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Environmental and Economic Assessment of Feed Phosphate Technology Modernization

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Abstract

Here we have briefly present the progress in technology of feed phosphates produced in Poland with different methods. Modernization of the production process and changing of the thermal method of defluorinated phosphate production with the low temperature method of dicalcium phosphate production process has strongly influenced environmental and economic figures and product quality. We also present an analysis of the feed phosphate thermal production method in comparison to the newly implemented low temperature process. The evaluation includes environmental and economical indicators. Results allow for estimated modernization as very effective from environmental and economic points of view.

Keywords: environmental assessment, technological quality, feed phosphate

Introduction

Until 1993, only one phosphate feed was produced in Poland: DFP (defluorinated feed phosphate) produced in the "Bonarka" Cracow Inorganic Works with a conventional method consisted in the decomposition of apatite and expelling of fluorine compounds by heating in temperatures of about 1723 K apatite with the addition of phosphoric acid and sodium carbonate. The final reaction is:

$$Ca_5(PO_4)_3F + H_3PO_4 + Na_2CO_3 = 2CaNaPO_4 + Ca_3(PO_4)_2 + CO_2 + H_2O + HF$$

The emitted hydrogen fluoride and other waste gases were absorbed in lime milk and formed a suspension of calcium fluoride, which was dumped into settling ponds [1]. A basic flow sheet of the thermal method is presented in Fig. 1.

The obtained DFP (CaNaP) contained 18% P, 46% CaO, 5% Na to 0.3% F. The product is used for manufacturing animals feed (0.5-1.5% in different feeds [1]). The basic problem of this method was fluorine emission (to 8g/lt of product) and produced wasted calcium fluoride slurry (80 kg/lt DFP). Only a small part of these wastes is utilized in cement production (2000 t/y). A disposal located

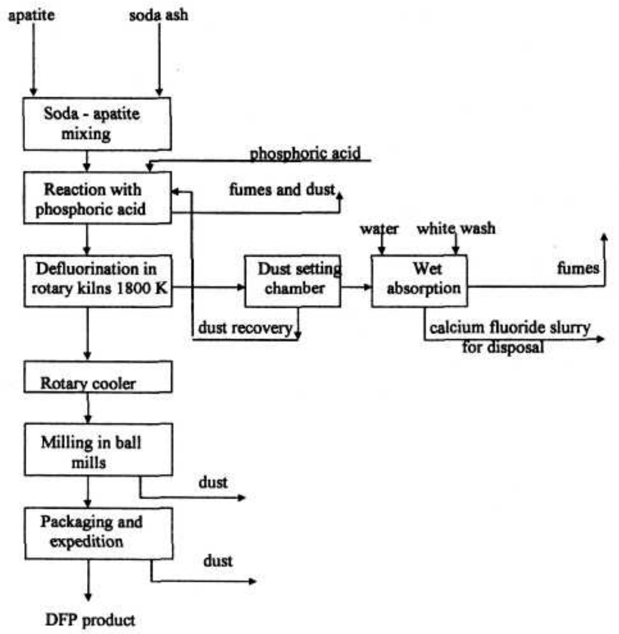

Fig. 1. Conventional thermal method of the DFP production process.

1 km from the centre of Cracow contains over 200,000 t of waste (disposed during 20 years of DFP production) and is serious problem for the city [2, 3].

Technological modernization involves using sodium phosphate instead of phosphoric acid and soda ash. This eliminates the first stage of mixing (soda ash with apatite) and emissions of acidic fumes occurring as a result of soda ash-apatite mixing and phosphoric acid reaction. Using sodium phosphates allows a decrease of over 15% natural gas consumption per It of produced DFP. Implementation of a recirculation system of DFP oversize particles (with too large fluorine content) allowed better product quality, with Fluor levels below 0.25% [1-4]. Changing a very old pneumatic system for a mechanical one (screw conveyors) decreased dust emissions to the environment [3].

DFP produced by the thermal method even after modernization made production costs too high to be competitive with other phosphates offered on the Polish market.

Experimental Procedure

A general process reconstruction resulted in the implementation of a new dicalcium phosphate (DCP) low-temperature technology in 1993 [4, 5]. This wasteless process was realized at the DFP unit with low investment costs. A new method based on the reaction of calcium hydroxide with phosphoric acid follows the formula:

$$Ca(OH)_2 + H_3PO_4 = CaHPO_4 + 2H_2O$$

Product contained 41-42% P_2O_5, 2% Mg and max. 0.2% F and was in compliance with the European standard. The new technology passed practical examination, but some old equipment (particularly the dedusting and raw materials preparation units) were not adaptable to the DCP process. These resulted in inferior product quality and in rather low production yield (~ 90%) [6]. A flow sheet of this method is presented in Fig. 2.

