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THE INFLUENCE OF BINDERS ON THE PROPERTIES OF DOLOMITE PELLETS FOR CALCIFICATION OF AGRICULTURAL LANDS

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SUMMARY

The research relates to determining the dependence of the strength and hardness, as well as the pH factor and solubility in water, of pellets made based on dolomite powder on the type and concentration of the binder. During the research, the technological parameters of the pelletizing device (speed and inclination of the disk, dosing speed of powder and binder suspension, and mixing time) were kept constant. Variations were made in the concentration of starch and molasses binder at values of 1.0, 2.5, and 4.0% and the control sample of 2.0 %. The purpose of pellets made of dolomite powder is to correct the pH factor of agricultural soil. The obtained results indicate that the production of pellets for the stated purpose requires an optimal choice of binder and its concentration due to the influence on the qualitative indicators of the pellet itself from dolomite powder. The research results are a partial extract of the Study: "Investigation of the optimal technology for the production of dolomite pellets from the "Očura" deposit for agriculture, Phase I".

Keywords: pellet, agriculture, binder concentration, strength, hardness, pH of pellets.

1. INTRODUCTION

In the conditions of climatic changes present in this period of civilization, as well as in intensive agricultural production with the use of artificial fertilizers, as a result, agrarian soils had a significant change in the pH factor in the direction of their acidification. Thus, managing acidic and highly acidic soils is one of the most critical issues of modern agriculture. Unfavourable chemical characteristics of acidic soils limit the growth and development of cultural plants, often to the point of justifying the use of these soils for the cultivation of various crops. If the pH value of soil falls below the optimal values, correction of the soil reaction is required, which is best carried out by calcification. Calcification increases production efficiency, has a favourable effect on soil biogenicity, and microbiological activity, and is ecologically completely acceptable for conventional and organic agriculture.

Calcification is carried out by different means; lime is the most commonly used. However, the tendency to protect the environment and the growing awareness of the impact of combustion products and carbon monoxide as a mandatory product on the air and consequently climate change significantly calls into question the justification of received lime from the aspect of an environmentally acceptable material. It is a well-known fact that in the production of lime (whether it is obtained from limestone or dolomite), during the thermal decomposition (baking) of Ca and Mg carbonates, up to 45% of CO_2 is released, which mostly ends up in the atmosphere. For this reason, the solution for the repair of agricultural materials is increasingly sought after in application, finely ground granulates of carbonate rocks, primarily limestone and dolomite.

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These rocks have a basic pH factor, so by introducing them into the soil, they repair the pH of acidic soils. However, the impact itself also depends on the level of comminution of the introduced soil repair products from these mentioned rocks. Increasing the fragmentation increases the activation of the mineral composition of the rock (mechatronic activation) with the chemical content in the soil, and the biological decomposition of carbonate rock grains intensifies to a considerable extent, which significantly increases the effect.

On the other hand, by reducing the grain size below 1 mm, significantly complicates the spreading technology itself, i.e. scattering and introduction of powdery particles obtained in this way. To that should be added the fact that in intensive agricultural production, machines and devices are used that have a technically solved system for spreading the necessary substances (mineral fertilizers) on the soil in accordance with the general physical condition of those products, i.e. the system disperses granules of a certain size. In order to use, almost, as a rule, the spreading technology that is already present everywhere in the world, for the agriculture of the necessary products, the aforementioned powdery particles need to be agglomerated into larger forms. This can be achieved by pelletizing or briquetting fine particles of crushed limestone or dolomite rock. Preference in these conditions should be given to the pelleting Method because the conditions for making pellets provide more useful characteristics of the product for the described purpose. They relate primarily to the favorable particle size of the crushed rock from the perspective of the requirements of the pelletizing process, because a successful process takes place if the particle size of particles smaller than 75 μm is greater than 70%.

The application of these agglomerates for the stated purposes under the present technical and technological conditions, partially stated, also requires special characteristics, i.e. properties of finished pellets. The finished product, limestone or dolomite pellets, should have the following properties:

- satisfactory impact strength due to the effect of the mechanism in the device for spreading on the ground,
- minimal wear due to abrasion, i.e. adequate pellet hardness,
- good solubility in water,
- must not have harmful substances present from the aspect of agriculture, i.e. production of healthy food.

