

Modification of manufacturing process of feed phosphates

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Introduction

Feed phosphates are of great importance among the feed materials produced for intensification of livestock farming. They are produced and applied in relatively large quantities, although for several years, both their production and use were often characterized by an unfavorable opinion resulting from the potentially adverse impact on the environment. Emergence of the “mad cow” disease BSE (bovine spongiform encephalopathy) and the Creutzfeldt-Jakob disease, which genesis was considered in the use of meat and bone meal - the main competitor of feed phosphates, have contributed to the change of this opinion. The products obtained in the chemical processes appeared to be much safer, which resulted in restrictions, introduced into the European legislation, on the use of products based on the utilization of products derived from slaughter wastes. Feed phosphates are one of the most important factors in the intensification of livestock farming [1 ÷ 3]. They enable compensation of phosphorus and calcium deficiency in the feeds. The estimated overall production capacity of worldwide industrial plants is about 4.5 mln Mg/year. The national prospective, differentiated by various experts, indicate the minimum demand of 90 thousand Mg/year, and in the next few years up to 130 ÷ 150 thousand Mg. Another important problem of the production of feed phosphates is introduction into their composition other chemical components which are essential for intensive methods of livestock farming. The most important are preparations containing calcium, sodium and selenium. Feed additives such as micronutrients or ultra-trace elements are applied in much smaller amounts. In this respect, products containing copper, zinc, iron, magnesium, cobalt and iodine can be distinguished among the feed materials.

The essence of the trends in development of the technology of feed phosphates production observed in recent years is aimed at reduction of manufacturing costs while preserving the basic operating parameters and better adjustability to the physicochemical properties of their operational applications. For this purpose, such issues like power consumption of manufacturing process, source of phosphorus compounds, water consumption balance, optimization of operations and unit processes used in technology, development of new apparatus and equipment used in the manufacturing process, are considered. These endeavors resulted in significant long-term manufacturing costs reduction, achieved by the leading world producers which cause price stabilization or even reduction for these products on global markets. In consequence ongoing elementary and development research of the process and the implementation of innovative alterations in techniques of feed additives manufacturing is required. Manufacturers that haven't changed their technologies in recent years are exposed to significant difficulties in range of relatively increasing production costs what makes their endurance, among the producers in a free market economy in Europe, limited and sometimes even impossible. The same situation can be found also in domestic industry. This paper focuses on several different technological options that allow to determine conditions under which the production of feed phosphates at reduced water amount in the process is possible. This is directly related to the possibility of reducing the energy demand of the process and therefore unit costs.

Development in technologies of feed phosphates production

Feed phosphates are mainly calcium, sodium, ammonium, magnesium hydrogen or dihydrogen phosphates [4,5]. Moreover, specific products such as urea-phosphoric acid adduct or liquid ammonium polyphosphates are also applied. Feed phosphates are currently apart from phosphate fertilizers (80%) and household chemical products (12%) the most important industrial products of inorganic phosphorus compounds (5%). Their development is directly correlated with the requirements for food production and thus the regional population of our planet. For this reason, over the past 15 years, 60% of the production capacities of new industrial plants have been located in China. The output of only one of the new industrial installations in this country, owned by the company Xuzhou Haijiang Imp. & Exp Trade Co., Ltd is 100 thousand Mg/month. An annual production capacity of 4 million Mg (about 85% of world production) is reached by industrial plants located in 3 regions and 4 countries:

- USA region (Asteairis, Cargill, IMC, Nutra – Flo, PCS, J. R. Simplot)
- European region
- Chinese region
- Industrial plants in Mexico, Japan, South Korea and Canada.

Production of feed phosphates, depending on the type of phosphate raw material, can be classified into one of the following groups:

- Produced from bones
- Produced from mineral fertilizers
- Produced from phosphate raw materials: apatites, phosphate rocks
- Produced from phosphoric acid solutions obtained by „thermal” method, based on absorption of elementary phosphorus combustion product by water
- Production on the basis of phosphoric acid obtained by dissolution of phosphate raw material by sulfuric acid.

