Production technology of nitrogen-sulphur-calcium fertilizers on the base of urea and phosphogypsum

Mieczysław BOROWIK - Fertilizer Research Institute in Puławy; Przemysław MALINOWSKI - The School of Higher Vocational Education in Nysa (PWSZ); Andrzej BISKUPSKI, Michał DAWIDOWICZ, Sebastian SCHAB, Piotr RUSEK, Janusz IGRAS - Fertilizer Research Institute in Puławy, Kazimierz KĘSIK - Institute of Soil Science and Plant Cultivation – State Research Institute

Please cite as: CHEMIK 2012, **66,** 5, 525-534

Introduction

Urea reacts with calcium sulphate with different levels of hydration forming $CaSO4·4CO(NH_2)_2$ adduct which in comparison with urea demonstrates reduced hygroscopicity and delayed action of fertilizers [1÷3]. Adduct-type fertilizers can be obtained through crystallisation from a hydrous solution of urea, to which calcium sulphate with different levels of hydration is added, or through melting a mixture of urea and calcium sulphate [4÷7]. The crystallisation method of obtaining adduct from the solution requires solving a problem of reusing the parent solution of urea which is diluted with water from gypsum. The melting technique for obtaining adducts is connected with conducting the process at high temperature at which urea condensates to biuret – a compound whose presence is not desirable due to its phytotoxic properties. Various forms of calcium sulphate can be used to produce calcium sulphate and urea adduct-type fertilizers. Regarding ecological and economic issues, the use of phosphogypsum seems to be the most favourable. As the result of research studies conducted at the Fertilizer Research Institute in Puławy so far, two methods of producing fertilizers containing calcium sulphate and urea adduct have been proposed. The first method is based on the screw granulation of the mixture of phosphogypsum and urea. The first stage of this process involves mixing of urea, phosphogypsum, and optionally water, in a course of which the reaction of adduct formation takes place. In the second stage, the obtained mixture is subjected to the screw granulation. The obtained fertilizer granules are dried, and then sieved to achieve an adequate particle-size distribution. Subgrain and sieve residue are returned to the granulation unit. In accordance with the second method, the fertilizer is produced neglecting the extrusion stage. The reaction of urea and phosphogypsum with reduced humidity content taking place in a blade mixer produces the pre-granulated material which is discharged on a granulating plate to form an adequate shape of fertilizer particles. Then, the fertilizer granules are dried. The product is sieved to achieve an adequate particle-size distribution. Subgrain and ground sieve residue are returned to the granulation unit. The production of urea and calcium sulphate adduct type fertilizers, in accordance with the proposed methods, requires the use of phosphogypsum or another sulphuric raw material with total water content not greater than 30 wt. %. Taking into account the above limitations, the tests have been undertaken to elaborate the granulation method for this type of fertilizers allowing the use of raw materials with higher water content.

Methodology

Phosphogypsum from ZCh "POLICE" S.A. *(Chemical Plant "POLICE" S.A.)*, GZNF "FOSFORY" Sp. z o.o. *(Gdańsk Phosphorus Fertilizer Plant "FOSFORY" Sp. z o.o.)* and ZCh "WIZÓW" S.A. *(Chemical Plant "WIZÓW" S.A.)* were used as a source of calcium sulphate (Table 1). Urea was used in its crystalline form (Zakłady Azotowe "KĘDZIERZYN" S.A.) *(Nitrogen Plant "KĘDZIERZYN" S.A.)* and prilled form (Zakłady Azotowe "PUŁAWY" S.A.) *(Nitrogen Plant "PUŁAWY" S.A.)*.

Table 1

Chemical composition of phosphogypsums used for tests

No.	Determination	Place of phosphogypsum production			
		ZCh "POLICE" S.A.		GZNF "FOSFORY" sp. z o.o.	ZCh "WIZÓW" S.A.
1	Calcination losses, 105°C, wt. %	33.21	24.90	24.46	19.21
2	Calcination losses, 400°C, wt. %	44.50	37.36	28.66	23.69
3	Calcination losses, 1000°C, wt. %	45.6	38.86	31.49	25.12
4	SO_3, wt. %	35.27	34.97	40.88	43.17
5	CaO, wt. %	24.08	24.10	26.51	29.25
6	P_2O_5, wt. %	0.60	0.52	1.00	1.25