These conditions, consequently, dictate limitations in the pellet production process for this purpose. They also dictate the tasks in the production and application of the product described in this way. In the process of pellet production, their qualitative properties are largely influenced by choice of binder, the granulometric composition of the material and the operating parameters of the device in which the process takes place. Limiting application conditions dictate the choice of binder, which directly affects the physical-mechanical characteristics of the pellets.

2. RESEARCH OBJECTIVE

The research aims to establish the influence of the selected type of binder, during the production of dolomite pellets for agriculture, on their hardness, due to the reduction of abrasive wear during their application.

3. BASICS, METHODS AND MATERIALS

Investigations of the influence on the mechanical strength of agglomerates are mainly found within the framework of various studies on the conditions and mechanisms of pellet formation. Thus, in his studies, Gluba considers the influence of the size and dynamics of the dosage of the liquid phase (binding suspension) on the growth of pellets at different operating parameters of the pelletizer. R. Ramachandran and colleagues consider a similar effect, focusing on the distribution of the binder within the pellet and the effect of this factor on the porosity of the pellet and the inhomogeneity of the layers in the pellet cross-section. It also considers consequences with an emphasis on inhomogeneity due to eniis glub, …

3.1 MECHANICAL PROPERTIES OF PELLETS

The mechanical properties of the pellets are reflected in: the impact strength of the green pellets, the strength of the pellets against uniaxial pressure and the strength of the pellets against wear. The strength of the pellets depends on the effective ratio of the grain of the material, the surface tension of the liquid phase, the porosity, the humidity of the pellets, the amount and type of binding agent, as well as the diameter of the pellets. Pellet strength increases with decreasing concentrate grain to porosity ratio and with increasing liquid surface tension and pellet diameter. The strength of green pellets is determined by falling from a certain height and the number of pellets that disintegrate after falling from a certain height or by measuring the minimum height from which all tested pellets disintegrate. The compressive strength is determined by clamping the pellet between two parallel surfaces and is expressed by force required to disintegrate the pellet.

Wear resistance is expressed by the number of small fractions formed after a certain number of revolutions of the test drum with pellets. Wear resistance is resistance to dust formation and material loss on the finished granule. It is obtained as a product of the friction of granules on granules and granules on different equipment during production, manipulation and application.

In addition to the influence of the type and amount of binder, the mechanical characteristics of the pellets are also influenced by the structure of the pellet itself, obtained as a result of the grain shape and granulometric composition of the pelletizing material, as well as the operating parameters of the device during their production. This structural influence is reflected in the porosity of the finished pellets. Porosity is a function of the mean grain size of the material (x), the pellet diameter (d) and the speed of pellet formation (v) in the pelletizing machine: $\varepsilon = f(x, d, v)$. It mainly depends on the granulometric composition of the raw material and on the mechanical forces acting during pellet formation, whereby the grain shape is not taken into account. Pelleting takes place in a three-phase concentrate-water-air system with percentage shares of 40÷45% concentrate, 10÷25% water and 35÷45% air. During pelleting, the proportion of air decreases, and the proportion of solid particles and moisture increases. It is generally considered that for further processing of green pellets, the porosity should not be less than 20%.

3.2 METHODS (RESEARCH METHODOLOGY)

The methodology or research model is based on the following principle:

- Determination of characteristic or representative (key) indicators in research;
- Determination of sample processing methods, namely:
  a. method of preparing samples for tests,
  b. selection of methods of laboratory tests,
- interpretation and processing of research results
- research conclusion

3.2.1 Representative research indicators

Of the mechanical properties when using pellets for this purpose, the most important is its strength under pressure and resistance to wear due to friction.

A representative indicator of compressive strength is expressed through the uniaxial strength of pellets. The indicator of research on the resistance of pellets to wear is represented by the coefficient of degraded grain ζ. This coefficient is calculated from the following relationship:

$$\zeta = (mdz/muz)*100\ \%, \quad (1)$$

where is :

- mdz - mass of grains that passed through the meritorious sieve after testing in the drum (g),
- muz – the mass of the sample during testing in the drum (g).

3.2.2 Sample and its preparation for testing

The basic material used in the test is dolomite powder obtained as a mixture of ground filler and as a product of dedusting during the production of technical stone from the Očura dolomite deposit (Lepoglava, Republic of Croatia), in a mass ratio of 10 : 90%. The physical and mechanical properties of the rock from the deposit are as follows: dry compressive strength 179.2 MPa, wear resistance according to Boehme 25.8 cm3/50 cm2, water absorption 0.154 wt. %, volumetric weight 2.821 t/m3, specific gravity 2.853 t/m3, degree of density 0.989, porosity 1.12 %. The moisture content of the sample was determined based on the delivered moisture. Tests were performed for the filler and the material taken from the dust collector.

