Review

New slow-release fertilizers – economic, legal and practical aspects: a Review**

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Abstract. The improper adjustment of the release characteristics of commonly used mineral fertilizers to the nutritional requirements of plants results in the loss of a significant part of them by infiltration into the soil profile or in the form of greenhouse gas emissions into the atmosphere. Legal regulations including the national emission ceilings directive, require the Member States of European Union to limit ammonia emissions from agriculture. In order to minimize the losses of valuable nutrients and to reduce greenhouse gas emissions it is necessary to find new solutions and technologies in agriculture. Specialists emphasize the beneficial effects of localized fertilization methods and the use of the slow-release/controlled-release fertilizers. Field studies conducted on newly obtained fertilizers prove their beneficial effect on the quality and quantity of the crop but currently the products offered on the market are too expensive to use in large acreage crops. This article presents an overview of some particular economic, legal and practical aspects of slow-release fertilizer production and use. Additionally, the results of field tests indicating their beneficial effect on plant yield, the plant response to stressful conditions and methods for environmental protection are also presented.

Keywords: slow-release and controlled-release fertilizers, national emission ceilings directive, greenhouse gas emissions, NH_3 emisions

INTRODUCTION

Nutrient losses from mineral fertilizers have persisted at a high level for several years (Barrows and Kilmer, 1963; Sharpley *et al.*, 2001; De Jong *et al.*, 2009; Dutta

et al., 2016). This adverse phenomenon not only has economic implications, *i.e.* the loss of the main components of costly fertilizers which enhance plant development (Vatn *et al.*, 2006), but also environmental consequences, *i.e.* the penetration of the components into deeper layers of soil (Drury *et al.*, 2014) and the contamination of soil and groundwaters (Bertol *et al.*, 2017). Some of the components are emitted into the atmosphere, in large part as greenhouse gases, thus contributing to progressive climate change (Parton *et al.*, 2001; Uzoma *et al.*, 2015; Congreves *et al.*, 2016a; Rochette *et al.*, 2018). The problem of irretrievable nutrient loss has been arousing increasing interest in recent times due to ongoing attempts at the reduction of environmental pollution (He *et al.*, 2018; Holly *et al.*, 2018). These considerations have resulted in the introduction of legal regulations at national and European levels, for instance, in the Act introducing changes to the National Emission Ceilings of 2016 for atmospheric pollutants (NEC Directive, 2016). Greenhouse gases include carbon dioxide, nitrous oxide and indirectly ammonia, which are released as a consequence of the application of fertilizers to soil. Apparently, the new emission limits may result in reduced levels of application or even in a complete ban on the use of urea-based fertilizers. An exception to this law, however, is the use of slow-release urea (Al-Zahrani *et al.*, 1999; Beig *et al.*, 2020).

Each manufacturer of slow- or controlled-release fertilizers is required to conduct a series of tests to characterize the properties of the substance added to new products, demonstrate the untypical mode of release of these components, and prove the absence of harmful effects of the materials on the environment (Ibrahim *et al.*, 2014; Babadi *et al.*, 2015). The solutions used to date do not meet all of the requirements introduced by the new law. The materials are often non-biodegradable and their residues decompose in the soil for several years or even decades (Boyandin *et al.*, 2016; Tan *et al.*, 2017). Hence, there is a clear tendency to return to materials of natural origin and their modified particles, which may become the only legal method of urea application from the point of view of the new requirements (Calabi-Floody *et al.*, 20018). In addition to typical laboratory tests, manufacturers are expected to carry out experimental field tests on the application of newly developed fertilizers. Multiyear field experiments are conducted on soils with strictly specified acidity, moisture, and other parameters that may affect the quantity and quality of crops (Perez and Francois, 2016; Zhang *et al.*, 2016). Additionally, such factors as different plant species and varieties as well as different climatic zones are frequently analysed in such experiments (Ransom *et al.*, 2020). The characteristics of the yields are influenced by the mode of fertilizer application (Wilson *et al.*, 2009; Nash *et al.*, 2012). The validity of introducing new trends based on localized fertilization in agriculture is worth emphasizing at this point.

This study is a concise compendium of the available data concerning changes in the law and economic environment as well as the methods that are currently used or being developed for the modification of mineral fertilizers contributing to the slow release of nutrients. The review presents examples of materials and the results of field tests of slow-release/controlled-release fertilizers (SRF/CRF). The study emphasizes the interesting relationship between legal changes and trends in the development of new products in agriculture. Furthermore, it presents the ongoing successive progress being made in the work on slow- and controlled-release fertilizers over the last twenty years.

LEGAL AND ECONOMIC ASPECTS

Plant nutrient requirements are fulfilled by the application of nutrient fertilization. One of the most important plant nutrients is nitrogen. Three forms of N are used for fertilization: nitrate, ammonium, and amide nitrogen; however, only the nitrate ion is readily available for plants (Masclaux-Daubresse *et al.*, 2010). The other two ions have to undergo characteristic transformations in soil in order to be absorbed by plants. The efficiency of fertilization is relatively low and often maladapted to the nutritional needs of plants (Hirel *et al.*, 2007). Simultaneously, fertilization exerts a negative impact on the environment. The

transformation of nitrogen forms in soil is accompanied by greenhouse gas emissions and ion leaching with groundwater (Matson *et al.*, 1998). Ultimately, the utilization of nitrogen originating from mineral fertilizers is in the range of 50-70% (Korzeniowska, 2009). As demonstrated by the official European Emissions Inventory (EMEP) and the analysis of the Department of the Environment, Food, and Rural Affairs (Defra), ammonia emissions from ammonium nitrate reach 10-13% and almost up to 60% in the case of urea (Fertilizers Europe, 2019). The urea ammonium nitrate solution is characterized by an intermediate level of emission somewhere between the two aforementioned fertilizers (Dampney *et al.*, 2004; Chadwick *et al.*, 2005; EMEP 2007). The average levels of emission from mineral fertilizers are presented in Table 1.