Currently, due to the availability of raw materials and energy consumption, methods based on natural products, fertilizers and using high-temperature processing of phosphate raw materials activated by addition of sodium bicarbonate, phosphoric acid and water vapor have less significant application. Also the cost of using in technology phosphoric acid obtained on the basis of elementary phosphorus, which can indeed meet the criteria of high quality product, does not allow for obtaining low unit costs of production, corresponding to the current levels of market prices of those products. The production is dominated by methods that implement the cheapest phosphoric acid obtained by dissolution of phosphate raw material with sulfuric acid, intended mainly for the production of phosphate fertilizers. Before using for the production of feed phosphates, it must be treated primarily in scope of content of fluorine compounds, heavy metals (As, Cd, Pb, Hg) and insoluble substances. The classic process for phosphate feed production consists of the implementation of sequential processes and unit operations:

- Purification of wet-process phosphoric acid from suspension, fluorine compounds and heavy metals
- Filtration of sludges containing impurities
- Neutralization of phosphoric acid

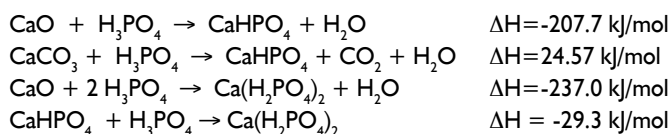
- Feed phosphates crystallization
- Filtration
- Drying
- Crushing and confectioning of product.

Rising prices of phosphate raw materials, high costs of the environment-oriented technical operations, and above all aiming to reduce manufacturing costs emphasised the role of several issues utilized in latest technological solutions, such as:

- Domination of low-grade but cost-effective phosphate raw material used in wet method phosphoric acid production
- Locating the treatment operations of the wet-process phosphoric acid in acid manufactures which positively affects the phosphate efficiency of the feed phosphates production process, furthermore it eliminates significantly amount of solid wastes and improves the economic indicators of the production
- Cancellation of crystallization and precipitation as the unit operations in technology of phosphate compounds production, which allows to limit the amount of water in the method and thus the energy demand of the processes associated with its removal from the installation
- Conducting the process under conditions of higher concentrations of the reactants as a consequence of the revised water balance of the technology
- Elimination of phase separation processes, especially filtration, generating large amounts of stem, washing fluid and sewages streams that are difficult to use directly in the technology, as well as affecting the high level of physically bound water in the product
- Increased concentrations of the reactants in the technology that deteriorate diffusion conditions of the reaction, increase viscosity and the presence of solid phase, forces the use of innovative reactors allowing to obtain under these conditions a homogeneous composition of the reacting mixture (blenders, ribbon mixers).

The concept of the feed phosphates production under conditions that reduce the energy demand of the process

The mainstream technologies in manufacture of industrial feed calcium phosphates (calcium hydrogen phosphates or calcium dihydrogen phosphates) due to energy reasons are dominated by two processes: neutralization of phosphoric acid with calcium compounds and removal of physically bound water which is present in the product after its separation from the stem fluid and washing with water. Neutralization reactions proceed with a significant energy effect:



Reactions are highly exothermic reactions when calcium oxide is used for neutralization of phosphoric acid. However, the removal of physically bound water is connected with expensive drying operation. The moisture content of precipitated calcium phosphates may indeed reach even up to 30% w/w H₂O and the situation is complicated by the fact that this process can't operate at too high temperature. The reason is that reactions of phosphates polycondensation can be initiated even below 200°C. For energy considerations, operating the process under conditions that allow to utilize the heat of neutralization reaction for the reduction of physically bound water content in the product would be therefore advantageous procedure. The process should be carried out by neutralization of phosphoric acid (or calcium hydrogen phosphate for the preparation of MCP monocalcium phosphate) with stoichiometric amount of calcium oxide or a mixture of calcium oxide and calcium carbonate in relation to calcium hydrogen phosphate or calcium dihydrogen phosphate which should be obtained in the reaction. Applying a mixture of calcium compounds allows for

controlling thermal effect of the process and thus physically bound water content in feed phosphate product. The first stage of neutralization reaction is carried out with intensive stirring, providing homogeneity of the chemical composition in the entire volume of the mixture while a maximum temperature should not exceed 160°C due to the possibility of phosphates condensation. The advantage of this method is the production of phosphate feed additives using highly concentrated phosphoric acid extraction without necessity of dilution of phosphoric acid with water, which allows to operate the manufacturing process without the need for additional methods of the acid pre-treatment, which is connected with the formation of liquid and solid (sludge form) wastes that are difficult to manage.

