POSSIBILITY OF USING CHALK IN PRODUCTION OF MINERAL-ORGANIC FERTILIZERS

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Abstract. Chalk, due to its physical properties and high reactivity, seems to be an interesting component for production of various types of fertilizers. This mineral can be mixed with other components both organic and minerals. Among the potential additives, we can indicate digestate, all kinds of biomass, elemental sulfur, phosphates, and nitrogen in the form of urea. The formulation of such fertilizers requires a series of investigations related to the physical and chemical effects on plants and soil environment. It is also important to select the best formulation method for specific mixtures. The paper presents comprehensive research on chalk based fertilizing mixtures. As additives several substances were chosen: digestate, biomass, sulfur, phospates, and urea. The formulation process was analysed form milling of the materials to fine powder, mixing to homogenise components, and agglomeration. The formulation of the granules was according to two most commonly used methods - pressure formulation on flat die granulator and the non-pressure method (disc granulator) most commonly used in fertilizer industry. In addition, chemical analysis of the proposed mixtures was performed to assign quality of the proposed blends. The presented results have shown that granulation of chalk both in combination with minerals and with organic materials is possible. Chalk with low water content can be very well mixed with all investigated materials. What is also important, dry material can be added to more wet (organic) substances and can be a very good material for balancing moisture in the final fertilizer mixture. It is also favorable, because drying of chalk is more effective than organic materials, where water molecules are more strongly associated. This would lead to lower energy consumption during production of the fertilizers. The tests carried out show clearly that chalk is a good ingredient in fertilizer production based on pressure and non-pressure agglomeration.

Keywords: lake chalk, compaction, agglomeration pressure, fertilizers.

Introduction

Proper management of nutrients and the maintenance of a high level of humus and a soil reaction that is appropriate to the type of the soil are prerequisites for maintaining a high level of productivity of agricultural land. Therefore, rational fertilisation, both with macro- and microelements and proper agro-technical measures are an integral part of appropriate agricultural management. For this reason, a very important element of the proper management of soil resources is the regulation of soil reaction through the use of calcium fertilizers [1; 2]. Due to the fact that the vast majority of soils in Poland were formed on acidic rocks, maintaining a proper reaction requires the use of large amounts of de-acidifying fertilizers. Maintaining the proper soil pH is one of the most important factors influencing the productivity of agro-ecosystems. The soil reaction influences the sorption complex capacity, microbiological activity and the effectiveness of the use of fertiliser ingredients and the availability of trace elements and heavy metals. Due to the low awareness of agricultural producers, the current consumption of agricultural lime in Poland is at a low level and amounts to approximately 40 kg of CaO per hectare of agricultural land.

The low level of calcium fertilisation does not speak well of the level of agriculture in Poland, but on the other hand, it informs of the market potential for calcium fertilizers, because increasing the effectiveness of agriculture is absolutely related to the maintenance of a proper soil reaction. On the market, there are many products that can be used for soil de-acidification. Depending on the type of soil and the level of acidification, calcium oxide, carbonate or silicate fertilizers can be used. Carbonate fertilizers are ground limestone and have a slow effect. Oxide fertilizers have a rapid de-acidifying effect, but their price per active ingredient is much higher.

An interesting alternative to the above-mentioned calcium fertilizers is chalk, which chemically is a carbonate fertiliser, but has a rapid de-acidifying effect due to its physical form, which is very valuable for agricultural producers and the marketing of this product. Chalk is the youngest calcium carbonate, which translates into its physical form. It is a very fine product with an amorphous structure, which makes the contact area between the fertiliser and the soil very large after it is applied in the soil. This translates into a high reactivity despite the fact that it is calcium carbonate from a chemical point of view. Other carbonate fertilizers have a crystallised structure, which results in longer calcium release times.