The process was free of solid waste, and fluorine emissions were eliminated too. Defluorination at a temperature ~ 1773K changed with a drying temperature of ~ 400K. This resulted in very low energy consumption. Total production costs for the DCP production process are comparatively about 33% lower than the thermal method.

The new DCP production process was named "low-temperature endothermic". Further technological modernization results in change calcium hydroxide-dolomite mixture used as raw material with calcium carbonate and elimination of the dolomite as raw material. These are rather not advantageous.

The produced DCP was competitive on the Polish market but dust emissions were still rather high and maintenance, repairs and labour demand costs were relatively high. To resolve this situation two possibilities were considered: the modernization of the old unit and the building of a new unit in another factory. Technical and economic analysis demonstrated building of the new unit to be more profitable [10].

Our research [6-9] has allowed us to propose new technological and engineering solutions. A new DCP unit was built in 1995 in the "Silikaty" Klucze factory. This project was preceded by detailed analysis made with the "reduction of source method" [10] and research suggested a new type of "low-temperature exothermic" technology based on the reaction of calcium oxide and phosphoric acid.

$$CaO + H_3PO_4 = CaHPO_4 + H_2O$$

A flow sheet of this process is presented in Fig.3

New technological solutions, modern project apparatus and equipment allow high production process yield (to 99.5%) to be achieved with very low energy consumption. Using a project time "reduction at source" analysis methodology allowed us to eliminate practically all dust emissions and fully protect the natural environment. Computerized process control resulted in higher product quality and low labour demand.

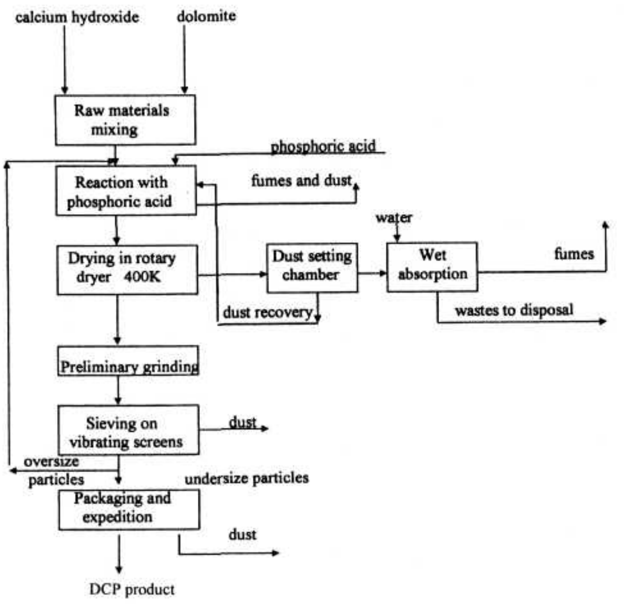

Fig. 2. Low-temperature endothermic DCP production process realized on DFP unit.

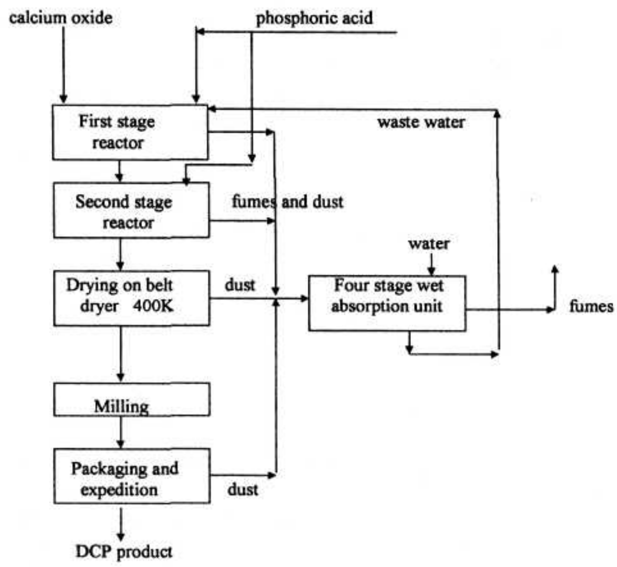

Fig. 3. Low-temperature exothermic DCP production process realized on new unit.