The laboratory tests to produce the granulated fertilizers of adduct-type were carried out using the mixer and plate granulator by ERWEKA company. The tests on a semi-technical scale were conducted in a granulating installation at the Fertilizer Research Institute in Puławy, the diagram of which is presented in Figure 1. The main installation elements are presented below:

1. Double shaft blade granulator. Length = 1000 mm , width = 240 mm, depth = 150 mm, number of blades on shaft = 92, shaft diameter = 30 mm, blade dimensions: width = 20 mm, length = 45 mm, rotary velocity = 80 rpm.
2. Granulating plate, diameter = 1000 m, edge height = 200 mm. Pitch angle 60°. Rotary velocity = 18 rpm.
3. Drum dryer: Length = 6000 m, diameter = 600 mm, number of rotations
4. 4 rpm. Pitch angle 3°. Dryer is heated with steam operating in a co-current mode. Air flow rate through the dryer - ca. 0.5 m/s.
5. Double-deck vibrating screen. Sown area 0.75 m^2.
6. Belt conveyor: Length = 6000 mm, width = 500 mm.
7. Bucket conveyor: Elevation height = 9000 mm.

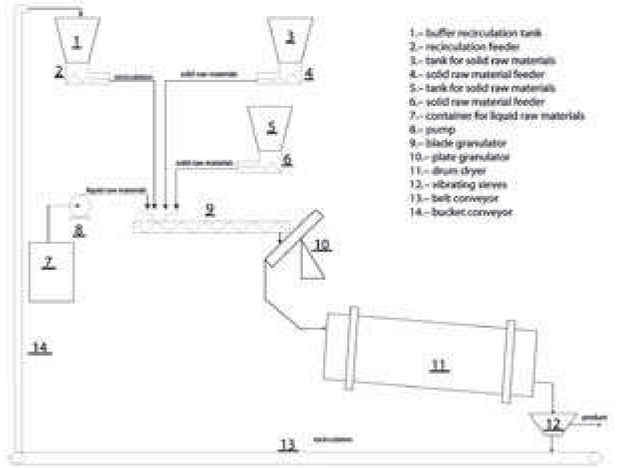

Fig. 1. Scheme of the semi-technical INS installation for granulation of fertilizers

Fertilizers produced during the research studies were subjected to chemical analyses and their utility properties were assessed (composition, particle-size distribution, granule hardness, hygroscopicity) [8, 9]. Urea content in the obtained fertilizers was determined with the spectrophotometric method using p-DMABA (p- dimethyl-aminobenzaldehyde) [10]. The conversion factor of urea in the adduct form was determined using the method based on the difference of solubility of free urea and urea bound into adduct in n-butanol [11]. The measurements concerning compression strength of granules from the produced fertilizers were performed using the apparatus ERWEKA TBH 200D. About 20-30 granules with a diameter from 2.50 to 4.00 mm were used for every measurement.

Test results

Phosphogypsum from Zakłady Chemiczne "POLICE" S.A. contains a significant amount of water (up to 45 wt. %). Considering the above, it is recommended to carry out a partial dehydration of phosphogypsum in the production process of adduct-type fertilizers in accordance with the proposed method. The tests conducted on a laboratory scale indicated that mixing phosphogypsum with such high water content and urea in the amount corresponding to the formation of $CaSO4{\cdot}4CO(NH_2)^2$ adduct resulted in the formation of pulp which probably could be discharged to the granulation unit. If phosphogypsum with lower water content (to 30 wt. %) is used,

Table 2

Composition of the pulp for producing of adduct type fertilizers in various raw material arrangement. Composition of the pulp is stoichiometric in relation to $CaSO4{\cdot}4CO(NH_2)_2$

No.	Raw material content in pulp, wt. %						Water content in pulp, wt. %	Pulp properties
	solid UREA	TUS 70 % $CO(NH_2)_2$	PHOSPOGYPSUM					
			WIZÓW 25 % H_2O	GDAŃSK WIZÓW 30 % H_2O	POLICE 37 % H_2O	POLICE 45 % H_2O		
1	51.5	-	-	-	48.5	-	18.1	pumpable pulp (T=70°C)
2	48.0	-	-	-		52.0	23.4	pumpable pulp (T=40°C)
3	-	64.2	35.8	-		-	28.2	pumpable pulp (T=20°C)
4	-	62.6	-	37.4		-	30.0	pumpable pulp (T=20°C)
5	-	60.3	-	-	39.7	-	32.9	pumpable pulp (T=20°C)
6	-	56.8	-	-		43.2	36.5	pumpable pulp (T=20°C)