Laboratory and industrial investigations of the process for feed phosphates production obtained from concentrated phosphoric acid

According to the concept for feed phosphates production presented in this paper, the use of phosphoric acid solutions at concentrations equivalent to 52 ÷ 65% w/w P₂O₅ was investigated under laboratory and industrial conditions [6,7]. The reaction was conducted under laboratory conditions in a ceramic evaporating dish which was filled with stoichiometric quantities of reagents calculated for 100 g of phosphoric acid obtained from the phosphoric acid pure p.a. POCH Gliwice (Poland). Furthermore calcium oxide and calcium carbonate of the same purity grade were also supplied by POCH Gliwice (Poland). Reactive mixture was intensively stirred using the IKA Ultra-Turrax homogenizer. The temperature of the reacting mixture was determined using the ST643 pyrometer. Parameters of the product were evaluated after 1 hour [8,9] including determination of total phosphorus (P_{total}), phosphorus soluble in 0.4% w/w HCl (P_{0.4%HCl}), water-soluble phosphorus (P_{H₂O}), phosphorus which is not present in the orthophosphate form (P_{unortho}), physically bound water, CO₂, pH and temperature. P₂O₅ content was determined colorimetrically at 420 nm wavelength, using the formation of yellow colored phosphate-vanadate-molybdate complex. The total phosphorus content (P_{total}) was determined on the basis of the form soluble in a mixture of hydrochloric and nitric acid (1:3). Determination of soluble phosphates was based on the extraction of phosphate with 0.4% w/w HCl or water. CO₂ was evaluated on the basis of TG analysis, using the weight loss during decomposition reaction of calcium carbonate at a temperature of 890°C approximately, whereas pH was measured directly in 10% w/w solution using pH meter. Phosphates occurring in the form other than orthophosphate was calculated on the basis of the difference between total phosphorus content and phosphorus soluble in 0.4% w/w HCl. Physically bound water content was determined by weight on the basis of differences between initial weight and after drying at 105°C (W_{H₂O}).

Laboratory studies revealed interesting, in consideration of technology, physically bound water level in the product which was obtained for the concentration of P₂O₅ in phosphoric acid solution applied for production at the level of 58.2% w/w. Table I shows the results of the laboratory tests where calcium oxide and its mixtures with the replaced part of CaO with the stoichiometric CaCO₃ content was used to neutralize this acid.

Table I

Results of laboratory tests of feed calcium hydrogen phosphate production using concentrated phosphoric acid

CaO/ ΣCaO+CaCO ₃	P _{total} , % w/w	P _{0.4HCl} , % w/w	P _{H₂O} , % w/w	P _{unortho} , % w/w	W _{H₂O} , % w/w	CO ₂ , % w/w	pH	T, °C
1.00	20.14	19.50	7.86	0.64	1.61	0.51	5.30	177
0.95	19.16	18.75	6.75	0.41	2.60	1.57	5.52	164
0.90	18.77	18.45	5.66	0.32	2.95	2.12	5.69	158

