AMMONIA AND FERTILIZERS

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Summary

Fertilizer use has been shown to be very effective in means of increasing agricultural productivity, estimated on 50% of crop production increase. About 40% of world protein production is based on synthetic ammonia. Recently, world agriculture uses about 400 million Mg of fertilizers (140 million Mg NPK).

Fertilizers are materials which supply to plants nutrients and improve soil fertility. Application of these simple chemical products belongs to the most effective methods of crop production, increasing and improving the yield and quality of food and fodder. Proper and balanced fertilizer use enhances agricultural production. Fertilizers and fertilizer industry plays very important role in ensuring that world food needs can be economically and sustainably produced.

Most of fertilizers are straight, mixed or compound products applied as solids, mainly as granules, or liquids, in the form of clear or suspension solutions. These products contain primary nutrients such as N, P, K, secondary nutrients, such as: Ca, Mg, S, and micronutrients, such as: Fe, Mn, Zn, Cu, B, Mo. The fertilizer nutrient content and rate are correlated with plant requirements, soil fertility, and planned yield of crops. Although fertilizer component belong to the simple substances, in practice there are many difficulties with their use, transport and storage, because they are frequently used as a mixture of straight products with various physical and chemical properties.

The main fertilizer products include: nitrogen fertilizer such as urea, ammonium nitrate, ammonium – calcium nitrate, ammonium sulfate; phosphate fertilizers such as single and triple superphosphate, mono- and diammonium phosphate and potassium fertilizers: potassium chloride and sulfate. The main raw material in fertilizer industry is ammonia, which is produced mainly from natural gas or other hydrocarbons. All phosphate fertilizers are derived from phosphate rocks and potassium fertilizers from deposits of potassium chloride or from salt brine.

The fertilizer industry is built of plants with huge capacity, producing daily even 5000 Mg of fertilizer products and is located near the fertilizer raw material resources. The fertilizer installations belong to the modern units with low emission parameters. The world fertilizer capacity is correlated with world population and is annually estimated to about 25 kg NPK per capita.

The main environmental fertilizer problems are related with the proper use of fertilizers. Estimated total environmental impact of fertilizers production is estimated on 8% but in agriculture 92%. This increasing trend is the result of revamping of technological facilities of the achievements of Chemical Engineering and Chemical Technology, in particular in the use of new apparatus and specific cycle of material streams which guarantee decrease of energy expenditures and better use of components in raw materials.

1. Introduction

1.1. Role of Fertilizers and Fertilization

[Bockman et al., 1990; EFMA, 1997a, EFMA, 2003; EFMA, 2006; FAO, 1998; FAO/IFA, 1999; FAO, 2000; Fink, 1982; Górecki 2000; Górecki, 2002a; IFA/UNEP, 1998; IFA, 2002; IFA, 2007a; Laegerid et al., 1999]

In agricultural practice the use of fertilizers is considered as one of the most important tools for raising crop yield and is known to have huge productivity – enhancing factor. About 40% of world cereal production has been contributed to mineral fertilizers.

Fertilizers are chemical substances which provide plants with the nutrients they need for their growth and development. Fertilizer implies the supply of one or more nutrients to the soil as chemical elements necessary for normal plant growth. In the "fertilizer law" fertilizers are defined as substance intended to be supplied directly or indirectly to crops in order to promote their growth, increase their yield of harvested mass and improve their quality. According to this law all commercial fertilizers sold must be identified with manufacturer or seller and chemical stable content of nutrients must be supported. Some national fertilizer regulations specify a degree of solubility of the nutrient in water or in defined special standard extraction procedure.

Actually the preferred term for manufactured fertilizer in USA and Europe is "commercial fertilizers". This term defines the products that are sold through commercial channels with warranted concentration of plant nutrients and physical properties. Commercial fertilizers are mineral fertilizers , mineral- organic fertilizers, organic fertilizers and also special fertilizers applied to foliar fertilization or horticulture and fertigation.

