Utilization of Industrial Wastes in Fertilizer Industry. Possibilities and Implementation

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Introduction

Mineral fertilization is one of the most important factors influencing crop quantity and quality [1]. So further development of fertilizer industry is justified and its products should be upgraded and its economical efficiency improved. The Polish fertilizer industry operates in difficult economic conditions because it must use mostly imported raw materials and it is faced with pressure of fertilizer producers working in more favourable conditions i.e. having access to raw materials of competitive prices. At present the local fertilizer industry covers fully the needs of Polish agriculture and even a big part of its production is exported.

Because of the high range of products fertilizer industry has a considerable impact on the natural environment using large amounts if unrenewable resources and producing huge quantity of wastes. Important changes had to be introduced to the local fertilizer industry in the pre-access period to the European Union and after access too. The European regulations forced actions which greatly reduced harmless effect of this industry branch on the environment. However, other actions are taken which aim at further reduction of detrimental impact of the industry on the environment. The subject of our study was how to utilize wastes produced both by fertilizer industry and other economy branches for fertilizer production.

Conditions and technical possibilities of waste utilization for fertilizer production

Possible application of various types of wastes for fertilizer production depends on their chemical composition, especially nutrient contents, harmful compounds, and other ones which can influence technological operations of fertilizer production process and properties of products. Physical state of wastes is also important because it can be an obstacle to process them profitably into a valuable fertilizer. Such waste properties as over-grinding, high mechanical strength, too buttery consistence, too high moisture content can make processing unprofitable. Other factors that influence possible utilization of wastes for mineral fertilizer production are: the type of available plants, their operational parameters, and the composition of produced fertilizers [2].

Chemical composition of fertilizers marketed in Poland, including allowable contents of plant harmful compounds, is determined by Regulation relating to fertilizers and fertilization [3] and Regulation of Minister of Agriculture and Rural Development [4], and that of fertilizers marketed in EU is determined by Regulation (EC) 2003/2003 of the European Parliament and of the Council of 13th October 2003 relating to mineral fertilizers and liming materials (agricultural limestone) [5]. According to the local regulations [4] allowable contents of toxic components in mineral fertilizers are the following:

As – 50 mg/kg of fertilizer,
Cd – 50 mg/kg of fertilizer,
Hg – 2 mg/kg of fertilizer,
Pb – 140 mg/kg of fertilizer,

As far as liming materials (agricultural limestone) are concerned, the contents of only two elements are limited, i.e. cadmium (8 mg Cd/kg of CaO) and lead (200 mg Pb/kg of CaO) [4].

11 Polish plants produce mineral fertilizers on industrial scale. They belong to Grupa Azoty: Grupa Azoty located in Tarnów-Mościce, Zakłady Azotowe „KĘDZIERZYN", Zakłady Chemiczne „POLICE", Zakłady Azotowe „PUŁAWY", Gdańskie Zakłady Nawozów Fosforowych „FOSFAN", and Zakłady Azotowe „CHORZÓW". Outside Grupa Azoty still are: ANWIL, FOSFORAN, „LUVENA", Zakłady Chemiczne „SIARKOPOL" in Tarnobrzeg, and ALWERNIA. Among 11 mentioned plants 10 produce granular fertilizers. They apply various granulation methods which can be described as:

- granulation of highly evaporated melt – prilling or belt granulation,
- pug mill granulation using the main raw material stream in the form of melt or suspension of concentration 70–95%,
- granulation by coating using the main raw material stream in a solid form and a granulating agent in the form of liquid, vapour or their combination (in such case there are two types of granulation: drum and pan granulations),
- granulation by compaction where raw material streams in solid form are used [6, 7].

The presented classification of granulation methods applied by the Polish fertilizer plants is not precise because some of them use combined systems connecting 2nd and 3rd granulation methods. Produced granular fertilizers are applied alone or as blends. The Polish plants produce also solid crystalline and powder fertilizers, which are used alone or as blends, and liquid clear fertilizers (where all fertilizer components are completely soluble). However, they do not produce suspension fertilizers which are two-phase fertilizers composed of a suspension and saturated solution of fertilizer components. Such fertilizers are produced by INS Liquid Fertilizer Station (Stacja Nawozów Płynnych). But its production capacity is smaller than that of industrial plants. However, if we consider possible utilization of wastes for fertilizer production we must take into account also this form. Physical fertilizer form (suspension of some components) and quite simple equipment enable duplication of such solutions what would make utilization of wastes from various sources possible.