While fertiliser chalk is available on the market, it would be an interesting idea from the marketing and practical point of view to create a fertiliser that contains chalk and other fertiliser ingredients. One can observe that the share of organic-mineral fertilizers in the fertiliser market is growing, which is a signal that the introduction of a product based on chalk and organic ingredients can be a successful project from the marketing point of view. The decline in the amount of organic matter in the soil is a growing problem in intensively used soils. For this reason, more and more farmers are relying on organic fertilizers. On the other hand, mineral fertilizers containing calcium and other ingredients, such as nitrogen and potassium, are frequently used by farmers due to the introduction of easily assimilated calcium.

Due to their dusty structure, calcium fertilizers, including fertiliser chalk, are usually granulated. The granulation process is usually carried out with the addition of raw materials that increase their agglomeration susceptibility. Organic or mineral substances with a positive fertilising effect are most often used. For this purpose, biomass bio-gasification digestates, sewage sludge and biomass combustion ashes are used [3-6].

Materials and methods

Lacustrine chalk is a type of limestone, which forms as a lake sediment in the continental environment. It is a limestone rock of chemical origin formed in lakes, marshes and waterlogged meadows. It is formed as a result of the chemical or biochemical precipitation of calcium carbonate in a freshwater environment that is poor in CO_2 (warmer standing waters or waters rich in phytoplankton and aquatic plants that absorb CO_2 from the water).

Lacustrine chalk is not only a formation that is forming nowadays, but also formed in the past, if the conditions for sedimentation were right (overgrowing freshwater reservoirs). The contemporary sediments are accumulations of Holocene lacustrine chalk. The active surface, which determines the speed and intensity of the reaction, is much higher for lacustrine chalk than for carbonate waste. Therefore, the expected result of the application of lacustrine chalk is much faster, and in the case of limestone – it is spread over a longer period of time. Almost every limestone contains a greater or less admixture of silica, which is an agriculturally neutral ingredient. On the other hand, lacustrine chalk is usually 90 % calcium carbonate, so there is a smallamount of admixtures and minerals that will not take part in the reaction. Due to these parameters, it can be directly used as a fertiliser. However, this raw material can be a potential basis or carrier for the creation of multi-compound mineral or mineral-organic fertilizers.

Research stages in the experiment being conducted

Drying – chalk specimens delivered for analysis were pre-treated by drying and crushing. The drying process was carried out to determine the moisture content and obtain a raw material that could be used for further research. The test specimen was placed in a chamber oven and dried at a temperature of 105°C ± 2 until a constant mass was established.

Fertiliser material thickening process – the main objectives of the fertiliser granulation process are to improve its flowability, density and transport properties, increase the size and mass of particles to enable safe and even spreading, reduce the content of dust and dustiness in transport and during processing, produce mixtures of non-segregating particles and give the particles planned essential physiochemical properties [7; 8].

Granulation, also referred to as agglomeration or pelletising, is a process of joining small particles, such as dust and powder, into larger aggregates (granules) with a specified mechanical strength, in which the initial grains of the material can still be distinguished. The agglomeration of fine grains of a solid into larger accumulations is achieved by physical or chemical binding mechanisms.

Granulation is widely used in many industries, including mineral processing, agricultural products, detergents, pharmaceuticals, foodstuffs and chemicals of various types. It is estimated that 60 % of products in the chemical industry are produced in powder or dusty form and another 20 % use additives in such a form. Granulation is a key stage in the production or processing of products in many of these industries. Incorrectly conducted granulation that produces a product with wrong parameters may cause significant problems in subsequent processing stages (such as lumping, segregation and low efficiency during tabletting) and impede the use of the final product.

In the case of the technology of high-pressure agglomeration of fertiliser materials, the pelleting process is most often used. Granulators with a flat or ring matrix are used, which are especially popular solutions in the production of animal feed. For this reason, the research on the pelleting process was carried out using a flat matrix machine. It was the Kovo Novak MGL 200 pelletising line with a capacity of up to 100 $kg \cdot h^{-1}$.