Tests on pulp consistency indicated that the minimum water content in urea and phosphogypsum pulp maintaining its pumpability at a temperature of 70°C was 18.5 wt.%. Pumpability restoration at a temperature of 70°C in the pulp stored for 96 hrs is possible if the total water content in pulp is increased to the level of 21.5 wt. %. Table 2 presents the exemplary feed composition (for the production of adduct-type fertilizers using solid urea, TUS and phosphogypsum from ZCh "POLICE" S.A., GZNF "FOSFORY" Sp. z o.o. and ZCh "WIZÓW" S.A.).

Taking into account the above considerations, two semi-technical tests were carried out to produce adduct type fertilizers in the system including feeding of urea and phosphogypsum mixture in the form of pulp to the granulation unit. The first test was performed using solid urea and phosphogypsum from ZCh "POLICE" S.A., and the second using 70 % solution of urea and phosphogypsum from ZCh "WIZÓW" S.A. The tests were conducted in the semi-technical INS granulating installation for fertilizers in Puławy. During the tests, the raw material feed in the form of pulp at a temperature of 60°C was fed to the double shaft blade granulator with a peristaltic pump. Also a stream of previously prepared recirculation was directed into the granulator. The fertilizer pre-granulate was discharged from the granulator to the granulating plate, and then to the drum dryer. After leaving the dryer, the granulate was directed to the double deck vibrating screens. When subgrain and sieve residue passed the screens through the system of belt, bucket and screw conveyors, they were discharged to the recovery unit. In the first stage of tests, in order to increase the recirculation mass, the specific fraction of product was not collected, but along with subgrain and sieve residue, it was directed into the circulation. After completing the tests, the produced fertilizer was divided into the proper fraction, subgrain and sieve residue, all of which were then subjected to further tests. In a course of the tests, it was found that the granulation process of adduct type fertilizers was stable at recirculation and feed ratio equal to 5:1. The product temperature at the dryer outlet was kept at the level of 90 - 110°C.

The properties of produced fertilizers are presented in Table 3. The tests resulted in products of expected content of nitrogen and sulphur in which urea conversion into adduct was ca.

70 %. Granule hardness reached the level of 20-30 N/gran. and did not demonstrate any radical changes during the storage.

Table 3

Properties of fertilizers prepared during tests

No.	Type of determination	Result of determination in product from test I		Results of determination in product from test II	
1	N_{og}, wt. %	27.6		29.5	
3	S_{og}, wt. %	8.6		8.2	
4	The compression strength of granule (fraction 2.5 – 3.15 mm), N/gran.	after 6 days	24.7	after 5 days	26.7
		after 60 days	23.2	after 21 days	30.8
		after 80 days	25.4	after 40 days	29.7
5	Conversion factor of urea, %	72.0		69.6	
6	Mass loss, 105°C, %	1.05		2.55	
7	Equivalent diameter, mm	4.01		3.24	

The extra drying of granulate produced during the test II resulted in a slight increase in granule hardness to 29.7 N/gran. During the tests, the granules were ground in the screw conveyor, and consequently, a significant amount of dust in the recovery material was produced. In the presence of the excessive amount of dust, the granulation of fertilizers was mainly based on the formation of granules by dust and feed sticking, and consequently the hardness of produced granules was low.

It was found that the fertilizers produced during the tests had a moderate hygroscopicity (Fig. 2 and 3). The samples of fertilizer produced in the test I, which were stored in the air atmosphere with relative humidity not greater than 50%, demonstrated low mass increase. At 65% relative humidity, the fertilizers absorbed moisture to the level of ca. 3-4% within 72 hours, and no significant changes in the mass were observed in the further storage period. It may indicate that calcium sulphate present in the fertilizer, which was not conversed into adduct form, was hydrated. The increase in mass was only observed for fertilizer samples stored in the air atmosphere with relative humidity exceeding 73%. Under the measurement conditions, the dewatering of the product obtained in the test II, due to increased moisture content, occurred.