Table 1. Nitrogen losses by ammonia emissions from typical fertilizers: ammonium nitrate (AN), urea-ammonium nitrate solution (UAN) and urea for two chosen agricultural ecosystems (based on Fertilizers Europe, 2019)

Fertilizer type	Volatilization losses (% N)	
	Arable land	Grassland
	(%)	
AN	0.6	1.6
UAN	6	12
Urea	11.5	23

Ammonia volatilization constitutes a considerable environmental burden (Congreves *et al.*, 2016b; Sun *et al.*, 2018). Therefore, the European Parliament and the Council of the European Union have resolved to prevent and reduce greenhouse gas emissions. In 2016, a Directive was introduced to reduce the emissions of some types of atmospheric pollutants. It also changes the emission ceilings for ammonia. The new Directive obliges all European Union countries to reduce ammonia emissions by 1% each year between 2020 and 2029 and to reach a 17% reduction in emissions by 2030 (NEC Directive, 2016; Suresh *et al.*, 2018). The implementation of this directive will have reduced ammonia emissions by almost 30% by 2030. The options suggested for the reduction of nitrogen losses include:

– the replacement of urea with ammonium nitrate fertilizers,
– the application of slow- or controlled-nutrient-release fertilizers.

The reduction of ammonia emissions through the total elimination of prilled/granulated urea and water solutions of urea and ammonium nitrate in Poland was expected to reach 55.5% by 2020 and a further 47% by 2030 in comparison with the NH_3 emissions from 2005 (Report by Grupa Azoty Puławy S.A., 2018). The lower rate of decrease in the percentage value of the reduction in the years 2021-2030, outlined in the report, stems from the estimated increase

in nitrogen fertilizer consumption. This demonstrates the possibility of meeting the requirements as implemented by the NEC Directive. It is noteworthy that in this scenario, the production of ammonium nitrate based fertilizers would have to be increased over a short period of time, while the domestic production of urea would be drastically limited or cease. This kind of solution would be economically unreasonable from the perspective of potential benefits and losses for Polish agriculture. Another scenario for ful-filling these requirements which was established by the European Parliament and the Council is to use some techni-cal measures which are applicable in the case of urea-based fertilizers that are capable of reducing ammonia emissions by 50% at least. This would result in a reduction of emis-sions by 28.8% by 2030 and ensure compliance with the novel emissions regulations. Currently, the methods used for such a high level of emission limitation in the context of economic profitability have as yet not been identified or fully explored. Nevertheless, a combination of current methods may yield the expected results, methods such as: urease inhibitor application, polymer coating applica-tion, larger fertilizer granules *etc.* (Report by Grupa Azoty Puławy 2018 – unpublished data).

Slow or controlled-release fertilizers have been designed to ensure that the delayed nutrient release is synchronized in time with the nutritional requirements of plants (Drury *et al.*, 2017). This in turn should result in an improvement of the efficiency of the utilization of fertilizer components and an increase in yields (Shaviv and Mikkelsen, 2005; Trenkel, 2010). A comparison between plant nutrient sup-ply by conventional and slow/controlled-release fertilizers is shown in Fig. 1. Figure 1a shows the highest concentra-tion of nutrients in the soil within a short time after the application of a conventional mineral fertilizer, *i.e.* when the lowest plant nutrient demand is noted. After that, the nutrient concentration declines, whereas the plant nutrient demand increases. During the application of SRF/CRF fer-tilizers, the rate of nutrient release is more suitable to meet the nutritional requirements of the plant (Fig. 1b).

The reduction of emissions associated with the use of mineral fertilizers is accompanied by an increase in the uti-lization of nutrients by plants which can be achieved in two ways. One approach is based on the application of urease or nitrification inhibitors, which slow down the transforma-tion of nitrogen compounds in the soil (Drury *et al.*, 2017; Rop *et al.*, 2018). The other method involves the use of a coating material, which is designed to be a physical bar-rier for nutrient transport (Guo *et al.*, 2005; Ransom *et al.*, 2020).

The effectiveness of inhibition for many soil enzymes mainly depends on the physicochemical properties of the soil and/or on the local climatic conditions (Masclaux-Daubresse *et al.*, 2010; Nash *et al.*, 2012). Chemical compounds that are widely known as urease inhibitors and nitrification inhibitors are able to limit nitrogen losses, including the gaseous forms such as: ammonia and nitrous oxide (Calabi-Floody *et al.*, 2018). These types of com-pounds must also meet plenty of requirements, *i.e.* with reference to non-toxicity, the low concentration required to act in an effective way, favourable stability versus time characteristics and a high degree of compatibility with urea-based fertilizers (solid and liquid) (Fu *et al.*, 2018). Another very important factor for urease and nitrification inhibitors is their degradability in the soil without any significant accumulation effect in the soil and/or in the roots of the plant (Jahns *et al.*, 1999; Boyandin *et al.*, 2016). Regulation (EC) No 2003/2003 directly defines the authorized sub-stances that are permitted to act as urease and nitrification inhibitors, while Regulation (EC) No 2019/1009 no longer defines inhibitors in detail. Regulation (EC) No. 2019/1009 is a novel guideline for EU fertilizers, which only intro-duces the general specification of urease and nitrification inhibitors, particularly those including the limitation level of the oxidation rate for ammonia/ammonium ions and also the limitation level of the urea hydrolysis rate with an inhibitor concentration of up to 2 wt. % in fertilizer.