The granulometric composition of the samples and input components for these tests was determined by sieve analysis on the following set of sieves: 200, 125, 90, 75 and 63 μm. Sowing was done in two ways: with a standard laboratory thresher and a ro tap system. The grain size characteristics of the input components and the research sample are given in Table 1.

Table 1. Granulometric composition of input components and dolomite sample

Size class	Sieve opening,	Sieve, filler	Sieve, duster	Sieve, sample
μm	d_i, μm	Yi_f , %	Yi_o , %	Yi_{uz} , %
(+200)	200	100,0	100,0	100,0
(-200+150)	150	98,0	100,0	98,4
(-150+125)	125	89,1	97,4	90,8
(-125+90)	90	78,6	94,8	81,9
(-90+75)	75	62,8	80,4	66,3
(-75+63)	63	40,1	49,1	41,9
(-63+0)	0	0,0	0,0	0,0

The granulometric composition of the sample is also shown in the diagram in Figure 1.

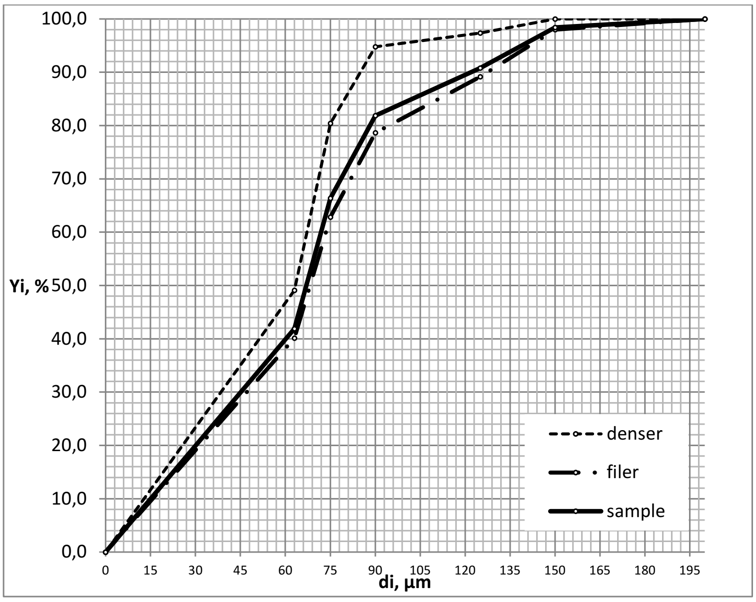

Figure 1. Granulometric composition of the dolomite sample

The following binding materials were used for the tests:

1. Sugar beet molasses. Sugar beet molasses has the following characteristics: hydrometric brix 79/80 degrees, total sugar 43/48%, organic matter without sugar 9 to 12%, nitrogen composition as protein equivalent 4%, carbohydrates: starch and other polysaccharides 4% and methoxy groups 3 up to 4%, organic acids: aconitic acid - average 2%, volatile fatty acids - average 1.3%, (formic acid, acetic acid, propionic acid, butyric acid and lactic acid), small amounts of malic acid, citric acid, etc. small amounts

of fat, resin and pigments, hydroxymethylfurfural about 40 mg/kg, humidity 22/25 %, ash 8/12 %, viscosity 5,000/15,000 CPS.
2. Starch binder produced by HG Helios Group d.o.o. Domžale Slovenia, under the commercial name, binder K. Binder K is hydrolytically and thermally processed starch. Yellow to yellow brown dust with the following properties: moisture (130°C). Max. 10%, solubility in cold water 96 – 100%, residue on sieve (1mm) max. 3%.

3.2.3 Laboratory procedures (tests)

The methodology for testing the compressive strength of pellets in this research was performed on a "mini" press, which, with accompanying equipment, is given in Figure 2.