Historically the term "fertilizer" was modified starting in the early 1900's as "chemical manure", "artificial manure", "chemical fertilizer" to "mineral fertilizers" and "commercial fertilizers". A very important goal of fertilization is improving the quality with regard to commercial quality, market value, nutritional quality for human and animals. Fertilizer use assures resistance of plants to noxious factors as freezing, drought and immunization against fungi disease and pests. The aim of fertilization is to achieve optimum nutrient supply for high-yield cultivated crops, reduce deficiency of soil nutrients which are removed with harvested crops and are caused by environmental losses. Fertilizers ought to improve soil fertility without negative effect on the environment, supplying deficient substances in the soil and their optimal use need avoiding chemical mistakes by taking into account soil fertility, soil texture structure, special plant nutrient requirements according to nutrient dose and NPK ratio.

Fertilizer production and fertilization are the factors which need chemical and agricultural knowledge and close interdisciplinary cooperation. The fertilizers are integral part of the world food supply chain without equivalent alternative, providing food for increasing population thanks to promoting crop yield with high economic benefits of agricultural productivity.

Mineral fertilizer often called artificial fertilizers in fact are natural products obtained from natural resources such as: natural gas, oil or coal (ammonia), phosphate are produced from phosphorities or apatities and potassium salts from salt deposits or marine brines. The term artificial creates negative sense, although exactly these products do not contain toxic components, pathogens and all ingredients originating from natural sources.

1.2. Definition of Fertilizers

[European Commission Directorate, 2006; Fink, 1982; IFA, 1980; IFA/UNIDO, 1996; IFA, 2002; IFA 2006a; IFA 2006b; Katyal and Randhawa, 1983; Nielsson, 1987b; Nelson, 1990]

According to Justus von Liebig theory of mineral nutrients of plants, nutrient depletion caused by crop productions need mineral fertilizer supplementation to maintain or to increase soil fertility enabling conditions for plants growth. Achieving these effects need to use proper rate, form and composition of these supplementing substances.

A plant contains practically all 92 natural elements but need only 16 for good growth. Thirteen of these are essential mineral nutrients, elements which must be provided by the soil either by animal manure or mineral fertilizer. Apart from carbon, hydrogen and oxygen, plants take their nutrients essentially from the soil or through leaves. The mineral nutrients are often classified into the “primary” plant nutrients – nitrogen, phosphorus and potassium which are required by plants in large amounts; “secondary nutrients” – calcium, magnesium and sulfur, which are need in smaller but still appreciable quantities; and the micronutrients boron, chlorine, copper, iron, manganese, molybdenum and zinc.
The primary and secondary nutrients are required in the largest amount, although there are large variations between crops. They are constituents of many plant components including protein, nucleic acid and chlorophyll and are essential for processes such as energy transfer, maintenance of internal pressure and enzyme function. On average, plants contain the elements N, P, K in a ratio N:P:K = 2:0.44:0.83, $N:P_2O_5:K_2O$ = 2:1:1.

The maximum nutrient uptake rate varies with crop species, climate and soil conditions. Common value for cereals in the temperate region are about 5 kg ha^{-1} day^{-1} for N and K and 0,5 kg P. These calculations result from composition of cultivated plants, composed of the nutrients: 95% basic elements - 44% C, 6% H, 45% O; 3.5% primary: 2% N, 0.5% P, 1.0% K; 1,3% secondary nutrients- Ca, Mg, S, and 0.1% micronutrients- B, Cl, Cu, Fe, Mn, Mo, Zn (Co, F, I in animals also). The usual sources of fertilizer primary nutrients are:

- Nitrogen compounds: ammonia, ammonium nitrate, ammonium sulfate, calcium ammonium nitrate, urea – ammonium nitrate solution
- Phosphate compounds: normal superphosphate, enriched superphosphate, triple superphosphate, ammonium phosphates, phosphate meal, partially acidulated phosphate rocks, nitrophosphates
- Potassium compounds: potassium chloride, potassium sulfate, potassium nitrate, potassium phosphate.