The use of urease inhibitors in agriculture is only pos-sible when the substances are authorized for use by the applicable law. Regulation (EC) 2003/2003 of the European
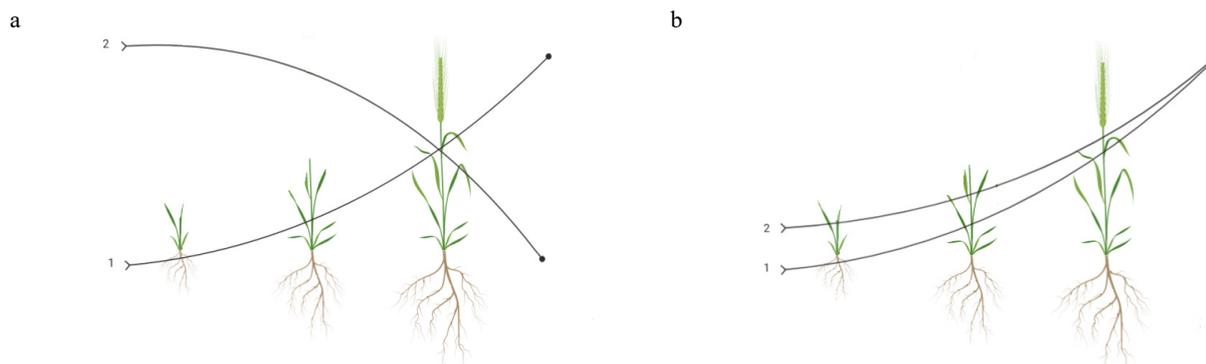
a

b

Fig. 1. Visualization of the differences between the nutritional requirements of plants (1) and supplementation of nutrients (2) depend-ing on the type of fertilizer: a) conventional fertilizers, b) slow/controlled-release fertilizers.

Parliament and Council contains a list of inhibitors that can be added to urea and other fertilizers as well as the amendments introduced in 2014. The EC has approved the following substances:

– N-(n-butyl-)thiophosphoric triamide (NBPT),
– N-(2-nitrophenyl)phosphoric acid triamide (2-NPT),
– reaction mixture of N-butyl-thiophosphoric triamide (NBPT) and N-propyl-thiophosphoric triamide (NPPT) (in a ratio of 3: 1) (Regulation EC 2003/2003).

The chemical structures of the inhibitors are shown in Fig. 2. All of them are thiophosphoric triamide structures with different substituents on one of the amide nitrogens. The groups may be aliphatic (n-butyl, n-propyl in NBPT and NPPT) or aromatic (2-nitrophenyl in 2-NPT). Because of the fact that these compounds are structural analogues of urea, they have an effect on urease activity in the soil.

The third of the substances listed by the EU Parliament and Council is a mixture marketed as a commercial product called LIMUS. As specified by the manufacturer, it offers an effective way to reduce emissions by delaying the hydrolysis of urea and its conversion to ammonium carbonates through the inhibition of urease activity. Emissions from fertilizers can be reduced by the LIMUS product by up to 90% (Li *et al.*, 2016). Nevertheless, investigations have suggested that the effectiveness of the application of this inhibitor varies depending on environmental conditions, primarily the type of soil treated (Bastos and Ferguson, 2015).

Another method used for the limitation of ammonia and GHG emissions involves the use of materials that form a physical barrier to nutrients. These include suspensions of active fertilizers in a hydrophobic material which hinders the solubility of the fertilizer or fertilizers coated with polymeric materials. As demonstrated by the current level of knowledge, urea can be coated with organic polymers (*e.g.* resins – Osmocote) and inorganic materials such as sulfur (Faber, 2016; Grönlund, 2007; Lubkowski and Grzmil, 2007; Majeed *et al.*, 2014.).

Despite their continuous development, slow-release fertilizer technologies still have few supporters in Europe, primarily due to the high prices of the SRF/CRF fertilizers. The prices of sulfur-coated fertilizers can be even 2-fold higher, while polymer-coated fertilizers can be up to 3 times more expensive than conventional agents (Carson and Ozores-Hampton, 2014). Hence, SRF/CRF fertilizers are used mainly in gardening and for the fertilization of lawns and ornamental plants. The data in Table 2 comes from three separate sources (Carson and Ozores-Hampton, 2014; Suresh *et al.*, 2018 and the author's own compilation of the data from the FOB Chinese ports database, 2020). It may be observed from Table 2 that the prices of SRF/CRF fertilizers have decreased in the last few years, which may be connected to the increasing popularity of these products. Table 2 also shows that the average prices in China are considerably lower than those in other markets. Currently, the major production and sales markets are those of China and the USA, where 94% of the world's production is purchased. China is the largest producer of CRF and SRF, also, it is the most dynamically developing market. Since 2012, China's production capacity has grown by an average of 9% per year and reached 5.95 mln t in 2017 (*vs.* the forecasted 3.5 mln t) (Suresh *et al.*, 2018). The same authors noted that the global consumption of slow-release fertilizers is set
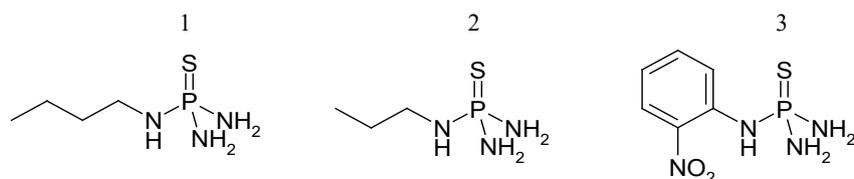

Fig. 2. Chemical structures of urease inhibitors: 1 – NBPT, 2 – 2-NPT, 3 – NPPT.