The experiments were conducted using a forming matrix with a diameter of 4.5 mm and a compression ratio of 4.2. The size of a single specimen for a given variant was about 20 kg.

In order to obtain varied information on the technical potential of the use of chalk as a basic ingredient in fertiliser production, the following fertiliser mixture variants were proposed:

- K1 – chalk 50 % – digestate50 %,
- K2 – chalk 75 % – digestate 25 %,
- K3 – chalk 45 % – digestate 45 % – sulphur 5 % – phosphorite 5 %,
- K4 – chalk 50 % – sewage sludge50 %,
- K5 – chalk 75 % – sewage sludge 25 %,
- K6 – chalk 45 % – sewage sludge 45 % – sulphur 5 % – phosphorite5 %,
- K7 – chalk 70 % – ash 20 % – sulphur10 %.

In the above-mentioned fertiliser variants, the share of both organic and mineral fractions was taken into account to a large extent in order to demonstrate whether such diverse fertiliser mixtures have properties that are conducive to agglomeration. The proposed additives perform the roles of raw materials evaluating the quality of the final product in terms of the fertilising value and physical characteristics.

Three basic characteristics were selected for qualitative evaluation of the obtained granules: i.e. mechanical durability, bulk density and static compression test.

The **mechanical durability** of the fertiliser granulate (DU) is a measure of its resistance to shocks and/or abrasion resulting from transport, handling and other distribution and storage processes. The specimen was subjected to a test, in which material in the form of fertiliser granules collided against itself and the walls of the test chamber. The tests of the fertiliser granules used a chamber which – as specified by the requirements of PN-EN 15210-1:2010 standard – had the shape of a cuboid with internal dimensions of 300 ± 3 x 300 ± 3 x 125 ± 1.3 mm. The specimens weighing 500 ± 10 g (weighed with the accuracy of 0.1 g) were placed in the test chamber. In accordance with the guidelines set out in the standard, the chamber rotated at a speed of 50 ± 2 revolutions per minute and the duration of one test was 10 minutes. The DU mechanical durability was calculated using the formula:

$$DU = \frac{m_A}{m_E} \cdot 100, \tag{1}$$

where DU – granulate durability;
m_A – specimen mass before the test;
m_E – specimen mass after the test.

The final result of the measurement is the average result obtained from two measurements.

The **bulk density** of the tested materials (*BD*) was determined in accordance with the procedure described in the PN-EN 15103:2010 standard by determining the mass of the material in a known volume from the relation:

$$DB = \frac{m_2 - m_1}{V}, \tag{2}$$

where DB – bulk density;
m_2 – mass of the container including the material;
m_1 – mass of the empty container;
V – volume of the container.

The tests used a standardised container with a volume of V = 0.001 m^3, into which the tested material was placed. Next, their masses were determined.

Static strength *TB* – in order to determine the strength under static conditions, specimen crushing measurements (the so-called Brazilian test) were performed to determine the force causing the cracking of the specimen. The failure stress value was determined from the following equation

$$TB = \frac{2Fn}{\pi dh}, \quad (3)$$

where *Fn* – specimen compression (failure) force;
d – diameter of the compressed specimen;
h – height of the specimen.

Results and discussion

Tables 1 and 2 present the results of the elementary analysis of the chalk specimens used in the tests.

