## Physicochemical properties of fertilizers available on market and possibility of production of blended fertilizers

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#### Introduction

Delivering high quality products is in every manufacturer's interest. Results of research on the evaluation of fertilizer products and ability to compound them into bulk blended fertilizers have many a time been published and discussed during symposia on granulation. Researchers at the Fertilizer Research Institute and the Institute of Inorganic Technology and Mineral Fertilizers of the Wrocław University of Technology have often compared and evaluated the various fertilizer products available on the Polish market. The situation in the Polish fertilizer sector, where supply exceeds demand, forces manufacturers to seek new processes for the already existing manufacture and to introduce new products. This is particularly evident in the case of nitrogenous fertilizers, where application of prilling is decreasing and preference is given to mechanical granulation which provides better quality. Due to this the market abounds in high quality granulated fertilizers that enable producing mixed fertilizers. This tendency, observed both in Poland and abroad, can be exemplified by the ammonium nitrate fertilizer.

In this paper we have collected the results of research on the physical and chemical properties of fertilizers selected to prepare fertilizer blends and we have evaluated physical and chemical compatibility of these products.

#### Criteria and methods of evaluating mineral fertilizers

The quality of a fertilizer, as of any other chemical product, is a set of features that define the functional properties of the product which differentiates it from other products of the same type, and define its performance during the time spanning from its manufacture to its application. The criteria applied in evaluating the quality of fertilizers are usually defined in standards applied to either broader classes of fertilizers or to single products of the fertilizer and related industries. A good quality fertilizer means one with its actual nutrient and contaminant content conforming to specifications and one of appropriate physicochemical properties. Quality related to different fertilizers is defined in a different way. To be able to compare various fertilizers, one must define universal notions that will enable comparison of functional properties of the individual products. With this understanding of fertilizer quality, the set of criteria for fertilizer quality evaluation should include size and additional features (complementary to those mentioned above), such as: total nutrient content, blendability with other fertilizers, required conditions of storage and application, and agronomic effects of application. The results of fertilizer quality evaluation by the user and the price thereof have an effect on the selection of the types and quantities of fertilizers depending on the planned crops under specific soil conditions. The fertilizer manufacturer makes the decision on production level and quality anticipating the attainable price that should ensure production profitability. Various fertilizers can be manufactured, but only some of them, produced in appropriately large quantities, will provide economic efficiency.

Crop cultivation requires simultaneous provision of various nutrients in quantities corresponding to the needs of the plants and soil. It is only rarely that the needs of a given plant can be fully met by applying only one multicomponent fertilizer. Usually it is recommendable to use a set of several fertilizers at defined ratio in one or more soil dressing operations. In the case of solid fertilizers, simultaneous application of several fertilizers is possible under a few conditions. The most important of those include:

- good physical and chemical properties of the blends (no reaction between the ingredients, maintaining flowability under storage)
- · intimate blending of the individual components
- no susceptibility of granules to segregation.

Important features of solid granulated fertilizers include compression strength, resistance to attrition and to other mechanical interactions, as well as retention of high strength during prolonged storage.

Selection of components of proper grain size distribution is an important condition for obtaining a fertilizer blend with desirable characteristics. Mixed fertilizers, despite many advantages, have one major drawback: tendency of the grains to segregate during transportation and application. Putting it in simple terms, the main causes of the segregation of particles of the various fertilizer ingredients, are as follows:

- different rolling speeds of granules (particles) of the various ingredients on the bed (e.g. when conveying to a warehouse)
- passing of the fine grains through spaces between coarser grains under the action of vibrations, e.g. during transport (generally particles smaller than 1 mm in diameter are sifted)
- relationship between fertilizer granule travel distance and its size and weight during fertilizer spreading effected with mechanical rotary equipment.

It should be pointed out that physical blends of mineral fertilizers are used mainly as pre-seeding fertilizers. These usually contain all macroelements, with a lower dose of nitrogen, and optionally microelements. The remaining portion of nitrogen and microelements are applied by top dressing. It is believed that the tendency of the particles of the various fertilizers to segregate is mainly dependent on:

- differences between particle sizes of the different fertilizers (smaller particles tend to accumulate in the lower part of the fertilizer mass)
- differences between the densities of the different fertilizers (particles of higher density gather in the lower part of the fertilizer mass)
- differences between particle shapes of the different fertilizers (fertilizer particles of spherical shape move more readily in the fertilizer mass than irregularly shaped particles).

For practical reasons it is assumed that similar size of particles is a sufficient criterion for selecting solid components of fertilizer blends  $[1 \div 3]$ .