The reaction of such phosphoric acid with calcium oxide proceed at a higher temperature than in the typical solutions, however, allows for production of nearly direct product devoid of physically bound water content. Also, the absolute phosphorus content is higher than in such solutions. Partial substitution of calcium oxide with calcium carbonate reduces the process temperature. Substitution at the level of 10% allows to reach a temperature not exceeding 160°C, which is considered as the limit temperature of security capabilities of the process in terms of elimination of phosphate polycondensation reaction. Variations in the level of available phosphates content in comparison with its total content in the product are minimal, which shows absence of such reactions. Furthermore, any significant change in moisture content in relation to the requirements of the feed industry was not observed. Trial production of feed calcium hydrogen phosphate under industrial conditions was carried out on the basis of laboratory tests results. Experimental installation for feed phosphates preparation, located in GZNF FOSFOR in Gdańsk, was used. The installation consists of a raw materials feeder unit, twin shaft neutralizer, and three conveyors connected in cascade to allow complete reaction and cooling of the product, and the hammer crusher with a screen to allow the classification of fineness of the final product. Taking into consideration the scale of planned industrial trial (several hundred kg of feed phosphate) a specially designed mixer equipped with a frame stirrer of about 0.5 m³ working volume was used instead of the twin shaft reactor. The reactor contents were stirred at 18 rpm for 2 hours. Phosphoric acid from Lithuanian manufacturer AB LIFOSA, and calcium oxide and calcium carbonate supplied by ZW KUJAWY (Tab. 2 and 3) were used as substrates.

Table 2

Characteristics of phosphoric acid from AB LIFOSA used for the preparation of feed phosphates under industrial conditions

Analysis indicator	Unit	Content
P ₂ O ₅	% w/w	56.900
F	% w/w	0.2400
SO ₃	% w/w	0.3300
Cd	mg/kg	1.2800
As	mg/kg	1.5500
Pb	mg/kg	0.4200
Hg	mg/kg	0.0051

Table 3

Characteristics of calcium oxide and calcium carbonate from ZW KUJAWY used for the preparation of feed phosphates under industrial conditions

Analysis indicator	Unit	Calcium oxide	Calcium carbonate
CaO	% w/w	89.200	50.900
F	% w/w	0.0039	0.0330
Cd	mg/kg	0.3040	0.4030
Hg	mg/kg	0.0020	0.0021
Pb	mg/kg	1.1630	1.1440
As	mg/kg	0.1440	0.2240

Stoichiometric calcium oxide calcium carbonate ratio of calcium hydrogen phosphate production was applied, while the carbonate mole ratio in this mixture constituted 10%. Under conditions of operated process, the reaction temperature reached 175°C. The result of the process was about 350 kg of feed calcium phosphate (Tab. 4).

Table 4

Chemical composition of feed dicalcium phosphate obtained under industrial conditions

Analysis indicator	Unit	Content
P _{total}	% w/w	20.0500
P _{0.4HCl}	% w/w	19.8500
P _{H₂O}	% w/w	3.4000
P _{citric acid}	% w/w	19.8000
P _{ammonia citrate}	% w/w	18.9500
P _{unortho}	% w/w	0.2000
W _{H₂O}	% w/w	1.8500
CO ₂	% w/w	1.6500
F	% w/w	0.1500
W _{H₂O}	% w/w	1.9000
Cd	mg/kg	1.6500
As	mg/kg	1.3000
Pb	mg/kg	1.5800
Hg	mg/kg	0.0095