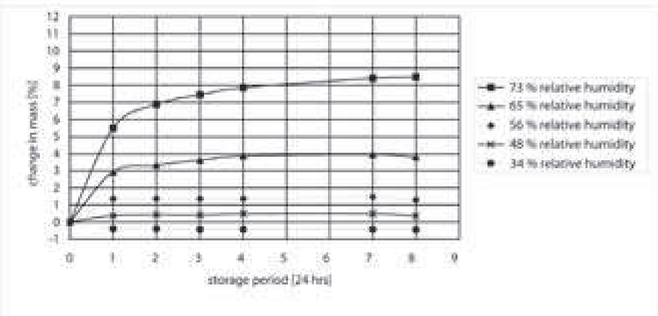

Fig. 2. Changes in mass of adduct type fertilizer samples kept in the atmosphere of various relative humidity values (test I)

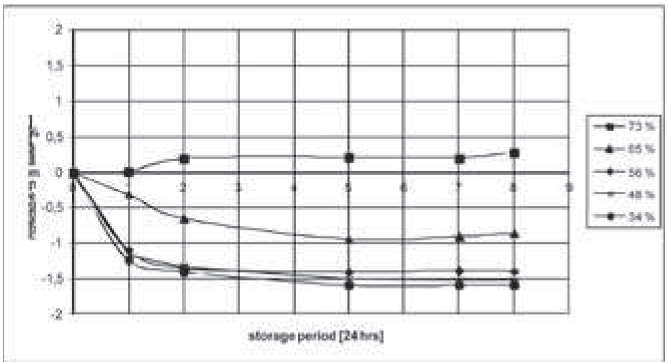

Fig. 3. Changes in mass of adduct type fertilizer samples kept in the atmosphere of various relative humidity values (test II)

According to the results of semi-technical tests, it is necessary to continue the works on improving the properties of obtained granulates. The laboratory tests and tests on a quarter-technical scale were conducted regarding the possible application of various additives to improve granule hardness. Magnesite, magnesite partly decomposed with sulphuric acid (MgO_{AS} = 13.53 % and MgO_{og} = 33.77%), bentonite, gypsum plaster and solutions of magnesium sulphate and urea were used as additives. The molar ratio of urea to calcium sulphate from phosphogypsum in the produced granulates was 4:1.The solutions of magnesium sulphate and urea were sprayed on granules present on the granulating plate. Table 4 shows the measurement results of the hardness of granule with additives in comparison to the hardness of the reference sample granules produced under the same conditions but with no additives.

Table 4

Hardness of adduct type fertilizers granules with various additives

No.	Type of additive	Additive content in granulate, wt. %	Granule hardness, N/gran	Hardness of granule from reference sample, N/gran.	Change in hardness %
1	$MgSO_4 \times 7H_2O$	2.0 MgO	12.8	10.7	+19.6
2	$MgSO_4 \times 7H_2O$	4.0 MgO	41.6	10.7	+288.8
3	Partly decomposed magnesite	2.0 MgO	22.1	10.7	+106.5
4	Partly decomposed magnesite	4.0 MgO	31.3	10.7	+192.5
5	Bentonite	5.0	40.0	10.7	+273.8
6	Gypsum plaster 3	3.0	25.4	29.7	-14.5
7	Gypsum plaster 5	5.0	19.6	29.7	-34.0
8	Solution of magnesium sulphate	1.0 $MgSO_4$	28.7	29.1	-1.4
9	Solution of magnesium sulphate and urea	1.0 $MgSO_4$ 0.5 $CO(NH_2)_2$	32.2	29.1	+10.7
10	Solution of magnesium sulphate and urea	2.0 $MgSO_4$ 1.0 CO(NH2)2	37.7	29.1	+29.6

Samples 1-5 were prepared on a laboratory scale.
Samples 6-10 were prepared on a quarter-technical scale.

The obtained results indicate that the granulates with the highest hardness are obtained using magnesium sulphate heptahydrate and bentonite. For these cases, the increase in granule compression strength by about 300 % was observed in comparison to the granulate without additives. The hardness of granulate samples with partly decomposed magnesite was increased to maximum by ca. 200 % in comparison to a sample without the magnesite raw material. The measured hardness of granules with gypsum plaster did not exhibit any impact of this additive on the increase in their hardness. The presence of unwashed phosphoric acid residues in phosphogypsum can be the cause. Phosphate ion has a negative impact on gypsum binding properties. None significant impact of magnesium sulphate solution on granule hardness was observed. The obtained results demonstrated the increase in hardness of products conditioned with the solution of magnesium sulphate and urea. The increased hardness of fertilizer granules produced with various different forms of magnesium sulphate was probably caused by the production of magnesium sulphate and urea adduct.