#### Chemical composition and physical properties of selected fertilizers

There are many types of fertilizers available on the market, both single-nutrient fertilizers, as well as compound fertilizers. The fertilizers selected for investigations included N fertilizers, P fertilizers, potassium fertilizers and NP fertilizers. The exceptions in this list were the nitrate fertilizer from ANWIL S.A., which is not available on the market, and USP fertilizer, which was manufactured in the past by Siarkopol, but the manufacturing process of which is still being worked on by the Fertilizer Research Institute (INS). Table I shows granulate strength test results and nutrient content figures according to manufacturer specifications.

All the fertilizers selected for preparing mixed fertilizers were characterized by high or at least sufficient compression strength. It is interesting that tests have shown that nitrate fertilizer from ZAK had good physical properties as compared to fertilizers offered by foreign manufacturers. This may be due to a different manufacturing process. Among CAN fertilizers, CAN 27 delivered by a foreign manufacturer was decidedly the best.

The USP fertilizer, prepared in a test plant at INS, had satisfactory compression strength. Its manufacture on an industrial scale would presumably improve the strength of granules significantly.

# Assessment of the suitability of granulated fertilizers for the preparation of mixed fertilizers

When considering the feasibility of preparing various mixed fertilizers, one should take into account the chemical compatibility given in the compatibility tables (Tab.2 and 3) and physical compatibility, that is grain size data (the values of SGN, UI and, where appropriate, MQI). The first type of data indicates whether mixing the components at any time, immediately before application, is practicable, or whether these components cannot be mixed.

As the USP fertilizer has not been included in any compatibility table before, chemical compatibility tests of this fertilizer with other known components were carried out. The test consisted in blending the USP fertilizer with other fertilizers and determining the strength of granules after defined time. Results of chemical compatibility tests are presented in an extended fertilizer compatibility table (Tab. 3).

It was found that the USP fertilizer was compatible with the other tested fertilizers. It will be possible to use it in the preparation of mixed fertilizers at any time before spreading. The exceptions are fertilizer blends with ammonium nitrate and ammonium sulphate. Such fertilizers can only be prepared immediately prior to application. Data on physical compatibility provide information whether the blend prepared from components of defined grain size will ensure uniform distribution of all components over the entire fertilized area. The values of SGN and UI are determined from the following formulas:

$$SNG = \left[\frac{\Delta r[PLUS(r_m) - 50]}{PLUS(r_m) - PLUS(r_m)} + r_m\right] \times 100 \tag{1}$$

$$UI = \frac{S}{L} \times 100 \tag{2}$$

$$S = \left[\frac{\Delta r[PLUS(r_w) - 95]}{PLUS(r_w) - PLUS(r_w)} + r_w\right] \times 100$$
(3)

$$L = \left[\frac{\Delta r[PLUS(r_m) - 10]}{PLUS(r_m) - PLUS(r_m)} + r_m\right] \times 100$$
(4)

where:

 $\label{eq:PLUS} \begin{array}{l} \text{PLUS}(r_{m}) - \text{fraction retained on smaller size mesh} \\ \text{PLUS}(r_{w}) - \text{fraction retained on larger size mesh} \\ \Delta r - \text{difference in larger and smaller size mesh} \end{array}$ 

The values of rm and rw are set so that for the granule diameter contained between them the fraction retained is 50% (when calculating SGN), 95% (when calculating S) and 10% (when calculating L).

When considering the feasibility of preparing various fertilizer blends, SGN and UI values are calculated for all components, mean SGN and UI values are calculated for the blend and deviations from these mean values are calculated for all components. Fertilizer blending is allowed when SGN and UI deviations for blend components are within  $\pm 10\%$  of the mean values. These value intervals are generally applied when evaluating fertilizers as possible blend components, and they are statistically justified [5,6]. If one of the values of SGN or UI is within permissible range, and the other is outside such range, then such blend (component) is not rejected and the value of MQI (Mixing Quality Index) is calculated:

$$MQI = 100 - (SrSGN + SrUI) 100$$
 (5)

where Sr is the relative standard deviation of SGN or UI of fertilizers included in the blend calculated from formulas:

$$S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \overline{x})^{+}}{n-1}}$$

$$Sr = \frac{S}{x}$$
(6)
(7)

The closer to 100 is the value of MQI, the better is the quality of the blend in terms of grain size distribution. According to the Canadian Fertilizer Institute the limiting value of MQI at which blend preparation is allowed is 85. If the value calculated is less than 85, we can still prepare the blend, its application, however, requires that it be used in an excess of 2% in relation to fertilizer requirement for each unit of MQI value deviation from the limiting value. American literature from the years  $1970 \div 80$  indicates that the principal requirement that prevents a blend from segregation is the use of fertilizers of grain size within 1.5-4 mm, preferably with 95% of grains within 2-4 mm range [7,8]. Numerous fertilizers can be taken into account for preparing fertilizer blends. Here a few examples were selected (Tab. 4).