In addition to the analysis described in the laboratory investigations the fluorine content was determined using ion-selective electrode connected to an ORION potentiometer for industrial investigations. Determination of phosphates soluble in citric acid and ammonium citrate was based on extraction of phosphate with solutions containing 2% w/w of these substances and colorimetric analysis of extracted phosphate. The sulfates content was determined by precipitation method (BaSO₄ precipitation). Heavy metals (lead, cadmium, arsenic) were determined by ICP, while the mercury by AAS method using an AMA apparatus (Czech Republic). The final product was characterized by a physically bound water content of less than 2% of w/w, despite using the maximal calcium compounds content in a mixture, recognized in laboratory testings to allow obtaining the product without the necessity of drying. This is mainly due to the influence of process scale. Industrial trials were undoubtedly carried out at less heat loss to the environment. Implementation of the process in a much larger twin shaft reactor and with much greater intensity of reagents feeding will allow for even more efficient use of heat of reaction to the removal of physically bound water from the system. Such solution should enable the possibility of applying phosphoric acid solutions with a lower content of H₃PO₄ in the process, similar to the typical acid products available on the market containing approximately 54% w/w of P₂O₅. The difference between total and soluble in 0.4% w/w HCl phosphorus compounds content in the product obtained in industrial trials has proved to be lower than that determined in laboratory studies. This gives evidence to the lack of condensed phosphates formation under such conditions which could impair the utility value of feed phosphates. Reaction temperature, responsible for such processes, has occurred to be relatively high and could constitute a threat to these orthophosphates transformations if the process will be carried out on a larger scale. In potentially realized production process, this factor will require careful laboratory monitoring, and for reasons of product quality is likely to receive the feed phosphate of a slightly higher moisture content which determines the implementation of drying device into the process line. The feed calcium hydrogen phosphate obtained under industrial studies was characterized by slightly higher levels of phosphorus compounds in relation to products available on the market. Moreover rate of available forms of phosphorus, was also high and is not inferior with these parameters to commercial feed phosphates.

Conclusions

In the technology of feed phosphates production the requirement of removal of physically bound water from final product, which is characterized by a high heat energy unit demand, constitutes an important technological problem. The research was performed under laboratory and industrial conditions using a modification of this technology in scope of higher H_3PO_4 content in the solution of applied phosphoric acid, increased ratio of calcium oxide in a mixture of calcium compounds used for acid neutralization, and modifying the reaction unit in range of homogeneity of reacting mixture. In such conditions, the process proceeds at a higher temperature whereas the heat effect of exothermic reaction is used for direct production of feed phosphate with low moisture content. The final product is characterized by the total P content of about 20% w/w where over 95% occurs as bio-available phosphates. Condensed phosphates were not observed in the product under elevated temperature conditions.

English translation by the Author

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Events IYC'2011

June 2011

Eröffnungsveranstaltung - opening ceremony at ETH Zurich and University of Zurich, Switzerland - Jun 01, 2011
- Calatrava Library, Rämistrasse 74, Zurich, Switzerland

The Combined XII Spring Meeting of the Division of Synthetic Chemistry and XXXIII Finnish NMR Symposium Synthetic Chemistry and NMR Symposium - Jun 07 - Jun 10, 2011 - Spa Hotel Rantasipi Laajavuori, Jyväskylä, Finland

Clusters: Physics and Chemistry in a Finite World Nottingham Chemistry Public Lecture Series - Jun 09, 2011
- Lecture Theatre XI, School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK.

75th Prague Meeting on Macromolecules Conducting Polymers - Jun 10 - Jun 14, 2011 - Prague, Czech Republic

Conferences "grand public" during the Week of Chemistry in Fribourg - Jun 14 - Jun 18, 2011 - Chemin du Musee 9, 1700 Fribourg, Switzerland

Chemspec Events - the fine and specialty chemicals connection - Jun 15 - Jun 16, 2011 - Hall I, PALEXPO, Geneva, Switzerland

Tag der Chemie, Universität Zürich and ETH Zürich, Switzerland - Jun 18, 2011 - ETH Hönggerberg und Universität Zürich-Irchel

4th International IUPAC Symposium for Trace Elements in Food (TEF-4) Trace Elements in Food - Jun 19 - Jun 22, 2011 - King's College, University of Aberdeen, Aberdeen AB24 3FX, Scotland, United Kingdom

Symposium of the Commission on the History of Modern Chemistry Renewing the Heritage of Chemistry in the 21st Century - Jun 21 - Jun 24, 2011 - ESPCI ParisTech, Paris, France

Joint 15th Annual Green Chemistry & Engineering Conference / 5th International Conference on Green and Sustainable Chemistry Green and Sustainable Chemistry and Green Engineering - Jun 21 - Jun 23, 2011 - Capital Hilton Hotel, Washington, DC USA

Schiff-Fahrt-Diskussion, Universität Zürich and ETH Zürich - Jun 23, 2011 - Zürichsee, Switzerland