If we analyse possible utilization of wastes for production of mineral fertilizers in terms of their physical form and that of wastes too, we must conclude that the lowest utilization possibilities are connected with liquid clear fertilizers. If we want to utilize wastes as a part of liquid clear fertilizers it is only possible to supplement their composition or to replace one of raw materials with a cheaper substitute. In such cases we must take into account limited solubilities of individual waste compounds and their possible reactions with components of the basic fertilizer which could result in formation of insoluble compounds. The most promising utilization of wastes is connected with a liquid-suspension fertilizer form. There are neither limitations concerning solubilities of individual components nor those concerning impurity

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contents; the only requirement is that the wastes must not contain substances harmful to plants. Also high water content in wastes is not disadvantage for this fertilizer form [8 – 9].

Quite serious restrictions concerning utilization of wastes for fertilizer production are imposed on the solid fertilizer form. The waste introduced to a fertilizer cannot cause losses of nutrients available for plants (e.g. as NH_3) or their retardation (e.g. as a result of phosphates binding into sparingly soluble compounds). It cannot also reduce substantially such product properties as critical moisture content, granule mechanical strength or stability of physico-chemical properties during a long storage period. Moreover, the introduced wastes cannot change process operating conditions, e.g. by evolution of substantial amount of water or by formation of low-melting phase systems with fertilizer components or compounds formed in reactions between individual system components. Considering utilization of wastes we must take into account rules applying to fertilizer blending which have to be verified at least in laboratory conditions because of presence of additional components in wastes as compared to the systems described in literature.

Technical safety considerations are equally important when we think about utilization of wastes for mineral fertilizer production. It refers most of all to waste utilization for production of nitrate fertilizers. There is explosion and fire hazard. In other cases there is hazard of possible waste over-reactivity and liberation of toxic gases (e.g. while utilization of waste mineral acids or desulfurization products) [9 – 10].

Results of important research and implementation work on utilization of wastes from various economy branches for production of mineral fertilizers

Polish fertilizer industry has harmful effect on the environment by emitting toxic gases, dust, sewage and producing substantial amounts of wastes because of applied technologies and high production capacity. At the same time fertilizer industry utilizes large amounts of wastes also from other economy branches. Many scientific institutions are interested in the problem of waste utilization. The paper presents selected results of research work on reduction of waste amounts produced by fertilizer industry carried out by New Chemical Syntheses Institute (INS, former Fertilizers Research Institute) and the Institute of Inorganic Technology and Mineral Fertilizers of Wrocław University of Technology (ITNiNM PWr).

Phosphogypsum is a waste material produced in highest amounts by the local fertilizer industry [6]. In the past, that waste was produced by three Polish plants: two of fertilizer character (ZCh „POLICE" and GZNF „FOSFORY") and one producing a component of washing powder (ZCh „WIZÓW"). Now it is formed in only one plant, i.e. Grupa Azoty Zakłady Chemiczne „POLICE". Production of wet process phosphoric acid (WPA) was shutdown in two plants and it resulted in substantial reduction of produced and stored phosphogypsum. Lately, work on further reduction of formed phosphogypsum has been continued (maintaining the amount of produced fertilizers) and studies on that compound utilization for fertilizer production and other purposes have been carried out. As far as the reduction of phosphogypsum is concerned we can mention the following actions [6]:

- compound fertilizer production on the basis of superphosphate pulp was started in ZCh „POLICE",
- compound fertilizer production on the basis of partly decomposed phosphate rock was started in GZNF „FOSFORY" instead of triple superphosphate production.

As far as utilization of produced phosphogypsum is concerned the following research work has been carried out:

- conversion of phosphogypsum to ammonium sulfate and fertilizer chalk with recycle of the formed ammonium sulfate to fertilizer production (ITNiNM PWr),
- utilization of phosphogypsum from ZCh „WIZÓW" for production of SALMAG with sulfur (ITNiNM PWr) [11],
- utilization of phosphogypsum for production of nitrogen-sulfur fertilizers of calcium sulfate with urea addition compound type (ITNiNM PWr and INS) [12],
- preparation of calcium-sulfur-magnesium fertilizers on the basis of phosphogypsum and calcium and magnesium oxides (GZNF „FOSFORY"),
- utilization of phosphogypsum for roadmaking (ICHN GLIWICE),
- utilization of phosphogypsum and anhydride produced from phosphogypsum for highway engineering purposes, in cement industry, and in agriculture as fertilizer on selected soils and selected crops (ZCh „POLICE") [13].