#### Suitability of granulated fertilizers for bulk blending

Proper fertilization requires the use of a complete set of nutrients in quantities adjusted to the needs of the cultivated plants. Plant needs may be satisfied either by using single fertilizers (usually applied in several spreading operations) or by using compound fertilizers. Solid compound fertilizers may have the form of complex fertilizers, where each granule contains all nutrient types, or that of mixed fertilizers, which are prepared by physical mixing of particles (granules, crystals, etc.) of various fertilizers. In the case of solid fertilizers, granular or large crystal products can be components of mixed fertilizers (bulk blending), crystalline products can be used as raw materials for preparing granulated fertilizers or powdery mixed fertilizers.

The advantage of mixed fertilizers is the possibility of accurate adjustment of the individual nutrients to the needs of plants, provided that the individual components are properly selected. The principal criteria for selecting components for mixed fertilizers are the indications of the compatibility tables and conformity of SGN and UI. The results of assessing the suitability of selected solid fertilizers for preparing mixed fertilizers are shown in Table 5.

The table shows that only twelve, out of the total of more than thirty suggested blends, proved successful. In most cases the incompatibility of just one value conduced to the rejection of the mixed fertilizer. Among Polish products, the CSF fertilizer from GZNF, provided very good results. Most of the blends containing it are usable.

**CHEMIK** nr 5/2012 • tom 66

The possibilities of mixed fertilizer manufacture are not broad, but these may be expanded by implementing organizational improvements with virtually no need for capital spending.

Physicochemical properties of selected mineral fertilizers

Table I

Table 2

ltem	Sample name	Manufacturer	Nutrient content	Strength (N)	Mean size (mm)
I	Saletra GM (nitrate fertilizer)	ZAK	32% total N (16% nitrate, 16% ammonium)	69.30	3.99
2	AN-32	Anwil S. A.	32% total N (16% nitrate, 16% ammonium)	53.50	4.08
3	AN I	Foreign manufacturer I	32% total N (16% nitrate, 16% ammonium)	36.15	4.15
4	CANWIL S	Anwil S. A.	27% total N	95.00	3.89
5	CAN I	Foreign manufacturer l	27% total N	82.80	3.78
6.	NS 32-5 II	Foreign manufacturer II	32% total N (16% nitrate, 16% ammonium), 5% S	81.30	3.45
7.	CAN GM	Foreign manufacturer III	27% total N	61.50	3.64
8.	CAN 27	Foreign manu- facturer IV	2/% total N		4.45
9.	Potassium salt, white	ZAP import	50% K <sub>2</sub> O	77.60	3.12
10.	Potassium salt, red	ZAP import	60% K <sub>2</sub> O	128.56	3.42
11.	CSP	GZNF	40% P <sub>2</sub> O <sub>5</sub>	158.45	3.84
12.	TSP	GZNF	46% P <sub>2</sub> O <sub>5</sub>	121.30	3.91
13.	USP	INS	INS 20% total N, 10% P <sub>2</sub> O <sub>5</sub>		3.01
14.	Polimap	Z. Ch. Police	n. Police P <sub>2</sub> O <sub>5</sub> as monoammonium phosphate		2.60
15.	Polidap	Z. Ch. Police	18% ammonium N, 46% P <sub>2</sub> O <sub>5</sub> as ammonium phosphate	72.10	2.81

Table 3 Chemical compatibility of mineral fertilizers and USP fertilizer

USP									
L	Ammonium nitrate								
ОК	х	Urea							
L	ОК	ОК	Ammonium sulphate						
OK	ОК	L	ОК	TSP					
ОК	ОК	L	ОК	ОК	SSP				
OK	ОК	ОК	ОК	L	L	DAP			
OK	ОК	OK	ОК	ОК	OK	OK	MAP		
ОК	ОК	ОК	ОК	ок	ОК	ОК	ОК	Potassium chloride	
ОК	ОК	ОК	ОК	ок	ОК	ОК	ОК	ОК	Potassium sulphate