Taking into account the test results on additive impact on granulate hardness, the semi-technical tests were conducted to produce adduct-type fertilizer with partly decomposed magnesite used for laboratory tests. The phosphogypsum from ZCh "POLICE" S.A. was used in the tests conducted in the identical apparatus arrangement as in case of tests without additives. One test (test III) was conducted by feeding partly decomposed magnesite into the blade granulator, to which the feed in the form of urea and phosphogypsum pulp and the recirculation were discharged. During the test, problems with magnesite feeding emerged. They were connected with the vibrations generated by the blade granulator and achieving the adequate temperature in the dryer. Because of the operational problems, it was decided to conduct another test (test IV) in which partly decomposed magnesite was fed to the urea and phosphogypsum pulp, and the whole was directed to the blade granulator. The product with hardness exceeding 40 N/gran. was obtained as a result of test IV (Table 5). After storing for 2.5 months the hardness was greater than 50 N/gran.

Table 5

Properties of fertilizers prepared during tests with addition of partly decomposed magnesite

No.	Type of determination	Result of determination in product from test III		Results of determination in product from test IV	
1	N_{og}, wt. %	24.7		25.3	
2	$N_{amon.}$, wt. %	0.52		0.52	
3	S_{og}, wt. %	8.4		9.7	
4	CaO_{og}, wt. %	15.7		16.1	
5	CaO_{AS}, wt. %	7.9		8.1	
6	MgO_{og}, wt. %	1.3		2.0	
7	MgO_{AS}, wt. %	0.75		0.80	
8	The compression strength of granule (fraction 2.5 – 3.15 mm), N/gran.	after production	27.6	after production	42.0
				after 20 days	43.0
				after 77 days	51.0
9	Conversion factor of urea, %	84.50		81.00	
10	Mass loss, 105°C, %	3.93		2.39	
11	Equivalent diameter, mm	3.12		3.26	

The granulate produced during the test IV is characterized with hygroscopicity comparable to the product without additives (Fig. 4). It was found that the samples in the air atmosphere at controlled relative humidity absorbed moisture expanding their mass from 0.5 % (33.8 % relative humidity) to ca. 8.5% (73.2 % relative humidity).

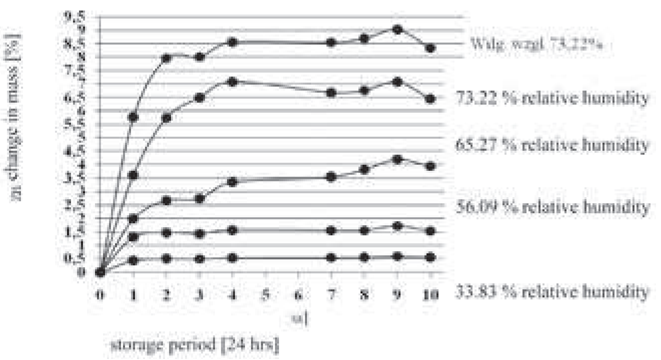

Fig. 3. Changes in mass of adduct type fertilizer samples kept in the atmosphere of various relative humidity values (test IV)

The agricultural usefulness of fertilizer was verified in the agriculture pot experiments and field experiments for the cultivation of spring wheat grain and corn grain. For field experiments, the fertilizer sample I was used in 3 versions: without coating, with coating of urea and formaldehyde resin in the amount of 3%, and the coating of technical waxes in the amount of 3%. The field experiments were carried out in RZD IUNG Kępa. It was a single-factor experiment conducted four times in a random block arrangement. The experimental scheme involved the following treatments for each plant separately:

The control without nitrogen;

Ammonium nitrate applied in two doses (60% + 40%)

N-S without coating

N-S coated with resin in the amount of 3 wt. %

N-S coated with 3% waxes in the amount of 3 wt. %.

The results from field experiments are illustrated in Figures 5 and 6.