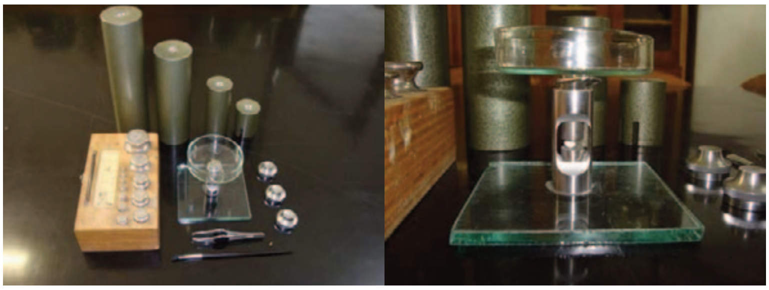

Figure 2. Laboratory "mini" press

The apparatus for testing the resistance of pellets to pressure consists of a mini laboratory press that has a tray for setting the load and a partially hollow static cylinder that has a stand for positioning the pellets. Through this cylinder passes the piston, which is connected to the tas. By placing a load on the tas via the piston, pressure is applied to the pellet, and the load is used until it breaks. The load is represented by weights of different masses: 4000, 3000, 2000, 1000, 500 and weights of 250, 100, 50, 20, 10, 5, 2 and 1 gram.

The load is applied in the following way: first, a weight of 500 grams is placed. If the pellet withstands this load, a weight of 250 is added, and then another of 250 grams. If the pellets did not burst with this load, the applied weights are removed, and a weight of 1000 grams is used as the basic weight. On top of this load, one and then two weights of 250 grams each are placed again. The procedure is repeated in the same way until the pellets burst. In this way, a continuous load of up to 250 grams is obtained on the pellet.

Granules of the size class -5+2 mm were tested. For all samples, the pressure resistance of 10 granules was tested, and the authoritative result is the arithmetic average of three series of results. Maximum and minimum results are not taken into account.

In this test, the wear resistance of the granules was performed using a rotating drum (Drum Method), which is shown in picture number 3.

Figure 3. Drum for testing the wear resistance of pellets

The apparatus consists of a drum that has six evenly spaced slats of a certain height inside. During testing, the drum is closed with a lid that is lined with rubber on its inside and has an opening in the middle through which the flow of the test can be seen. If necessary, this opening can be closed with a wooden or rubber plug.

The drum is placed on the apparatus so that its central axis of rotation is horizontal. The drum rotates at 30 revolutions per minute. The rehearsal lasts a total of five minutes. For the test, it is necessary to provide a sample with a total mass of 100 ±0.1 grams.

The granules for these tests are of the size class -5+2 mm. For testing, it is necessary to prepare sieves with circular openings of 5 and 2 mm, and seeding after the test must be done with the ro tap system. Metal spheres are separated on a 5 mm sieve, and degraded granules are classified on a 2 mm sieve. Classified granules are weighed on a scale with an accuracy of 0.1 grams.

To test the solubility and pH of pellet solutions in redistilled water, basic solutions with a concentration of 5% (w/v, 5g in 100 ml of redistilled water) were prepared. The basic solutions were prepared by weighing the appropriate amount of pellets in the form of granules on a precise analytical balance with accuracy to 4 decimal places. Accurate pH-value determination was performed on a laboratory pH-meter GLP 21 Krison, with resolutions of 0.1, 0.01 and 0.001. Electrodes: Indicator - glass electrode, reference - saturated calomel electrode. Measurements were made after the ageing of the solution/suspension for 3h, for samples that had rapid destruction of the structure. Thermostat was done at a temperature of 25°C. The measurement was performed in three repetitions.

3.2.4 Method of making agglomerates in research

Pellets for these studies were made in a laboratory plate (disk) pelletizer. Pellet growth in this pelletizer takes place in two stages. In the first stage, sprouts are formed, and their centrifugal force increases, which becomes greater than the frictional force, thus leading to a rapid increase in the mass of the pellets. When the pellets reach a certain size, they pass over the edge of the disk and leave it. The following operating parameters of the device favour the creation of sprouts and then the increase in pellet size: the angle of inclination of the disk of the plate to the horizontal (β) and the speed of rotation of the disk (no).

The angle of inclination of the plate disc to the horizontal is usually between 45 and 65°, and it is a function of the characteristics of the material that is subjected to this process, so it should be greater than the angle of the natural slope of that finely chopped material. The speed of rotation of the plate is reflected in the process through the influence of the centrifugal force on the compactness and dimension of the obtained pellet. With higher disk rotation speeds, with other constant parameters, the obtained pellet has a smaller dimension but is more compact than is the case with smaller values of this parameter. In essence, the inclination and speed of the disk dictate the path of the material along its bed in the pelletizer, thus influencing practically the formation of sprouts and the growth of pellets, as well as their compactness and the duration of the pelletizing process. In addition to the mentioned operating parameters of the device, the process of pellet formation and their final properties from the aspect of the process itself are also influenced by: the time, speed and Method of adding the binder suspension, the flow of input material into the working area of the pelletizer, and the size and characteristics of the coarseness of the input material.