Available nutrients are those available to the plant for absorption those that can be absorbed However the degree of availability may vary within wide limit. Nutrients are absorbed by plants through the roots – water, oxygen, mineral and organic substance and through the leaves: CO_2, O_2, H_2O water and its solutes via stomata and micropores in the outer stein.

The major nutrients N and P are absorbed by plants as anions K, Ca, Mg and micronutrients: Fe, Mn, Zn, Cu as cations and Cl, B, M are absorbed as anions. The modern and environmentally safe use of mineral fertilizers is recommended that knowledge of the nutrients content of the soil and nutrient requirements of the crop are carefully balanced with application of nutrients in organic fertilizer, especially. This process is called nutrient budgeting. By careful monitoring of soil conditions it is possible to avoid wasting expensive fertilizers and avoid leaching nutrients to the ground water.

1.3. History of Fertilization and Fertilizers.

[Górecki, 2002a; IFDC, 1992; IFDC/UNIDO, 1998; Nelson, 1990; Palgrave 1991]

Development of the fertilizer technology and their use called "fertilization" is an important part of agriculture history which appears to have started in Mesopotamia, Nile Valley, China. The roots of fertilization knowledge were based on observations of effects on plant growth after the use of many natural soil amendments. Philosophical idea presented in Ancient Greece times by Plato, Aristotle, Theophrastus tried to explain increasing soil productivity through the application of manures compost, ashes, agricultural wastes and minerals. The similar solutions were proposed by Romans such as Varro, Pliny, Columella, Palladus, which recommended increase of soil productivity by using human excreta, waste from oil press, dregs from wine production, vegetable refuse, pigeon manure and inorganic substances such as ashes, marl and lime kiln. This idea was developed in the Middle Ages and in the beginning of XIX century in European and US agriculture were the first commercial fertilizer products used for arable land improving. In England the milled and partially acidulated bones as phosphorus source were used, and guano birds imported from Peru natural sodium from Chile. The import of these natural fertilizers was about 100 000 Mg annually.

The modern era of fertilizers began with the Justus von Liebig theory published in 1840 in "Organic Chemistry and Its Application to Agriculture and Physiology". The theory of mineral nutrition of plants and law of minimum were the turning point in fertilization, resulted in demand for mineral fertilizers and emerging fertilizer industry. In the Table 1 the most important facts in fertilizer technology development are presented.

Year(s)	**Developed technologies and place(s)**
1710-1800	Chemical discoveries of obtaining ammonia, sulfuric acid, urea phosphoric acid
1800-1840	Cargo of guano from Peru, sodium nitrate – from Chile
1826	Sulfuric acid chamber plant in Baltimore (USA)
1831	Phosphoric acid from bones by sulfuric acid route (England, France)
1831	Contact process for making sulfuric acid, patent granted to P. Philips (England)