However, results of the research work were not very effective. For several years phosphogypsum from ZCh „WIZÓW" was applied as a partly substitute of anhydride in production of SALMAG with sulfur in ZA „KĘDZIERZYN" (complete anhydride substitution would require phosphogypsum drying before feeding it to a nitrate fertilizer production plant). At present almost all produced phosphogypsum is stored on a dump in GA ZCh „POLICE". Only a part of phosphogypsum is utilized for production of compound fertilizers on the basis of superphosphate pulp in GA ZCh „POLICE". It is worth mentioning that phosphogypsum utilization in Poland is similar to that in the whole world. The main barrier of that waste utilization is its content of impurities (including radioactive ones in phosphorite phosphogypsum) and high water content. Another disadvantage is easily available gypsum from flue gas desulfurization which is free from some phosphogypsum drawbacks. Research work carried out in recent years indicates that both phosphogypsum and gypsum from flue gas desulfurization with wet method can be used as sulfur components of mineral fertilizers, including sulfur ones.

Crystalline sodium nitrates (V and III) were by-products formed in „old" nitric acid plant (Nitric acid I) in GA ZA „KĘDZIERZYN". Moreover, it was necessary to discharge a part of the circulating solution from the plant because of growing content of impurities, including chlorides. The solution discharged from sodium nitrates (V and III) crystallization unit was used for potassium nitrate production in ADIPOL (now ZA „CHORZÓW"). Chemical reaction describing that process can be expressed by the following equation:

$$KCl + NaNO_3 = KNO_3 + NaCl$$

and both products formed in this process were utilized (potassium nitrate as explosive component, preservant, and fertilizer and sodium chloride as road salt).

Periodically there were troubles with utilization of crystalline sodium nitrate (V) formed as a by-product in nitric acid production. It resulted in development of a production method of mechanically granulated nitrogen-sodium fertilizer (SALMAG with sodium) by ZA „KĘDZIERZYN" in co-operation with ITNiNM PWr. Such fertilizer was designed for sugar beets and for a short time it was on the market but situation of crystalline sodium nitrate was improved and this solution was no longer applied in practice because of more favourable prices of crystalline $NaNO_3$ than those for the form of granular fertilizer called SALMAG with sodium.

Waste solution of sodium nitrate is formed in catalyst production plant of Grupa Azoty in Tarnów-Mościce. For some time it was utilized for potassium nitrate production by ADIPOL. However, periodically it was difficult to sell that solution so a method of their utilization for fertilizer production was developed. Formula and production technology of nitrogen-sodium-boron fertilizers were developed and a fertilizer was produced in such amount to utilize $NaNO_3$ solution. This method is no longer applied because a new more profitable demand for sodium solution was found [9].

Bio-mass combustion in power plants and in heat and power generating plants results in formation of ashes that contain valuable nutrients such as potassium and calcium. The ashes have strong alkalizing properties. From environment protection point of view it seems that return of ashes from bio-mass combustion to soil is the most ecological method of their utilization in agreement with balanced development principles. Such solution would enable come back of substantial amounts of macro- and micronutrients uptaken by plants to soil closing nutrient cycle. However, there are waste regulations which prevent such utilization of ashes. They refer to *recovery conditions with R10 process (spreading on soil surface to enrich or improve it)*.

Feasibility studies on possible utilization of ashes from bio-mass for fertilization purposes were carried out in INS. Strongly alkaline reaction of ashes and substantial content of calcium would suggest their application as a soil liming agent. However, it turned out that such utilization is not possible because of the content of harmful elements (lead and cadmium) exceeding allowable values for agricultural limestone [*Regulation relating to fertilizers and fertilization*]. Possible application of bio-mass ashes as a potassium source in compound fertilizers was also investigated. Because their alkaline properties the ashes cannot be used with ammonium salts. In such mixtures ammonium nitrogen would be lost as a result of ammonia displacement by alkaline ash components. As far as phosphorus components are concerned alkaline reaction reduces phosphorus availability by plants (so called phosphorus retrogradation). Because of that application of bio-mass ashes in a mixture with other fertilizer agents requires their prior processing with mineral acids to stabilize them.