T a b l e 2. Price list of different types of fertilizers

Fertilizer	Price ($ t[-1])		
	2014[1]	2017[2]	2020[3,*]
Soluble urea	380 – 560	178 – 326	260 – 270
Controlled-release urea (sulfur coated)	775 – 875	327 – 950	300 – 450
Controlled-release urea (polymer/sulfur coated)	500 – 1 000	528 – 1 130	300 – 520
Controlled-release urea (polymer)	700 – 1 500	905 – 2 940	350 – 600

Based on 1. Carson and Ozores-Hampton (2014), 2. Suresh (2018), and 3. authors' own compilation of the data from the FOB Chinese ports database, 2020. *Data considering only the Chinese market.

to increase annually by 5.5% in 2017-2022. The majority of slow-release fertilizers applied in agriculture are coated fertilizers (approx. 75%), mainly polymer-coated products. Argium, Everris, Aglukon, Haifa, and Chisso are the main producers (Carson and Ozores-Hampton, 2014).

Table 3 presents examples of products manufactured with the granule coating process together with their N-P-K composition. It includes both pure urea and conventional NPK fertilizers with different compositions as well as sulfur or magnesium oxide additions. They differ in the ratio of their components, release time, and coating composition. There are fertilizers with polymer (*e.g.* polyurethane), mixed sulfur-polymer, and resin coatings (Carson and Ozores-Hampton, 2014; Suresh *et al.*, 2018).

In Europe, the CRF production capacity is approximately 50 t per year of sulfur-coated urea, 352 t of polymer-coated urea, and 136 t of CRCU (Controlled-Release Coated Urea). The main producers are Sulfur Hellas in Greece, Haifa and ICL in Israel, and Everris/ICL in the Netherlands (Suresh *et al.*, 2018).

TECHNOLOGY OF THE PRODUCTION OF COATED SLOW-RELEASE FERTILIZERS

The fertilizer coating process delays nutrient release through a physical barrier. The coating is an outer layer in direct contact with the environment and is poorly soluble in soil conditions. The inner core of fertilizer granules consists of easily soluble nutrients. Nutrient release is

Table 3. Examples of products and producers of SRF/CRF (PC – polymer coated, RC – resin coated, S/PC – sulfur/polymer coated)

Trade name (Manufacturer)	Formulation N-P-K	Coating description
ESN (Agrium, Inc.)	44-0-0	PC urea: Flexible micro-thin polymer coating
Polyon (Agrium, Inc.)	20-6-13 or 41-0-0	PC: Ultra-thin ployurethane coating that uses patented "Reactive Layers Coating"
Duration (Agrium, Inc.)	44-0-0 or 9-6-13	PC: Micro-thin polymer membrane
Nutricote (Chisso-Asahi Fertilizer Co.)	28-0-0	RC: Resin coating with a special chemical release agent
Meister (Chisso-Asahi Fertilizer Co.)	21-7-4 or 19-5-14	Resin-coated: Granular urea coated with a polymer composition of natural products, resin, and additives
Osmocote (Everris, Inc.)	8-16-12 or 16-9-12 or 17-11-10 +2MgO+TE	RC: Alkyd-resin coating made in a batch process from
Poly-S (Everris, Inc.)	37-0-0	S/PC urea: Urea coated first with sulfur and then with polymer
Agrocote (Everris, Inc.)	39-0-+11% S or 0-0-42+14% S	S/PC and RC: Either 100% N or K fully coated with polymer/sulfur and resin coatings
Multicote (Haifa Group)	34-0-7 or 22-8-13 or 34-0-7 or 34-0-7	RC: Water-soluble nutrients encapsulated in a polymeric shell
Florikote (J.R. Simplot)	12-0-40 or 19-6-13 or 40-0-0	PC: Dual-layer technology coats the fertilizer with a smooth exterior coating with no breaks

determined by the following factors: temperature, moisture, pH, the presence of salt in the soil and the composition and mechanical strength of the coating (Carson and Ozores-Hampton, 2014). Another important factor is the size of the granules, which determines the specific surface area to volume ratio. For instance, 1 kg of a coarse and fine-grained fertilizer will exhibit differences in the nitrogen release rate. With its lower specific surface area to volume ratio, a large granule will release nitrogen more slowly (Carson and Ozores-Hampton, 2014).

Liu *et al.* (2008) and Shaviv and Mikkelsen (2005) conducted research concerning the mechanism of action of coated fertilizers. They suggest that nutrient release should be based on a multi-stage diffusion model (Fig. 3). After the application of fertilizer, moisture penetrates the granules through the coating pores or micropores (Fig. 3a), next, the pressure inside the granules increases gradually and the nutrients in the core are dissolved (Fig. 3b). The subsequent stage consists of nutrient release (Fig. 3c), which may proceed in two ways:

1. Stepwise "catastrophic" release – the coating bursts due to the internal pressure and the entire content of the granule enters the soil.

2. Gradual release – the pressure inside the granule does not exceed the coating strength and the elevated pressure causes nutrient release via diffusion (Shaviv *et al.*, 2001; Azeem *et al.*, 2014).

The stepwise release is characteristic for non-elastic fragile coatings, whereas the gradual release is typical of polymeric coatings made from *e.g.* polyurethane, alkyd resins, or polyolefins (Korzeniowska, 2009). The third phase of the diffusion model is the slow decay of release. The decreasing pressure inside the granule slows down nutrient release until the nutrients are depleted and release ceases to occur. Examples of the studies concerning the most promising coating materials are presented in Fig. 4.
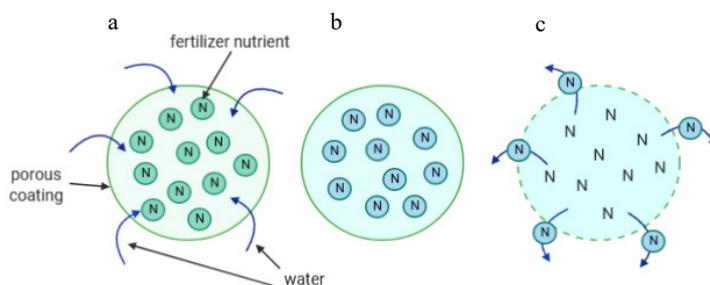
Fig. 3. Diffusion mechanism of controlled release.