1840	First nitrogen fertilizer – ammonium sulfate from coke production (Germany)
1842	First fertilizer patent on single superphosphate granted to Sir John Lawes (England)
1846	First industrial plant for commercial fertilizer – superphosphate (Liverpool)
1851	Batch phosphoric wet-process acid by Albright & Wilson (England)
1860	Potassium salt deposits were opened (Germany)
1862	Continuous single superphosphate (England)
1870	Continuous triple superphosphate (Germany)
1870-1890	Wet-process phosphoric acid for fertilizers (Germany, England, USA)
1870-1920	Golden age for normal superphosphate (Europe, USA)
1873	First fertilizer Law (Massachusetts USA)
1878	Thomas phosphate slag from steel industry (Germany)
1890	Commercial nitrogen fertilizer – ammonium sulfate from coke production (Germany)
1890	Fertilizer mixing plants (USA)
1891	Commercial electric furnace for phosphorus by Coignet (France)
1900	Industrial phosphate rock mining (USA)
1901	Sulfuric acid contact process (Coult Coast. USA)
1903	Catalytic process of NH_3 synthesis by K. Haber
1903-1910	Program Nitrogen Fixation Processes sponsored by Ampere Electrochemical Company BASF, Norks-Hydro, American Cyanamid
1903	process for nitric acid production (BASF, Germany)
1907	Calcium cyanamide plant (Italy)
1907	Saltpeter from atmospheric nitrogen by arc-gap process (Norway)
1908	Oxidation of ammonic to nitrogen oxide plant according Ostwal process (Gerthe, Germany)
1913	Industrial ammonic production in Oppau (Germany) according Haber-Bosch process
1913	Sulfuric acid from elements sulfur (USA)
1915	Continuous process of wet-process phosphoric acid (Dorr Co. USA)
1916	Ammonium phosphate by American Cyanamid Co (USA)
1916	Rhenania phosphate through alkaline phosphate decomposition (Germany)
1916	Wet-process phosphoric acid continuous process for fertilizer use (USA, Sweden)
1916-1920	Development of ammonic production plant (Leuna, Germany)
1921	Urea from ammonic plant (Germany)
1923	Liquid fertilizer plant (Lignid Fertilize USA)
1926	Ammonium nitrate as fertilizer (Germany)
1927	Nitrophoska NPK multicomponent fertilizers (Germany)
1927	Calcium ammonium nitrate CAN (Germany)
1929	Triple superphosphate (Dorr USA)
1930	Nitrophosphate fertilizer (Germany, Norway)
1930	Ammoniation of superphosphates (Germany, USA)
1930	Injection of anhydrous ammonia to the soil (USA)
1932-1952	Slurry recycle of wet process-phosphoric acid (USA, England, Germany)
1950	Urea – ammonium nitrate solution (USA)
1950	Granulation of fertilizers (USA, England, Germany)
1955-1965	Ammonium phosphate and polyphosphate for liquid fertilizer (TVA, USA)
1955	Superphosphoric acid for Liquid fertilizer (TVA, USA)
1960	Development of suspension fertilizers (TVA, USA)
1970	Slow-release fertilizers (Japan, Israel, Germany)

1970	Foliar fertilizer (Germany, Poland).

Table 1. Development of fertilizer technologies.

Since the 1970-ties - revamping of the industrial installations, introduction of The Best Available Techniques, decreasing of energy consumption, unit capacity increase.

1.4. Classification of Fertilizers

[Fink, 1982; IFA, 1980; EFMA, 1995; Hodge and Popovici, 1994; IFA, 2002; Mortvedt et al.,1998]

The elements recognized as being necessary for cultivated plants are introduced to the fertilizer products mainly in the form of inorganic salts, although also some organic compounds such a slow-release fertilizer and urea are used. The fertilizer, are classified:

- according to chemical composition
  - “organic fertilizer”, containing organic compounds as manure, peat, organic wastes, urea, organic compounds, slow-release fertilizer
  - “mineral fertilizer” – containing mineral salt or salts, which according to the their proportion are available to plant or easy converted in soil to available substances.
- according to source of obtaining
  - “commercial” – obtained through trade network, subjected to the fertilizer regulations produced by fertilizer industry
  - “natural” in the form of manure, liquid manure, compost, straw, peat, NPCa containing agricultural wastes, used on the farmer own arable land
- according to number of ingredients
  - “single nutrient fertilizer” containing only one essential nutrient
  - “multicomponent fertilizer” – containing at least two nutrients
  - “complete fertilizers” containing 3 essential nutrients NPK in the form of mixtures or as granulated chemical compounds
- according to the physical form
  - “solid fertilizer” in the form granular or powder
  - “fluid fertilizer” in the form of fertilizer solution, fertilizer suspension
  - “gaseous fertilizer” anhydrous ammonia
- according to type of fertilization
  - “to soil application” – soil fertilizer
  - “to fluid application” used to direct application on top soil or under soil
  - “hydroponics fertilizers” – used in system of growing plants without soil
  - “fertigation fertilizer” – used to irrigation with nutrient supplement
  - “foliar fertilizer” used for supplying nutrients through leaves
- according to mode of plant availability
  - “direct acting” – containing essential component of available plant nutrients for direct received by plants
  - “indirect – acting” (soil fertilizer) – improve the nutrient substrate (soil in agriculture, substrate in horticulture) for future source of nutrients
- according to concentration fertilizer nutrients
  - “major nutrients” containing essential concentration of primary or secondary