Table 1. Quality of some produced feed phosphates.

DCP producer/ Method	Content [%]			Solubility in [%]		Heavy metal concentration [ppm]								Estimation of the quality			Remarks
	P	Ca	F_{max}	0.4% HCl	citric acid 2%	Zn	Cu	Mn	Pb	Cd	As	Hg	Cr	Granula-tion	Package	General	Estimation of the level
- top European Rhone Poulenc BASF Albright - Wilson Tessenderloo	to 20 17-20 17-21 18.1	24-25 24-27 24-28 24	0.1 0.1 0.1 0.15	> 99.5 > 99.5 > 99.5 > 99.5	> 99 > 99 > 99 > 99	370 8-156 7 –	37 15-27 5 –	117 30-61 51 –	19 25-51 51 8	9 3-8 1 0.9	< 1 < 1 < 1 2.5	< 0.1 < 0.1 < 0.1 0.03		pulver or granulated E - 4	E - 4	E - 4	E-4 - -European E-3 - good E-22 - average E-1 - slight
Bonarka -DFP thermal method	17.5 -18.5	32-34	0.3	> 98	> 98	120	40	70	15	1.5	3	< 0.1	15	pulver E-2	E - 1	E - 1	5% Na content
Bonarka -DCP low-temperature alternative I	17-18	24-27	0.2	> 99	> 98.5	80	40	30	5	0.5	2	< 0.1	16	pulver	E - 1	E - 2	2% Mg content
alternative II	17-18	24-27	0.2	> 99	> 98	80	43	35	4	0.5	2	< 0.1	15	E-2	E - 1	E - 2	
Silikaty - DCP low-temperature	17-19	23-27	0.15	> 99.5	> 99	75	37	45	3.4	0.2	1.5	< 0.1	10	pulver E - 3	E - 3	E - 3	1% Mg content
Polish standard BN-84/9164-23	16-21	21-30	0.2-03	–	–	–	–	–	< 30	–	< 10	–	–	pulver 90% < 0.3 mm	50 kg paper bags, bulk		

According to detailed technical and economic analysis, production costs for the exothermic alternative of the low-temperature DCP technology were estimated to be 30% lower than in the endothermic process. At the new unit we could produce all dicalcium phosphate grades (with P content from 16 to 20%).

Table 1 presents a detailed description of dicalcium feed phosphate quality produced with different methods used in Poland and also sealed on the Polish market product of top European producers. Macro- and microelements, impurities (especially heavy metals), and packaging quality are compared.

Comparison results of DCP produced in Poland with low-temperature method as comparable with European products. In some cases packing is also good quality.

Discussion

Environmental assessment of the change DFP production with DCP production were made on base process analysis in the quantification of cumulated calculation [11-12]. This method basis determine on the process material balance effects of fume and dust emissions to the - cumulated hazard ZS defined as a sum of the emission E or dump O of the same type substances in process phases sequences *f=1....n:*

$$ZS_E = \sum_{f=1}^{n} E \tag{1}$$

$$WS = \frac{ZS}{P} \tag{3}$$

- cumulated hazard index WS defined as the quotient of cumulated hazard ZS and production quantity P:

- cumulated hazard index with allowances for toxic coefficient K:

Toxic coefficients are determined on our method basis

$$\overline{WS} = WS \cdot K \tag{4}$$

[3, 11-12], with late modifications. For fume and dust emission K is defined as quotient of the acceptable concentrations of SO_2 and analyzed substances, multiplicand with 1 t SO_2 to the air emission fee (in US dollars). For solid waste dump - K is a quotient of analyzed toxic substance concentration in waste and lowest acceptable concentration of this in the waste, multiplicand with It IV category waste dump fee (in US dollars).

The sum of WS coefficients for all phases of the process allow us to determine cumulated hazard total coefficient GWS (as appropriate for gases, wastes and solid wastes):

$$GWS = \sum_{f=1}^{n} \overline{WS} \tag{5}$$

Table 2a. Calculation of the cumulated hazard total coefficients of the feed phosphate production process (capacity 20,000 t/y).