In the formation of pellets for this research, the value of the static and dynamic angle of filling dolomite was determined for the previously described characteristic of the coarseness of the excavation sample. Taking into account that all the listed parameters are variable, and in terms of answering the hypothesis, they were determined as constants in the pellet production phase. Thus, the following values of the enumerated parameters were chosen during the conducted experiments:

- plate inclination angle β = 52˚,
- number of revolutions of the plate no = 7.5 rpm,
- material dosing speed in the pelletizer is 3.8 g/s.

The total mass of the sample for each test was 1.2 kg, and the process lasted 10 minutes. In this regard, the total planned amount of binder suspension was added during this time, which allows the dynamics of binder addition in the process to be calculated. The Method of adding the suspension was via a manual sprayer, which provided 2g of suspension per application, with a droplet diameter of 100 μm.

Working parameters set in this way during the process of obtaining pellets provide a suitable opportunity to observe the influence of the type and amount of binder on the resistance of pellets to wear, i.e. wear and tear due to the manipulation of pellets during the application phase.

4. RESEARCH RESULTS

The key influence on the binder choice is the pellets' purpose. Considering the purpose, the pellet should be soluble under the influence of moisture and should not affect the value of the pH factor of the pellet itself. For this reason, starch and molasses were chosen as binders. Another factor for analysis was the influence of the amount of added binder on the hardness of the pellets. The amount of binder undoubtedly affects the repair of all mechanical characteristics of pellets, but in terms of the possibility of application, it is limited (restricted) by economic parameters. In this connection, two groups were formed with three differently obtained pellet samples, namely:

- one group of pellets with a starch binder and with three different binder concentrations i
- the second one with molasses binder, also with three different binder concentrations,
- pellets were made for both cases with binder concentrations (ρv) of 1.0, 2.5 and 4.0%,
- a control sample was made for both binders with a concentration of 2.0%.

The results of research for pellets obtained using a starch binder are given in table 1, and the results of research for pellets obtained using molasses as a binder are given in table 2.

Table 1. Characteristics of pellets with a starch binder

Sample	Binder concentration ρ_v, %	Strength of pellet σ_p, N/pellet	Non-degraded grains (+2 mm), %	Degraded grains ζ, %
1.	4,5	90,74	96,2	3,8
2.	2,5	57,3	92,9	7,1
3.	1,0	21,5	67,6	32,4
4.	2,0	36	89,1	10,9

Table 2. Characteristics of pellets with molasses

Sample	Binder concentration ρ_v, %	Strength of pellet σ_p, N/pellet	Non-degraded grains (+2mm), %	Degradation coefficient ζ, %
1.	4,5	84,45	91,7	1,091
2.	2,5	46,9	75,3	1,328
3.	1,0	12,7	35,9	2,786
4.	2,0	44,9	67,2	1,488

Sample number 4 in both tables was the control sample.

Considering that the indicator of the pellet for this purpose is its value of the pH factor, as well as its solubility in water, the obtained samples were controlled by measuring these two parameters. The results of testing the pH factor of the obtained pellets and solubility in water are given in table 3, for pellets with starch binder and table 4. for pellets with molasses.

Table 3. Value of pH and solubility in water for pellets with starch binder

Sample	Binder concentration ρ_v, %	pH	Dissolution time in water, s	Decomposition description
1.	4,5	9,32	27,000	broken structure, without fine sediment
2.	2,5	9,83	6,000	Rapid disintegration of granules
3.	1,0	10,03	0,001	Instant decomposition
4.	2,0	9,87	0,006	Instant decomposition

Table 4. Value of pH and solubility in water for pellets with a molasses binder

Sample	Binder concentration ρ_v, %	pH	Dissolution time in water, s	Decomposition description
1.	4,5	9,71	0,001	Instant decomposition
2.	2,5	9,99	0,001	Instant decomposition
3.	1,0	10,09	0,001	Instant decomposition
4.	2,0	10,05	0,001	Instant decomposition

5. DISCUSSION OF OBTAINED RESULTS WITH CONCLUSIONS

It is a clear indication that the binder concentration has the most significant influence on the mechanical characteristics of the agglomerates obtained in this way. From the results of the conducted research, the influence of the type of binder itself on the mechanical characteristics of the binder can be clearly observed. The results given in Tables 1 and 2 give a clear idea of this statement, which can also be seen from the diagram in Figure 3.