Sulfur	Synthetic polymers	Starch	Ethylcellulose
Liu *et al.*, 2006	Rosa and Rocha, 2010	Naz, 2016	Sadłowski *et al.*, 2015
Detrick, 1997	Alemzadeh and Vossoughi, 2002	Trenkel, 2010	Szymański *et al.*, 2015
Detrick and Hargrove, 2002	Suresh *et al.*, 2018	Naz and Sulaiman, 2014	Myasoedova, 1999
Choi and Meisen, 1997	Yang *et al.*, 2012	Singh and Nath, 2012	Grönlund, 2007
Liu *et al.*, 2008		Wang *et al.*, 2014	Perez-Garcia *et al.*, 2007
Naz, 2016		Azeem *et al.*, 2016	
Blaylock, 2010		Han *et al.*, 2009	
		Suherman and Anggoro, 2011	

Fig. 4. Examples of the studies concerning some coating materials.

The simplest method for the application of the coating material on fertilizer granules is the non-pressure pan-coating process. The process parameters depends on chemical factors, *i.e.* the chemical composition of the granulated material, material factors, *e.g.* grain structure, grain surface, wettability, hygroscopicity, plasticity, equipment factors, *e.g.* the diameter of the granulator plate, frequency of plate rotation, angle of plate tilt, type of granulation liquid, and process factors, *e.g.* the rate of the granulation liquid flow, the temperature of the liquid or the residence time of the material in the granulator (Kołaczkowski *et al.,* 2003). The solid fertilizer encounters the coating solution on the rotating plate. A spherical granule is formed as a result of this contact and material dumping. Granules with a predetermined diameter, depending on the process parameters, leave the device. In turn, spray drying is a material encapsulation method. The encapsulating material is dispersed in a solvent with surfactants or another dispersion-supporting agent. Next, the core material is added into the mixture and the solution becomes homogenized thereby producing an emulsion (the core phase is the dispersed phase). Spraying is performed by means of a spray disk in the spray dryer chamber, where the solvent evaporates and the coating solidifies (Janiszewska and Witrowa-Rajchert, 2006). Another method is the fluidized bed coating process (Fig. 5). Fluidization ensures a high level of control and flexibility in running the process. It consists of the formation of a fluidized bed from the coating material, which is sprayed in a supporting air stream (Roy *et al.,* 2014). After the addition of the fertilizer, the substance coats the granule, thereby creating a new material characterized by slow nutrient release.

The first attempts at coating were made with the use of sulfur (Fig. 6). Sulfur was used as a middle layer between a sealant sublayer of petrochemical waste (*e.g.* car oils or paraffin) and a polymer layer which improved the mechanical parameters and was applied using a rotating plate (Liu *et al.,* 2006). Subsequently, there were attempts at the application of polymer coatings after the sulfur was preheated in a fluidized bed as well as in a polymer-sulfur-polymer combination. Such fertilizers exhibited a 38% solubility (7-day test) (Detrick, 1997; Detrick and Hargrove, 2002). In order to apply the sulfur as an independent layer, a coating of liquid sulfur in a fluidized bed was tested (Choi and Meisen, 1997). The fertilizer obtained with this approach exhibited 32.8% solubility in a 7-day solubility test. The possibility of using sulfur in combination with polymeric compounds depends on the form of the element. Crystalline sulfur (α-S) is unsuitable, as its presence causes cracks and fissures to form in the coating. By contrast, β-S is an amorphous form of sulfur that easily binds to polymers. However, β-S may be transformed to α-S at a relatively low temperature, *i.e.* even at approximately 60°C.
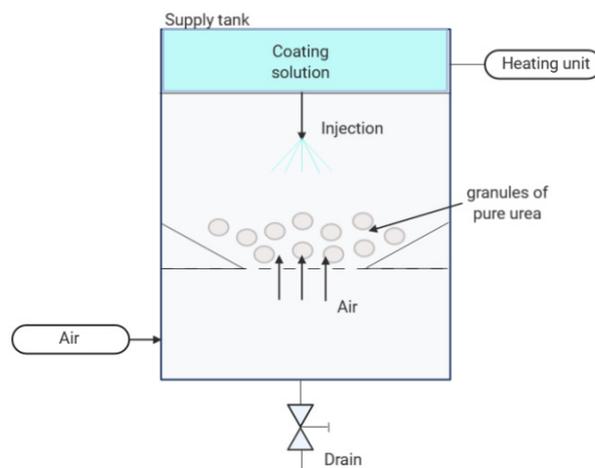

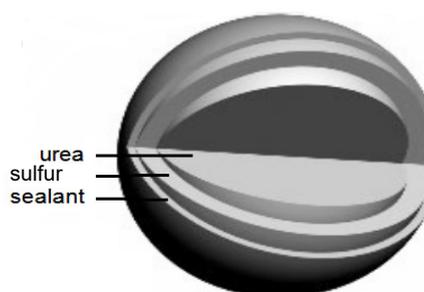**Fig. 5.** Scheme of a fluidized bed coater.

Fig. 6. Composition of sulfur-coated urea.

In order to limit the adverse transformations, various additives were introduced. One of them was DCPD (dicyclopentadiene) (Liu *et al.,* 2008). A 7-day solubility test showed a DCPD-induced reduction in the solubility of coated urea from 83 to 54%. However, the sulfur-coated fertilizers did not meet the controlled release standards. The material turned out to be sensitive to temperature, light, mechanical pressure, and soil properties. Additionally, the level of water penetration was relatively high, which indicated the poor sealing properties of the sulfur coatings. However, the sulfur coatings exhibited biodegradability and had relatively low production costs. As shown by various studies, the nutrient release was slowed down, but in an uncontrolled and largely unpredictable manner (Naz, 2016). The nutrient release from polymer-sulfur-coated fertilizers proved to be more predictable. These fertilizers were less sensitive to temperature, water penetration into their core was impeded, and the release was slower and also predictable. Unfortunately, the hybrid material solutions were substantially more expensive and, at the same time, exhibited sensitivity to soil properties (Blaylock *et al.*, 2010).