N-S fertilizer, being an adduct of urea and calcium sulphate from ZCH "POLICE" S.A., used in the tests is undoubtedly ammonium fertilizer which, regarding the yield forming effect, does not differ considerably from pure ammonium sulphate applied in two doses, and is more effective than the pure urea for pre-plant application. The facts collected in a course of the research studies demonstrate slower release of nitrogen from urea adduct and limiting action of resin coating in this scope. It also has some impact on the root protection against the excessive concentration of fertilizer in the initial period of plant growth, and probably on the level of nitrogen losses. Thus, only the pre-plant application of this fertilizer in the cultivation of plants sown and planted in spring seems to be well-grounded. The accumulation of nitrogen in one pre-plant dose may balance the average total needs of plants in the vegetation period in contrast to pure forms of urea and ammonium nitrate.

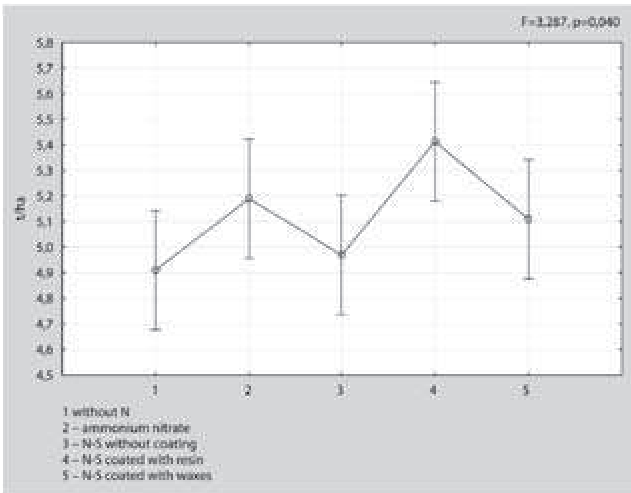

Fig. 5. Spring wheat grain yield in t/ha

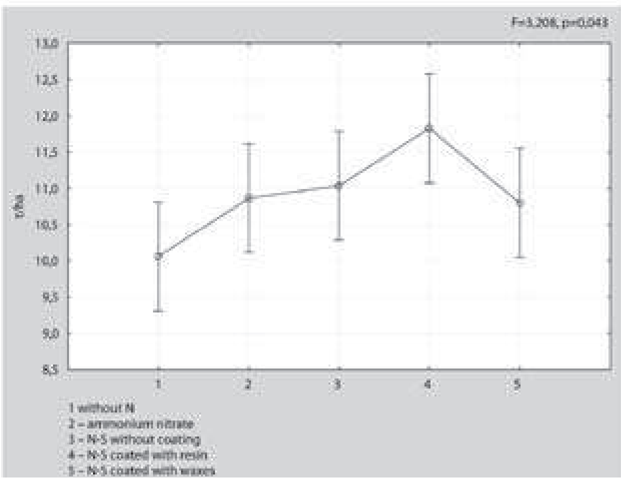

Fig. 6. Corn grain yield in t/ha

Summary

The conducted research studies presented the possibility for the production of nitrogen - sulphur - calcium fertilizers based on urea and phosphogypsum by granulating the urea and phosphogypsum pulp with dried recirculation. The obtained granulate was dried, and then sieved to achieve an adequate particle-size distribution. Subgrain and ground sieve residue were returned to the granulation unit. The pulp can be formed using solid urea and phosphogypsum with high water content, e.g. from ZCh "POLICE" S.A. or using technical urea solutions ($(CO(NH_2)_2$ 70 wt. %) and any phosphogypsum. In the second case, the application of phosphogypsum with the lowest possible water content seems to be the most reasonable. The application of proper additives is required to obtain the desired hardness of granules. The additive of partly decomposed magnesite was found to cause the increase in the hardness of obtained granulates with 2% of MgO total content - the content at which this element can be guaranteed in the fertilizer. Magnesite can be partly decomposed with sulphuric acid at the stage of pulp formation. The increase in hardness of adduct-type fertilizer granules can be also achieved by adding 5 wt. % of bentonite in the dried granulate to the granulation unit.

The agriculture tests for field crops of cereals have indicated that, regarding the yield forming effect, the obtained fertilizer is nitrogen fertilizer which does not differ considerably from the pure form of ammonium sulphate applied in two doses, and is more effective than the pure urea for pre-plant application. The retarded release of nutrient elements allows for the pre-plant application of the total content of nitrogen in one dose, which reduces the number of treatments and cultivation costs.

