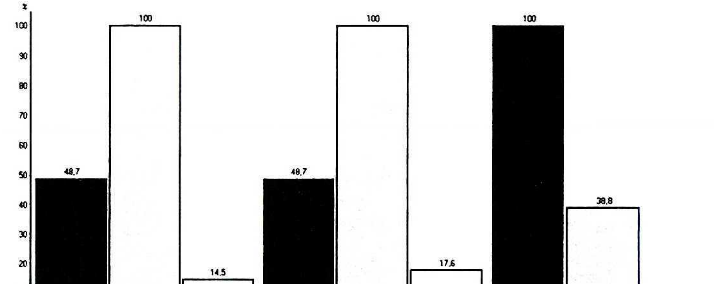

Fig. 8. Comparison of three processes of feed phosphates production (evaluation of environmental hazard from the point of view of impact categories)

In three end-points categories, evaluation of DCP and DFP processes from different units returns the best results for DCP "Fosfory", i.e. 14.5% in the area of human health, 17.6% for ecosystem quality, and 5.49% in the area of resources. But there is a significant difference for the DCP processes in "Fosfory" and "Bonarka" (in the area of ecosystem quality the value is 100% in DCP "Bonarka" and only 17.6% for DCP

"Fosfory"). The reason for such large differences in the environmental impact of these two DCP units may be:

- the technical condition of the unit (DCP "Bonarka" is an old unit for DFP adapted to DCP production, while DCP "Fosfory" was designed from scratch);
- differences in dust removal stages (in DCP "Bonarka" there were dry dedusting stages, while a wet absorption unit was designed for DCP "Fosfory").

Environmental impact can also be calculated and analyzed for 10 mid-point categories, e.g. minerals, land use, acidification, etc. For three analyzed methods in the minerals category the DCP "Fosfory" works shows 5.54% compared to 38.8% at DCP "Bonarka" and 100% at DFP "Bonarka", while in the land use category DCP "Fosfory" shows 16.4% compared to 45.3% for DFP "Bonarka" and 100% for DCP "Bonarka". Generally, for 10 impact categories DCP "Bonarka" shows the highest (100%) impact 9-times, and DCP "Fosfory" shows the lowest values 8 times. Even based on such a predominate position of DCP "Fosfory" it could be difficult to conclude that this is the best technological method. The interpretation of these scores (in 10 mid-point categories) may be confusing, because it would be difficult to compare score for acidification, with score for climate change, etc., it could be done only if all the scores for one process are higher than those for another in every category.

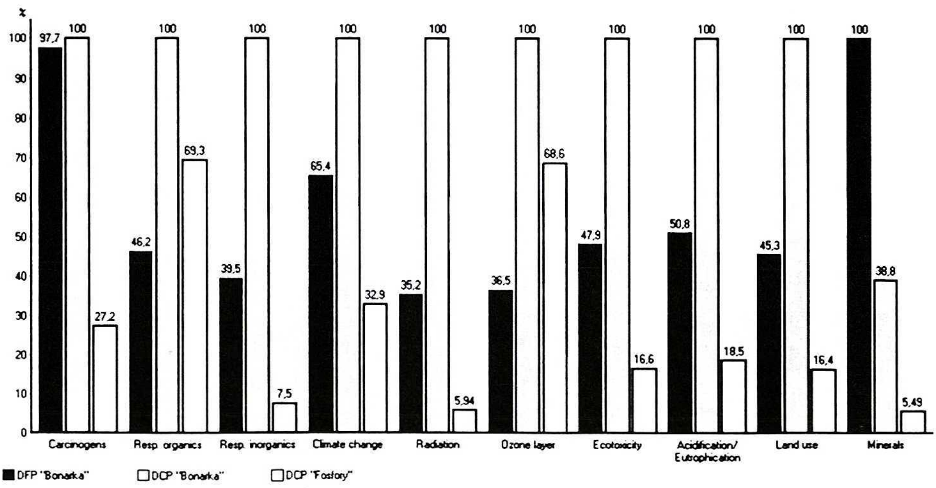

Fig. 9. Comparison of three processes for feed phosphates production (evaluation of hazard broken down by impact categories)

The histogram analysis showed that the best method (according to this method of analysis) is the low-temperature endothermic method used in the "Fosfory" DCP unit. The results for DCP "Bonarka" were worse than those for the old DFP "Bonarka" method. However, this could be due to the fact that the Sima Pro software accounts for decreases in the material consumption of energy-consuming processes to the smallest degree.

CONCLUSIONS

On the basis of performed LCA it was possible to formulate following conclusions:

- LCA showed that the modern low-temperature endothermic method designed (DCP) in Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk is the most environmentally friendly (based on the databases of the Sima Pro 5.0 software with the Ecoindicator 99 system in individual form).
- DCP method applied in Phosphoric Fertilizers Works (PFW) "Fosfory" in Gdańsk shows the lowest value (8 out of 10) in mid – point categories, mainly due to effective utilization of resources and land use.
- The main factor affecting the results of LCA for every analyzed methods was phosphoric acid, whereas electric power had marginal significance in the processes analyzed.
- LCA can be an effective method of evaluating potential environmental impact. However, the results can be surprising (even in comparative analysis). It should be compared with other types of environmental assessment.

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