The use of polymer-based coating materials may yield thinner layers with very favourable mechanical properties. Given the diffusive mechanism of nutrient release, an important aspect of the coating materials was the possibility

of nutrient solution penetration. The permeability of bio-polymers justified the choice of these coating materials. With their more predictable physicochemical traits, stable properties, and ability to be designed during synthesis, synthetic polymers have become highly popular. The permeability of polymeric materials can be controlled by the optimization of their composition. This also contributes to the improved predictability of nitrogen release than is the case with inorganic compounds (Shaviv and Mikkelsen, 2005). The first method for the application of polymer coatings consisted of polymer dispersion in organic solvents. The use of volatile organic compounds increased the costs and posed an environmental threat. Therefore, research concerning water dispersions was instigated. One of them was the aqueous dispersion of a 2-methylpropenoic acid copolymer with the addition of talc, magnesium, triethyl citrate, polyethylene glycol, and titanium dioxide. In such conditions, the ammonia losses were reduced by 3-57% (Rosa and Rocha, 2010). Polyurethanes were also tested in previous studies by Ge *et al.* (1998). The process involved the application of isocyanate, polyol, and wax onto fertilizer granules. The reaction induced the formation of coatings and delayed nitrogen release by 40-50 days. Additionally, there were attempts at coating urea with poly(vinyl alcohol) (Alemzadeh *et al.,* 2002), which proved to be too expensive for high-scale applications despite its high degree of biodegradation. In order to produce low-cost materials, the use of recycled polymers was proposed (Yang *et al.,* 2012). The use of waste polystyrene in a mixture with wax and a polyurethane sealant even resulted in a 7-fold reduction in costs relative to polymer-coated fertilizers with a similar N release rate (Faber, 2016). The mixture was applied to urea in a Wurster fluidized bed. Three main types of natural polymers were tested to assess their potential to be used as coating materials: cationic (*e.g.* chitosan), neutral (hydroxymethylpropyl cellulose), and anionic (sodium poly-alginates) polymers (Jintakanon *et al.,* 2008). It is worth emphasizing that starch derivatives may be applied using this process due to their non-toxicity, complete biodegradability, and water storage capacity (Majeed *et al.,* 2014).

Starch may be regarded as a semi-permeable or impermeable membrane with fine pores that provides temporary isolation of urea granules from the soil environment (Naz, 2016). The migration of nitrogen in such a material is influenced by the physicochemical properties of the coating rather than the soil properties. The rate of nutrient release from starch-coated fertilizers should be under greater control than is the case with simple sulfur coatings. Unfortunately, starch is a fragile material due to the high level of interchain interactions which limits the mobility of entire polymer segments (Trenkel *et al.*, 2010). The interchain distance can be increased and the strong interactions between them can be disrupted by using plasticizers. In this way, the elasticity of the coating can be increased by the addition of urea or borates (Singh and Nath, 2012; Naz,

2016). Urea may be applied at a dose of 5-20% of starch dry matter. Hydrogen bonds are produced upon the addition of *ca*. 10% urea. Larger amounts promote the absorption of moisture by free molecules, which results in a plasticizing effect (Wang *et al.,* 2014). Excessive amounts of plasticizer leads to the transformation of the coating material into a paste or gel, which may barely adhere to the surface of the fertilizer granules. Therefore, an optimized amount of urea should be used in the case of the application of a starch-based coating material. Apart from urea, boron ions obtained *in situ* via the dissociation of di-sodium tetraborate were added to the starch-based materials (Naz and Sulaiman, 2014). In this case, the urea particles functioned as a plasticizer, while the boron ions were reactive particles responsible for crosslinking. The sodium ions remaining in solution counterbalanced the negative charge of the mixture.

In another experiment, polyvinyl alcohol (PVOH) and citric acid or formaldehyde were added to the starch as a crosslinking agent to improve its mechanical properties (Azeem *et al.,* 2016; Han *et al.,* 2009). The parameters of the coating depended not only on the composition of the coating mixture, but also on the process parameters (in the fluidized bed), *i.e.* the temperature and pressure of the auxiliary gas, the rate and temperature of the spray, and the coating time. Coatings made from a mixture of starch, acrylic acid, and polyethylene glycol were also applied in a fluidized bed (Suherman and Anggoro, 2011). Analyses of the surface of coated urea granules have demonstrated differences in the morphological structure between thin coating layers and thicker coatings. The former are more compact and do not exhibit disturbances in the crystalline structure. As indicated in many studies, there is a directly proportional relationship between the time of nutrient release and the thickness of the coating, the parameters of which differ depending on the material used (Azeem *et al.,* 2016).

Cellulose is another biodegradable natural-origin polymer. It is a polysaccharide from the polyacetals group with structural units linked via glycosidic bonds. Cellulose is a linear polymer consisting of glucopyranose residues linked *via* 1,4-β-glycosidic bonds.