nutrients

- "micronutrients" – containing mixture or chelated micronutrients in composition according to special plant requirements.

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Biographical Sketch

GÓRECKI, HENRYK JAN, chemical technologist, educator; born in Oleśnica, Poland, February 25, 1946; son of Wladyslaw Górecki and Stefania Górecka; married with Helena; children Katarzyna Wanda Chojnacka and Jan Wladyslaw Górecki. Master Thesis at Department of Chemistry on the Wroclaw University of Technology in Poland in 1970, PhD in 1974, DSc in 1980. Professor title in 1987. At 1974-80 a tutor in the department of chemistry at the Wroclaw University of Technology, at 1980-86 a director of Institute of Inorganic Technology and Mineral Fertilizers, at 1987-91 a manager of scientific division, at 1992-96 a manager in Institute of Inorganic Technology and Mineral Fertilizers, at 1996-2002 dean of the Department of Chemistry. 1978-89 a manager of industrial research group in Chemical Works Police SA (Poland); at 1998-2000 a chief of technology council in Chemical Works Alwernia SA (Poland); at 1992-2002 an expert in Ministry of Environmental Protection in Warsaw; from 2000 an expert of environment protection in the Lower Silesia Voivodeship in Wroclaw, Poland. Contributor: of a book "Pollution Control in Fertilizer Production", an author of "Waste Free Method of Phosphate Fertilizer Production", awarded an Award of Polish Ministry of Education in 1981; an editor of "Pollution Control in Agriculture in Fertilizer Industry", "Chemical Products in Agriculture and Environment". Member of State Committee for Scientific Research in Warsaw at 1999-2002; at 2000-02 a chairman of advisers group in Ministry of Science in Warsaw. V-ce Predsident of the Polish Council of Science and president of the Committee on Research for the Development of the Economy. Recipient of a Meritorious award for Polish Chemistry Industry Development from Ministry of economy in 1991, an Order of Merit at the University of Technology in Lodz in 1998 and at the University of Technology in Szczecin in 1997, a Medal of National Education President of Poland in 2000, an award for Industrial Success from a Prime Minister of Poland in 2001. A member of: Polish Organization of Chemical Engineering (Gold Medal in 1999), Polish Technology Organization (assoc. Silver Medal in 1998), Polish Chemistry Society, International Union of Pure and Applied Chemistry. Achievements include research in "Toxic heavy metals circulation in environment"; "Pollution Control in Agriculture and Fertilizer Industry"; "Application of urea phosphate in argochemicals production"; "New forms of fertilizers and technologies of foliar, liquid and suspended fertilizers"; "Technology of feed phosphate for husbandry"; "Recovery of uranium from wet-process phosphoric acid"; Utilisation of waste fluoride compounds from fertilizer industry"; " New methods of fertilizer granulation"; patents in field. In the year 2007 was awarded with title of Doctor Honoris Causa of Wroclaw University of Environmental and Life Sciences. Recently, president of the Science Council of Fertilizer Institute in Pulawy, Institute of Inorganic Chemistry in Gliwice and Institute of Heavy Organic Synthesis in Blachownia. He is also the member of scientific council in: Institute of Chemical Engineering in Gliwice, Institute of Atomic Energy and Institute of Non-Ferrous Metals in Gliwice. Home address: Lakowa 17, Kamieniec Wroclawski 55-002 Poland; office address: Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, Poland.