The research was conducted under the Development Programme No. N R05 0054 06 "Production technology of nitrogen-sulphur-calcium fertilizers on the base of urea and phosphogypsum" co-financed by the State Research and Development Centre

Literature

1. Whittaker C., Lundstom F., Hendricks S.: *Reaction between urea and gypsum*. Ind. & Eng. Chem. 1933, 11, 1280.
2. Uno S.: *Studies on the higroscopicity of chemical fertilizers, I – on the hygroscopicity of gypsum-urea*. J. Soc. Chem. Ind. Japan 1940, 43, 274.
3. Achard P., Schwob Y., Limousin L.: *A new route for urea-superphosphate fertilizers*. Phosphorus & Potassium 1994, 191, 27-29.
4. Patent US 2 074 880, 1937.
5. Patent US 3 976 467, 1976.
6. Patent ZSRR 1 063 800, 1983.
7. Patent RO 111 183, 1996.
8. Rozporządzenie (WE) Nr 2003/2003 Parlamentu Europejskiego i Rady z dnia 13 października 2003 r. w sprawie nawozów. Dziennik Urzędowy Unii Europejskiej L 304/1, 21.11.2003.
9. Pawlikowski S., Szymonik S.: *O metodyce określania higroskopijności*. Przem. Chem. 1959, 8, 598-599.
10. Maciaszek S.: *Mocznik*. WNT, Warszawa 1967.
11. Malinowski P., Biskupski A., Głowiński J.: *Preparation methods of calcium sulphate and urea adduct*. Pol. J. Chem. Tech. 2007, 9, 4, 111-114

Mieczysław BOROWIK - Ph.D. (Eng), graduated from the Faculty of Chemistry at Wrocław University of Technology in 1986. He is currently working at the position of the Assistant Professor in the Fertilizer Department, at the Fertilizer Research Institute. Specialization – inorganic technology.

Przemysław MALINOWSKI - Ph.D. (Eng), the professor at PWSZ *(State Higher Vocational School)* in Nysa, graduated from the Faculty of Chemistry at Wrocław University of Technology in 1998. He is currently working in the College of Fundamental Sciences, at the State Higher Vocational School in Nysa. Specialization - inorganic technology.

Andrzej BISKUPSKI - Ph.D. (Eng), graduated from the Faculty of Chemistry at Wrocław University of Technology in 1969. He is currently working at the position of the Head of the Fertilizer Department, at the Fertilizer Research Institute. Specialization – inorganic technology.

Michał DAWIDOWICZ - M.Sc., graduated from the Faculty of Chemistry at Maria Curie-Skłodowska University in 2008. He is currently working at the position of the chemistry engineer at the Fertilizer Research Institute. Specialization – inorganic technology.

Sebastian SCHAB - M.Sc., graduated from the Faculty of Chemistry at Rzeszów University of Technology in 2006. He is currently working at the position of the Assistant Lecturer at the Fertilizer Research Institute. Specialization – inorganic technology.

Piotr RUSEK - Ph.D. (Eng), graduated from the Faculty of Chemistry at Maria Curie-Skłodowska University in 1998. He is a senior specialist in the Fertilizer Department at the Fertilizer Research Institute in Puławy. Specialization – inorganic technology.

Janusz IGRAS - Professor (D.Sc., Eng), at INS, graduated from the Faculty of Agricultural Sciences at the University of Life Sciences in Lublin in 1989. After completing the studies, he was working at the Institute of Soil Science and Plant Cultivation in Puławy until May, 2011 where, in years 1999÷2011, he was the Head of the Department of Plant Nutrition and Fertilization. In 1998, he defended his doctoral thesis and in 2005 - habilitation dissertation. Since May, 2011 he has been a Director for Scientific Purposes at the Fertilizer Research Institute in Puławy. Specialization - agricultural chemistry.

Kazimierz KĘSIK - Ph.D.(Eng), graduated from the Faculty of Agricultural Sciences at the University of Life Sciences in Lublin in 1973. He is currently working as a chief specialist in the Department of Plant Nutrition and Fertilization, at the Institute of Soil Science and Plant Cultivation in Puławy. Specialization - agricultural chemistry.