Table 1

Results of the elementary analysis of chalk specimens used in the tests

Parameter	dry matter content	general alkalinity	carbon content
Unit	%	% CaO	%
Value	54.50	56	14
SD	2.31	1.2	1.3

Table 2

Results of the elementary analysis of chalk specimens used in the tests

Parameter	Ag	Al.	B	Ba	Ca	Cd	Co	Cr	Cu	Fe	Ga	K
Unit	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	%	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.
Value	0.385	13.55	2.517	11.68	32.65	0.086	0.083	0.266	1.083	771	0.717	2078
SD	0.021	0.77	0.21	0.26	2.33	0.018	0.023	0.047	0.07	76.36	0.07	114.5

Parameter	Li	Mg	Mn	Na	Ni	Pb	Sr	Tl	Zn	P	As	S
Unit	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.	mg·kg^{-1} s. m.
Value	0.483	1881	349.2	83.95	0.116	0.733	98.5	0.083	0.35	110.6	0.283	597.5
SD	0.07	70.71	26.9	21.14	0.023	0.047	2.1	0.023	0.07	31.60	0.023	41.71

The following figures show example specimens of the obtained granules, which were then subjected to qualitative evaluation.

Fig. 1. **View of obtained granulates from feedstock mixture – from left: variants K2, K3, K4**

The table below shows the results of the durability, density and compressive strength tests performed on the produced granulates.

Table 3

Results of the tests of the bulk density of fertiliser feedstock

Raw material	Bulk density, kg·m^{-3}
Ground chalk	596.1
Phosphorite	1487.7
Ash	478.1
Sulfur	523.3
Digestate	167.2
Sewage sludge (dry, ground)	681.7

Table4

Results of the qualitative tests of the analysed fertiliser granulates

Variant fertilizer	Moisture M, %		Durability DU, %		Bulk density BD, kg·m^{-3}		Brazilian test TB, MPa	
	$\overline{M}$	SD	$\overline{DU}$	SD	$\overline{BD}$	SD	$\overline{TB}$	SD
K1	9.24	0.41	94.2	4.6	658.2	26.4	1.29	0.07
K2	6.07	0.57	91.6	5.4	794.5	22.6	0.97	0.04
K3	10.57	1.23	96.9	5.1	648.3	31.8	1.02	0.04
K4	8.32	0.72	94.5	3.6	695.6	30.7	1.23	0.07
K5	12.88	0.69	93.7	4.6	705.4	32.3	1.29	0.05
K6	9.34	0.98	95.5	4.7	716.6	32.9	1.51	0.07
K7	11.21	0.71	92.2	3.5	759.7	25.5	1.97	0.11

The obtained results have shown unequivocally that high-pressure granulation of chalk with the addition of organic fractions makes it possible to obtain granules with very good physical properties, which predispose it to applications in technological systems. The determined quality parameters have shown that they have properties comparable to other commonly used fertilizers (peat or animal manure granulates, etc.) and organic granulates for other applications (use as a fuel and mulching) [9-12].

Conclusions

Due to its physical properties and high reactivity, agricultural chalk can be an interesting base ingredient for the production of various types of fertilizers. Other components may include organic and mineral materials. Among potential additives, one can indicate waste from methane fermentation, the so-called digestate, and various types of biomass, elemental sulphur, phosphates and nitrogen in the form of urea. However, the development of such fertilizers requires a number of studies relating to the physical and chemical properties, the impact on plants and the soil environment and the methods of formulation of the developed mixtures, which will require determination of the specific granulation process parameters because of different proportions of mineral and organic ingredients. Throughout the process of preparation and production of fertiliser granulates, chalk had properties conducive to production. Starting from the preparation of the raw material, chalk has properties that allow for easy reduction of the water content, the conciseness of the raw material does not pose problems with its grinding (which is important for grinding processes) and the prepared raw material can be easily mixed and granulated. The tests have shown that chalk easily undergoes granulation, both in combination with mineral and organic materials. Chalk with low water content allowed for easy mixing with organic raw materials (digestate and sewage sludge) with an increased moisture content, which makes it possible to assume that it is a very good raw material for moisture content balance in fertiliser mixtures in the long run. It should be remembered that the dehumidification process of chalk will be more effective than that of organic raw materials, where water molecules are more strongly bound, which in turn translates into an increase in energy expenditures and thus financial outlays. The tests clearly show that it is a good ingredient of fertiliser mixtures in the production of granulated fertilizers.

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