Possibility of potassium recovery as potassium salts from the ashes was also preliminarily studied in INS. Investigation results indicate that it is possible to recover potassium from the ashes as potassium nitrate (V) of 95% purity and also as potassium sulfate (VI) of 98.5% purity. Until now, none of the bio-mass ash utilization methods for fertilizer production investigated in INS has been practically applied on a large scale but because of expected increase of bio-mass combustion in future the work is continued [14].

Potassium and sodium hydroxides are applied as catalysts in preparation processes of higher fatty acid methyl esters for fuel purposes. Potassium hydroxide is more expensive but it has better catalytic properties and that is why it is applied in practice more often. When potassium hydroxide plays its part in the fat transestrification process it is removed from the reaction environment in so called acidulation with a mineral acid. Taking into account the price of used acid and practical value of the product it seems rational to apply sulfuric acid for removal of the transestrification catalyst from post-reaction mixture. In Trzebinia Refinery where biofuels are produced such solution is applied and potassium sulfate is formed as a by-product. It is contaminated with organic matter which limits its utilization for production of some fertilizers, e.g. nitrate ones. However, this by-product is used as a component of PK and NPK fertilizers, e.g. in ALWERNIA.

Post-nitration mixture containing sulfuric acid, nitric acid and organic impurities is a waste product formed in nitro compound and nitric acid ester production processes. Such mixture cannot be applied directly because of the content of organic matter having disagreeable odour and explosive properties. So, only a recovery process of sulfuric and nitric acids from the mixture is carried out. Quality of the recovered acids is poorer than that of acids coming from H_2SO_4 production plant but they are easily applied for production of crystalline and granular magnesium sulfate and calcium and magnesium nitrates in the form of flakes or solution.

In production process of nitro compounds and nitric acid esters waste water containing ammonium nitrate and sulfate is formed. The waste water is concentrated by reverse osmosis method and solutions of the above salts are obtained with total content of dissolved components of 20–30%. The solutions are utilized as granulating liquid in one of the plants producing compound fertilizers.

Titanium white production is a process generating large amounts of waste sulfuric acid (post-hydrolytic acid) and iron (II) sulfate (VI). Trials to purify that acid and recycle it to the main production were unsuccessful so the post-hydrolytic sulfur acid found application in production of wet process phosphoric acid. The waste iron (II) sulfate (VI) is utilized for production of building materials, pigments, and water conditioning agents. Trials to utilize iron (II) sulfate (VI) for production of granular and liquid – clear fertlizers were conducted. The first solution is not promising but the other one, in our opinion, can be implemented [15].

ZCh „Wizów" produced large amounts of phosphate sludge which was stored on a phosphogypsum dump. INS developed an utilization method of that waste for production of suspension fertilizers and applied it practically in Stacja Nawozów Płynnych (Liquid Fertilizer Station) in Łagiewniki Średzkie. Phosphate sludge from production of phosphorus compounds in ZCh "ALWERNIA" and waste phosphate solutions from polyether production in PCC "ROKITA" were utilized in a similar way.

For many years Zakłady Chemiczne „ALWERNIA" have been producing technical phosphates using thermal phosphoric acid from their own plant. However, because of striking changes of phosphorus prices it turned out that production of technical phosphates based on thermal phosphoric acid was unprofitable. So a new method was developed and implemented. It uses imported wet process phosphoric acid instead of the thermal type. Application of this solution resulted in formation of waste phosphate sludge dump. INS in co-operation with ZCh "ALWERNIA" considered utilization of that sludge for production of suspension fertilizers. But because agricultural farms in ALWERNIA region are quite scattered this form of fertilizers might be unaccepted by farmers and this idea was rejected. So both companies developed production technology of granular compound fertilizers on the basis of phosphate sludge and also on magnesium sludge formed in the ALWERNIA plant as a waste product of crystalline magnesium sulfate production. This solution is applied up till now [16].

Other studies on utilization of waste products for fertilizer production were conducted in INS and in ITNiNM PWr. They concentrated on recovery of nitrogen and phosphorus compounds from waste waters and their recycle to the main production process and also on utilization of solid wastes containing nitrogen, phosphorus and potassium for fertilizer production. Investigation results have already been published [2, 8].