 $\mathsf{L}-\mathsf{blending}$  possible immediately before spreading

OK - blending possible at any time before spreading

X – blending not possible

Table 4	4
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#### Values of SGN, S, L and UI for selected fertilizers

ltem	Sample name	Manufacturer	SGN	s	L	UI
I	Saletra GM (ni- trate fertilizer)	ZAK	387.17	295.64	440.76	67.07
2	AN-32	Anwil	374.18	265.96	482.72	55.09
3	CAN	Foreign manufacturer I	357.30	250.00	465.00	52.80
4	CANWIL S	Anwil	419.80	324.20	532.4	60.90
5	CAN I	Foreign manufacturer l	371.76	266.47	481	55.40
6	NS 32-5 II	Foreign manufacturer II	302.52	222.70	388.77	55.09
7	CAN GM	Foreign manufacturer III	401.38	297.97	503.00	59.24
8	CAN 27	Foreign manufacturer IV	377.82	272.02	486.74	55.89
9	Potassium salt, white	ZAP import	311.00	240.40	392.60	61.20
10	Potassium salt, red	ZAP import	250.00	116.70	317.90	36.70
11	CSP	GZNF	315.54	216.02	423.77	50.97
12	TSP	GZNF	315.84	203.63	425.25	47.88
13	USP	INS	305.90	207.90	390.70	53.20
14	Polimap	Z. Ch. Police	256.00	134.10	321.60	41.70
15	Polidap	Z. Ch. Police	280.00	202.20	355.40	56.90

Chemical compatibility of mineral fertilizers [4]

Ammonium nitrate								
Х	Urea							
ОК	ОК	Ammonium sulphate						
ОК	L	ОК	TSP					
ОК	L	ОК	ОК	SSP				
ОК	OK	ОК	L	L	DAP			
ОК	OK	ОК	ОК	ОК	ОК	MAP		
ок	ОК	ОК	OK	ОК	ОК	ОК	Potassium chloride	
ок	ОК	ОК	OK	ОК	ОК	ОК	ОК	Potassium sulphate

 $X-blending \ not \ possible$ 

 $\mathsf{OK}-\mathsf{blending}$  possible at any time before spreading

### **CHEMIK** nr 5/2012 • tom 66

	Table 5
Evaluation of usefulness of selected solid fertilizers	
to prepare blended fertilizers	

	Blend com	Evalu	Final			
ltem	I	н	SGN	UI	MQI	result
Ι	CAN WZ I	Potassium salt, granulated (red)	-	-	43.59	-
2	CAN WZ I	CSP	+	+	82.53	+
3	Nitrate fertilizer WZ I	Potassium salt, granulated (red)	-	-	48.29	-
4	Nitrate fertilizer WZ I	CSP	+	+	87.39	+
5	USP	Potassium salt, granulated (red)	-	-	56.43	-
6	USP	Potassium salt, granulated (white)	+	+	91.04	+
7	Nitrate fertilizer ZAK	Potassium salt, granulated (red)	-	-	28.16	-
8	Nitrate fertilizer ZAK	Potassium salt, granulated (white)	-	+	78.09	-
9	Nitrate fertilizer ZAK	CSP	-	-	66.28	-
10	CAN Hungary GM	Potassium salt, granulated (red)	-	-	33.90	-
11	CAN Hungary GM	Potassium salt, granulated (white)	-	+	79.75	-
12	NS 32-5 WZ II	Potassium salt, granulated (red)	+	-	55.57	-
13	NS 32-5 WZ II	Potassium salt, granulated (white)	+	+	93.37	+
14	NS 32-5 WZ II	CSP	+	+	88.77	+
15	AN-32 Anwil	Potassium salt, granulated (red)	-	-	38.36	-
16	AN-32 Anwil	Potassium salt, granulated (white)	+	+	84.94	+
17	Nitrate fertilizer ZAK	CSP	-	-	66.28	-
20	CAN WZ III	Potassium salt, granulated (red)	-	-	33.90	-
21.	CAN WZ III	Potassium salt, granulated (white)	-	+	79.75	-
22.	CAN WZ III	CSP	-	+	72.44	-
23	NS 32-5 WZ II	Potassium salt, granulated (red)	+	-	55.57	-
24	NS 32-5 WZ II	Potassium salt, granulated (white)	+	+	93.37	+
25	NS 32-5 WZ II	CSP	+	+	88.77	+
26	AN-32 Anwil	Potassium salt, granulated (red)	-	-	38.36	-
27	AN-32 Anwil	Potassium salt, granulated (white)	+	+	84.94	+
28	AN-32 Anwil	CSP	+	+	77.07	+
29	CANWIL S	Potassium salt, granulated (red)	+	-	29.08	-
30.	CANWIL S	Potassium salt, granulated (white)	-	+	78.59	-
31.	CANWIL S	CSP	-	+	67.38	-
32.	CAN 27 WZ IV	Potassium salt, granulated (white)	+	+	79.86	+
33.	CAN 27 WZ IV	CSP	+	+	80.77	+

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