Cellulose is practically insoluble in aqueous and organic solvents, therefore, its alcohol groups have to be esterified for the chemical modification of its properties. The potential of using an ester terminated with ethyl groups as a fertilizer coating has been assessed (Sadłowski *et al.,* 2015). Ethyl cellulose is produced in a reaction of alkaline cellulose with ethyl chloride and then impregnated with an aqueous sodium hydroxide solution. This reduces the molecular mass of the polymer and disrupts the crystalline structure, which results in an easier and more homogenous alkalization of the cellulose (Szymański *et al.,* 2015). Ethyl cellulose may be applied to urea from alcoholic solutions or organic solvents. It exhibits a favourable degree of miscibility with oils and waxes and can be plasticized (Myasoedova, 1999). In the process of spraying ethyl cellulose onto granules,

special attention should be paid to the possibility of the formation of explosive mixtures with alcohol vapours. It should therefore be applied in an open rotary drum granulator thereby minimizing the amount of dispersed solvent. After the coating process is complete, the granules should be dried. The low efficiency of the drying process and contact between the granules may cause disturbances in the coating continuity. Therefore, anhydrous solvents or fluidized bed processes are recommended (Grönlund, 2007). The delay of emissions depends on the thickness of the coating, the type of additional substances (*e.g.* plasticizers), and the size of the granules. The relationship between the release of nitrogen (nitrate ions) over time and the coating thickness was also demonstrated by (Perez-Garcia *et al.,* 2007). This work includes graphs with a presentation of the effect of ethyl cellulose content on the release of the active ingredient from the uncoated form (NH_4NO_3) and coated ammonium nitrate. As the coating on the granule becomes thicker the slower release of fertilizers ingredients is noted.

LABORATORY TESTS AND FIELD INVESTIGATIONS OF SLOW-RELEASE FERTILIZERS

The slow release of active ingredients is tested in preliminary laboratory tests followed by field tests. One of the simplest laboratory methods consists of weighing the fertilizer granules before and after the procedure. This is applied to the investigations of the coating process, where a specific amount of the fertilizer is weighed before and after the coating process. This allows for the calculation of the ratio of the mass of the applied coating to the total mass of the fertilizer. Additionally, in order to determine the diameter of the modified fertilizer granules, a specified number of randomly selected granules can be measured with a digital calliper (uncoated form of fertilizers and coated samples) (Naz and Sulaiman, 2014; Naz, 2016). Laboratory tests are based on an analysis of the nutrient release rate in aqueous solutions. The level and duration of the release of a substance can be determined using conductometric and colorimetric methods. The former approach is characterized by a low degree of complexity and the possibility of determining the amount of all fertilizer components released into the solution and changing its conductivity. The analyses may be carried out in both static and dynamic conditions. Intensive mixing contributes to a several-fold increase in the fertilizer dissolution rate. It is noteworthy that the conditions of the application of fertilizers to the soil are more similar to those used in static tests. A similar effect on nutrient release is exerted by temperature – an increase in the solution temperature is accompanied by more rapid nutrient release. The nutrient content may also be determined by capillary electrophoresis. Samples for this analysis are prepared through the dissolution of a specified mass of coated granules in an appropriate solvent and the extraction of the mixture. Undissolved fertilizer granules should be filtered out prior to the analysis. The content of nitrogen components may be determined with an ultraviolet (UV) detector (Perez-Garcia *et al.,* 2007). The most common method, however, is the determination of the water-dissolved total nitrogen using the distillation or formalin methods. The outer and inner structure of the coating was examined with the use of stereoscopic microscopes, scanning electron microscopes (SEM), and X-ray diffraction (XRD). It is important to note that, if necessary, the crystallographic structure of the coating may be determined using a diffractometer. Infrared (IR) and nuclear magnetic resonance (NMR) tests are performed to evaluate the structure and to determine the reaction of coating components and changes in the structure depending on the amount of additives (Han *et al.,* 2009; Perez *et al.,* 2016). The wide range of methods used facilitates the performance of complementary analyses corresponding to the needs and focus of the relevant investigations.

The behaviour of a slow-release product should also be analysed in the target environment. Therefore, nutrient release is analysed after the application of fertilizer to the soil with specific parameters, e.g. pH and moisture, with the maintenance of an appropriate temperature during the experiment. Such a fertilizer is then analysed based on the difference in the nitrogen content of the granules before and after application to the soil (Perez-Garcia *et al.,* 2007). At the same time, it is possible to study gas emissions from the soil in special laboratory measurement chambers in a system equipped with an external analyser of the air composition. Similar analyses are carried out in field experiments, but the chambers are substantially larger and the analysers have a higher degree of efficiency, especially those with a limited range of operation. The use of a chamber with a very small volume leads, for these analysers, to the upper limit of the measuring range being reached too rapidly, which has a negative impact on the effectiveness of the measurement. The main aim of the field studies is to determine the yield and, especially in the case of slow-release fertilizers, to examine the ratio of lost and absorbed nutrients introduced into the environment with fertilizers. The cultivation yield size depends primarily on the ability of plants to uptake nutrients, which is associated with the fertilizer dose, fertilization regime, weather conditions, and the form in which the nutrient was applied. In 2014-2016, the effects on the yield and selected quality traits of potato tubers which were exerted by a nitrogen fertilizer was investigated at the Plant Breeding and Acclimatization Institute, Jadwisin Branch (Trawczyński, 2017). The experiment had a 2-factorial design. The primary factor was the type of fertilizer (1. Control object (no fertilizer), 2. Slow-release fertilizer (29% N), 3. Urea – 46% N, 4. Ammonium nitrate – 34% N, 5. Nitrochalk – 27% N) and the secondary factor was the fertilization regime (1. Before planting, 2. Split dose – 50% before planting + 50% before plant emergence).

The investigations of potato tubers were conducted in sandy loess soil (granulometric composition of loamy sand). The soil was acidic and had a high content of available phosphorus and moderate levels of potassium and magnesium. Nitrogen fertilization was applied at a dose of 100 kg N ha^{-1}. During harvest, the total yield, the percentage proportion of deformed tubers, and the content of starch and nitrates (V) were determined. The change in the yield induced by the application of a slow-release fertilizer was clearly favourable compared to the quick-release fertilizers, *i.e.* ammonium nitrate and nitrochalk. However, compared to the slow-release fertilizer, this difference was not as significant, *i.e.* 4%. In the case of the secondary factor, higher yields were achieved after the application of one dose before planting the tubers. In addition to the beneficial effect on yield, the slow-release fertilizer exerted a positive effect on the tuber size and reduced the nitrate content in the plants (Trawczyński, 2017). Furthermore, it was proven that the application of a 110 kg N ha^{-1} dose of the slow-release fertilizer produced the same effect as 260 kg N ha^{-1} of the conventional mineral fertilizer (Shoji *et al.,* 2001).