Process phase	DFP production with the termal method							
	Dust and fume emission [t/y]							
	Apatite	Soda ash	Phosphoric acid	DFP dust	Calcium oxide	Sulphur dioxide	Nitrogen oxides	Fluorine
Raw materials unloading and transportation	150	20	–	–	20	–	–	–
Preparation and transportation of the dry mixture	450	50	–	–	–	–	–	–
Phosphoric acid dosage into the mixture	5	6	50	–	–	–	–	–
Calcination in rotary kiln, dedusting, absorption	0.5	0.5	–	15	–	0.001	0.05	0.5
Milling of the product	–	–	–	225	–	–	–	–
Sieving of the product	–	–	–	25	–	–	–	–
Product transportation, packaging and expedition	–	–	–	500	–	–	–	–
Cumulated hazard ZS	605.5	76.5	50	765	20	0.001	0.05	0.5
Cumulated hazard index WS	0.030275	0.03825	0.0025	0.03825	0.001	5.00E–07	2.50E–05	3.25E–03
Toxicity coefficient K	31	31	98	31	31	49	73	978
WS = WS*K	0.938525	0.118575	0.95	1.18575	0.031	0.00000155	0.0001825	0.31785
GWS — dust and fume emission	2.686865							
Calcium fluoride slurry dump [t/y]								
ZS	2800							
WS	0.14							
K	20							
WS = WS * K	9							
GWS — solid waste dump	2.8							
GWS — sum	5.486865							

The sum of GWS coefficients determines total coefficient for all wastes dumped and emitted from the process.

Comparative analysis of the dump, emission and cumulated hazard coefficients for the old DFP process and realized different new alternatives of DCP production processes are presented in Tables 2a and 2b.

Calculated cumulated hazard total coefficients are as follows:

- DFP thermal production process $Z\ GWS^1 = 5.486865$
- DCP Bonarka low-temperature endothermic process $\Sigma\ GWS^2{}_a = 2.181715$ (alternative I) $\Sigma\ GWS^2{}_b = 2.5716$ (alternative II)
- DCP Silikaty low-temperature exothermic process $\Sigma\ GWS^3 = 0.212$

On coefficient GWS base could we calculate relative index of the natural environment hazard decrease WZZ defined as quotient [in *%]* of the difference Σ GWS indexes for the old and new processes and Z GWS of the old process.

$$WZZ = \frac{\Sigma\ GWS^P - \Sigma\ GWS^N}{\Sigma\ GWS^P} \cdot 100\% \qquad (6)$$

Comparing three alternatives of the new low-temperature process to the old thermal method calculates WZZ indexes accordingly [in %] 60.2, 53.1 and 96.1

Estimating economic effects of the new feed production process implementation taken in advance comparison of the production costs and energy and materials consumption index.

Energy consumption index X_J is defined as a sum of energy consumption in all phases of the process (GJ/t of product).

This quantity for the DFP production process was $X_J^P = 8.375$ GJ/t, for low-temperature endothermic DCP process in Bonarka $X_J^N = 0.502$ GJ/t for both alternatives. The DCP Silikaty low-temperature exothermic process has energy consumption index $X_J^N = 0.3$ GJ/t. So big differences between thermal and low-temperature methods resulted in decreasing natural gas consumption figures from 250 to 15 m^3/t of product and electricity from 260 to 135 kWh/t of product (in Bonarka). The new projected Silikaty DCP unit has even better consumption figures.

Material consumption index is a sum of the all raw material quantities used for It of the product manufacture. In thermal method and in first alternative Bonarka process material consumption indexes were the same $M^p = M^N = 1250$ kg/t of product. In second Bonarka alternative this index increased to $M^N{}_1 = 1825$kg/t.

Comparing production costs (1997 year price basis) helped us estimate these figures as follows:

$K_1 = 1074.5$ zl/t for DFP Bonarka product

$K_2 = 714.3$ zi/t for DCP Bonarka product according alternative I

$K_3 = 705$ z!/t for DCP Bonarka alternative II

$K_4 = 538.4$ zl/t for DCP Silikaty

Calculated indexes of the ecological and economic effects of feed phosphate production process modernization were the basis of complex evaluation of the process modernization made with complex quality method, characterized

Table 2b. Calculation of the cumulated hazard total coefficients of the feed phosphate production process (capacity 20,000 t/y).