Conclusions

Fertilizer industry is one of economy branches that reduced substantially detrimental effect on the natural environment in the last few years. Several solutions were implemented which greatly reduced amounts of harmful gases, dusts, and waste waters discharged to the environment. The solutions partly consisted in recovery of valuable components from waste streams and their utilization in principal processes (e.g. recovery of nitrogen compounds from condensates and their recycling to the main production) and partly in their processing into substances neutral for the environment (e.g. selective catalytic NO_x reduction and N_2O decomposition). Reduction of detrimental effect of industry on the environment was also achieved by utilization of some wastes by fertilizer industry, including wastes generated by other economy branches. The most important solution is utilization of waste mineral acids (from production of titanium white and explosives, from petrochemical industry) for fertilizer production. The acids play two parts in fertilizer production processes. They are used for processing of water insoluble raw materials containing phosphorus, calcium, and magnesium into products of good availability for plants and they are a source of valuable nutrients such as nitrogen and sulfur. Very important processes are such solutions which utilize wastes from various industries for fertilizer production because they contain valuable plant nutrients. Thus, wastes from: bio-fuel production, food industry, technical phosphorus compound industry, and polyether production are utilized for that purpose. It is worth mentioning that the processes have low detrimental effect on the natural environment and in a small degree they influence economic efficiency of fertilizer production.

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SPOTKANIA

AgroFesta 2015 – dokąd zmierza polskie rolnictwo?

Czy polskie rolnictwo ma szanse stać się najnowocześniejszym w Europie? Co zrobić żeby dalej mogło się rozwijać i wzmacniać swoją pozycję na europejskich rynkach? To pytania na które odpowiedzi szukali uczestnicy AgroFesty – corocznego spotkania liderów branży rolnej i rolno-spożywczej. W tym roku spotkanie zorganizowano w dniach od 4 do 5 września w ośrodku Jakubus na Opolszczyźnie, własności Państwa Osadkowskich, od lat związanych z branżą rolną. Partnerem strategicznym wydarzenia był PKO Bank Polski SA, organizatorem Grupa Azoty.

– Dialog, który dziś Grupa Azoty prowadzi z rolnikiem ma swój wymiar strategiczny. Wspólnie dążymy do lepszej efektywności, dbamy o bezpieczeństwo w zakresie produkcji żywności i jej rentowność. Jesteśmy świadomi wielu wyzwań, które swoją przed nami i wspólnie widzimy możliwość ich przezwyciężenia – podkreślał Paweł Jarczewski, Prezes Zarządu Grupy Azoty.

Głównym zadaniem AgroFesty jest stworzenie platformy wymiany wiedzy i doświadczeń pomiędzy czołowymi gospodarstwami rolnymi w Polsce, światem nauki i firmami takimi jak Grupa Azoty, czyli takimi których działalność bezpośrednio wpływa na polski rynek rolny.

– Grupa Azoty traktuje spotkania z rolnikami jako najwyższy priorytet do opiniowania ram prawnych, które służą kreowaniu wizerunku nowoczesnego polskiego rolnictwa na tle pozostałych krajów UE – mówił Zenon Pokojski, Wiceprezes Grupy Azoty Puławy. *(abc)*

(inf. Rzecznik Prasowy Grupy Azoty, 10 września 2015)

XXV Forum Ekonomiczne w Krynicy

Jubileuszowe XXV Forum Ekonomiczne w Krynicy obradowało pod hasłem „Jak zbudować silną Europę? Strategie dla przyszłości", co nawiązywało do najważniejszych wyzwań przed jakimi znalazła się Europa, zarówno w obliczu zagrożeń zewnętrznych, jak i braku stabilności wewnątrz UE. Kryzys finansowy Gracji, wzrost nacjonalistycznych nastrojów, zagrożenie państwem islamskim, problem imigrantów, a także agresywna polityka Rosji i nierozwiązane strukturalne problemy europejskiej gospodarki stanowiły tło dyskusji podczas jubileuszowego Forum. Na stronie internetowej Forum można znaleźć obszerne relacje ze wszystkich paneli dyskusyjnych. *(abc)*

(inf. http://www.forum-ekonomiczne.pl/dla-mediow/informacje-prasowe/, 15 września 2015)

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