Another example of field research is the experiment concerning the cultivation of spring wheat and barley, which was carried out in Alberta and Saskatchewan in western Canada in 1998-2000 (Haderlein *et al.,* 2001). The experimental factors included both conventional and controlled-release urea. Localized fertilization was applied, *i.e.* fertilizer granules were placed at a distance of 30 mm from the seeds or 30 mm under the plants. In order to assess the possibility of reducing this amount, the fertilizer was applied in doses of 25, 50, 75, and 100 kg N ha^{-1}. A reference plot (0 kg N ha^{-1}) was also established. The soil had a neutral to acid pH. The slow-release fertilizer applied had been previously tested in laboratory analyses. It released all of its nitrogen after 40-50 days of granule immersion in water. The experiment conducted by Haderlein demonstrates that the application of the Commodities Research Unit (CRU) fertilizer under the plant may be an alternative to the conventional placement of urea beside seeds. The absence of significant differences in efficiency may be determined by certain specific aspects of the experimental area. Soil moisture is a determinant of nitrogen losses through leaching and the emission of gases. The soils in Alberta and Saskatchewan have a low moisture content and winters are characterized by relatively low air temperatures. No conditions promoting nitrogen losses were observed during the experimental period. However, distinct changes were noted in the nitrogen content of the grain. It turned out that the grains of plants supplemented with the slow-release fertilizer had a higher level of nitrogen (protein). This implies a higher intensity of nitrogen absorption by the plants in the latter stages of plant development. Hence, it may be concluded that the nutrient losses associated with leaching and emission are lower, as a large part of the applied nitrogen is absorbed by the fertilized plant. This brings greater financial benefits for the farmer, despite the comparable yields. An example of other benefits may be that the different nitrogen contents in the grain depend on the applied dose of conventional urea and slow-release fertilizer. Because of the lower N losses by leaching and denitrification, the application of slow/control release fertilizers at the same rate as pure urea guarantees a higher protein content in the plant (Haderlein *et al.,* 2001).

The next example is a field experiment with winter wheat and barley conducted in Alberta Province in 2002-2005. The experiment included three factors: fertilizer application mode (seed-placed, side-banded), fertilizer type (conventional urea, 20-day CRU, 40-day CRU) and nitrogen dose (0, 30, 60, 90 kg N ha^{-1}) (McKenzie *et al.,* 2007).

The investigations have shown the possibility of supplementing higher doses of nitrogen with slow-release fertilizers even in adverse weather conditions (drought). CRU application did not reduce the number of germinating plants even at a dose of 120 kg N ha^{-1}. The efficiency and effectiveness of nutrient utilization were inferior, compared to the conventional mineral fertilizer. Even worse, the coatings were damaged during transport and during the application of the fertilizer (McKenzie *et al.,* 2007). These problems emphasize the importance of considering many additional aspects (such as adjusting the mechanical properties of the fertilizer with regard to the adverse effects of its transport and storage in the future) even at the stage of designing and obtaining the fertilizer.

SUMMARY

This review indicates the increasingly important role of SRF/CRF fertilizers in agricultural production and their positive role in environmental challenges connected with climate change and the increasing global population. The presented economic and legal aspects of SRF/CRF fertilizer production confirm the necessity of developing new technologies for their production and distribution while taking into account sustainable agricultural production. The enhanced effectiveness of the use of nutritional components compared to conventional fertilizers has been confirmed.

There are two main methods for the production of SRF/CRF fertilizers. One of them involves the use of substances that slow down the transformation of nitrogen forms in the soil, *i.e.* urease/nitrification inhibitors. The other approach relies on the creation of a physical barrier for nutrients by coating fertilizers with organic (polymers, copolymers) or inorganic substances, *e.g.* sulfur. Coatings are most often formed in an immersion process, by mechanical granulation, in drum coaters, or in a fluidized bed apparatus to coat fertilizer granules with a plastic protective material. However, the traits of the product have to be characterized in various ways and with the help of many laboratory tests. The demonstration of delayed nutrient release necessitates structural tests of the coating surface as well as analysis

of the composition of the coating material (SEM, XRD, IR, NMR). One important aspect is the characterization of nutrient release and, more particularly, the time of release of most of the nutrients contained within the fertilizer. Such a declaration should be provided by each manufacturer on the label of the product, if it is intended to serve as a slow or controlled-release fertilizer.

Field experiments that were conducted using newly obtained fertilizers demonstrate their beneficial effect on the quality and quantity of the yield. Cereals fertilized with SRF/CRF have a higher protein content, while tuber plants exhibit a lower level of harmful nitrates and a larger tuber size. It is noteworthy that the advisability of the application of a specific slow-release product depends on soil properties such as pH and moisture. Investigations of the applicability of the product should be carried out on target soils or at least in similar climatic zones.

The SRF/CRF products currently available on the market typically do not meet the requirements for the biodegradation of the coating material within 24 months after the application of the fertilizer. Moreover, their price prevents their use in large-scale cultivation. This product gap can be filled by cheaper slow-release products. The growing interest in slow-release fertilizers reflects the impact of the legal changes concerning the development of new products and solutions in the agricultural sector. Due to the regulations imposed on the sale of mineral fertilizers in Europe, European manufacturers and importers will be forced to adjust their products to comply with the current legal requirements for slow-release fertilizers.

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