Process phase	DCP lowtemperature production production process alternative (capacity 20,000 t/y) – dust and fume emission (t/y)									
	Bonarka endothermic I				Bonarka endothermic II			Silikaty exothermic		
	Calcium hydroxide	Phosphoric acid	Dolomite	DCP dust	Calcium carbonate	Phosphoric acid	DCP dust	Calcium oxide	Phosphoric acid	DCP dust
Raw materials unloading and transportation	50	–	8	–	120	–	–	35	–	–
Preparation and transportation of the dry mixture	50	–	8	–	60	–	–	35	–	–
Phosphoric acid dosage into the mixture	5	50	2	–	12	75	–	4	6	–
Calcination in rotary kiln, dedusting, absorption	300	–	50	200	450	–	200	4	–	10
Milling of the product	–	–	–	10	–	–	10	–	–	10
Sieving of the product	–	–	–	70	–	–	70	–	–	10
Product transportation, packaging and expedition	–	–	–	500	–	–	500	–	–	10
Cumulated hazard ZS	405	50	68	780	642	75	780	78	6	40
Cumulated hazard index WS	0.02025	0.0025	0.0034	0.039	0.0321	0.00375	0.039	0.0039	0.0003	0.002
Toxicity coefficient K	31	98	31	31	31	98	31	31	98	31
WS = WS*K	0.62775	0.245	0.1054	1.209	0.9951	0.3675	1.209	0.1209	0.0294	0.062
GWS – dust and fume emission	2.18715				2.5716			0.212		
Σ GWS	2.18715				2.5716			0.212		

by qualitatively compared technologies [2, 4]. According to complex quality method value assessment (Wj), importance degree (aj) and assessment value criterion (w_c) were arbitrarily assumed.

For complex evaluation of the technology progress total cumulated hazard total coefficients, energy and material consumption indexes, quality level and production costs evaluation were taken in advance.

These could be also accepted as estimation of the technological quality [13] according to the equation:

$$Q_T = Q_{ED} + Q_E + Q_M + Q_K + Q_J \quad (7)$$

Calculations of the complex evaluation for the technological quality are presented in Table 3.

Calculated in Table 3 technological quality figures Q_T for low-temperature method alternatives much lower than for thermal. The best low temperature Q_T figure 299 point is 75% lower than the thermal method figure. This very effective modernization resulted from a decrease of the natural environment hazard and energy consumption index.

Table 3. Complex evaluation of the technological quality for feed phosphate production processes.

Technology quality characteristic	Feed phosphate technology alternative figures (F)				Technologic quality assessment			Technologic quality [points] $Q_T = F/w_c * a_i$			
	DFP Bonarka thermal method (A)	DCP Bonarka low-temperature I (B)	DCP Bonarka low-temperature II (C)	DCP Silikaty low-temperature (D)	Value assessment criterion w_c [1 point =]	Value assessment W_i [points]	Importance degree a_i	A	B	C	D
Cumulated hazard total coefficient GWS	5.4869	2.1817	2.5716	0.212	0.055	0-100	4.0	400	159	187	15
Energy consumption index X [GJ/t]	8.375	0.502	0.502	0.3	0.084	0-100	3.0	300	18	18	11
Production costs index K [zł/t]	1074.5	714.3	705	538.4	10.74	0-100	3.0	300	200	197	150
Material consumption index M [kg/t]	1250	1250	1825	1090	18.25	0-100	1.5	103	103	150	90
Product quality (as in Table 1)	E-1	E-2	E-2	E-3		0-100	1.0	100	66	66	33
Technologic quality Q_T							Σ	1203	546	618	299

Confirmed it also very low technological and ecological level, and low economic effectiveness too of the DFP production process with thermal apatite defluorination method changed now with a much move profitable low--temperature DCP production process.

Conclusions

Realized implementation of new low temperature DCP feed phosphate production process has changed energy consumption and dangers for the natural environment through DFP thermal defluorination of the apatite technologic process with more environmentally safe DCP technology. This implementation characterized low level of investment costs and effective economic figures.

Environmental assessment of the change DFP production with DCP production were made on base process analysis in the quantification of cumulated calculation. This method on the process material balance basis determines effects of the fume and dust emission to the air and waste or solid waste dump.

Calculated indexes of the environmental and economic effects of the feed phosphates production process modernization were the basis of complex evaluation of the process modernization made with complex quality method, characterized by qualitatively compared technologies.

This method allows versatile comparison of modernization degrees of the technology connected with the changed DFP process and DCP technology. Three new alternatives of DCP low-temperature production process were evaluated, too. Complex evaluation of the process modernization method confirmed as suitable for determination of the effectiveness of realized feed phosphate technology modernization. It could also be used for other chemical processes. With this method it is possible to indicate some new modernization direction on the basis of the analysis of environmental and economic figures.

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