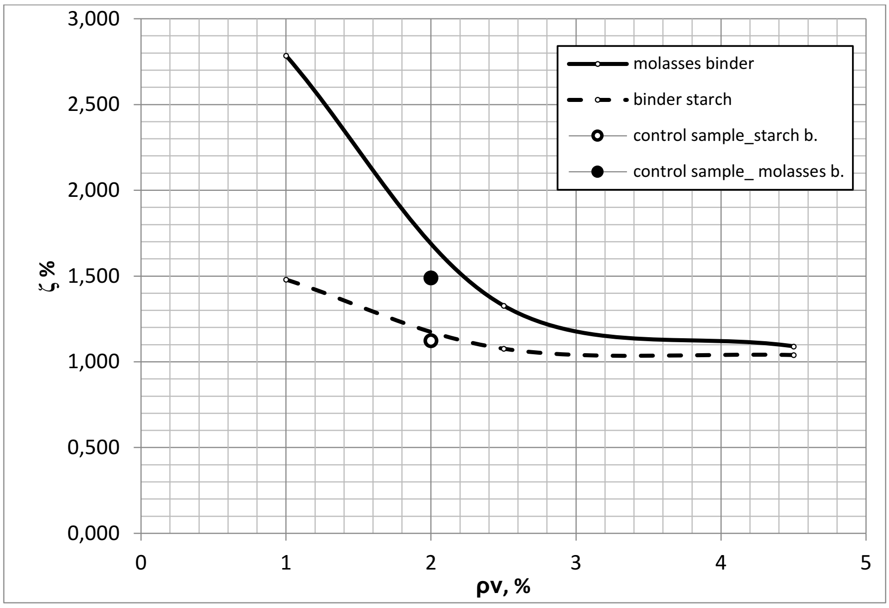

Figure 3. Strength of the obtained pellets

The strength and hardness of the material are interrelated. Usually, as the strength increases, so does the material's resistance to wear and tear, i.e. its firmness. However, the surface structure of the material has a significant impact on wear. A more pronounced roughness of the same material surface will degrade (wear out) more when exposed to wear. The diagram in Figure 4 shows the results of the wear resistance test of the obtained pellets.

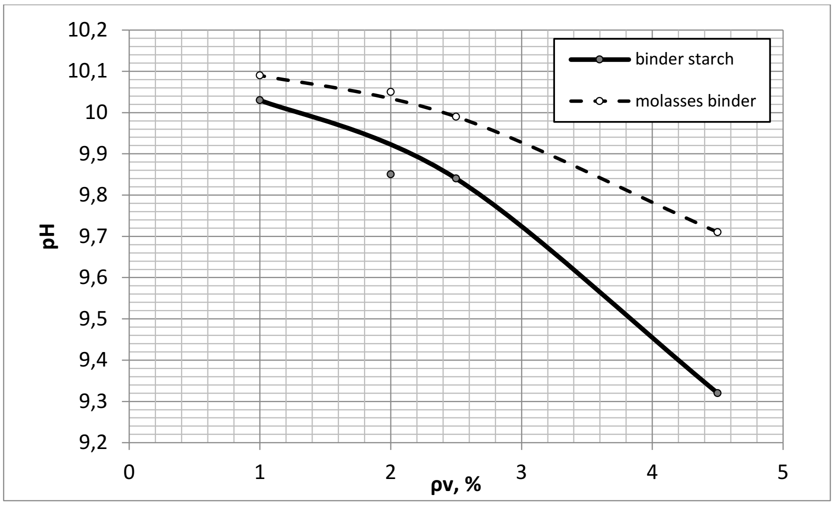

Figure 4. Coefficient of degraded grains (ζ) depending on binder concentration (ρv)

According to these results, the areas of change in the observed mechanical characteristics of the pellets can be clearly observed depending on the amount of added binder. This change is particularly pronounced in the pellet strength, which is expected. It can be said that in the observed range of binder concentration in the pellet, the dependence of power is approximately linear with the amount of added binder. However, the hardness shows a growth trend up to a certain percentage of the added binder of about 2.5%, after which the value of hardness (abrasion resistance) does not change significantly, regardless of the increase in the amount of binder.

Now let's look at the results of testing the influence of the concentration of both types of binders on the pH factor of the obtained pellets. The values of the pH factor of the pellets depending on the type and amount of binder from Table 3 are given in the diagram in Figure 5.

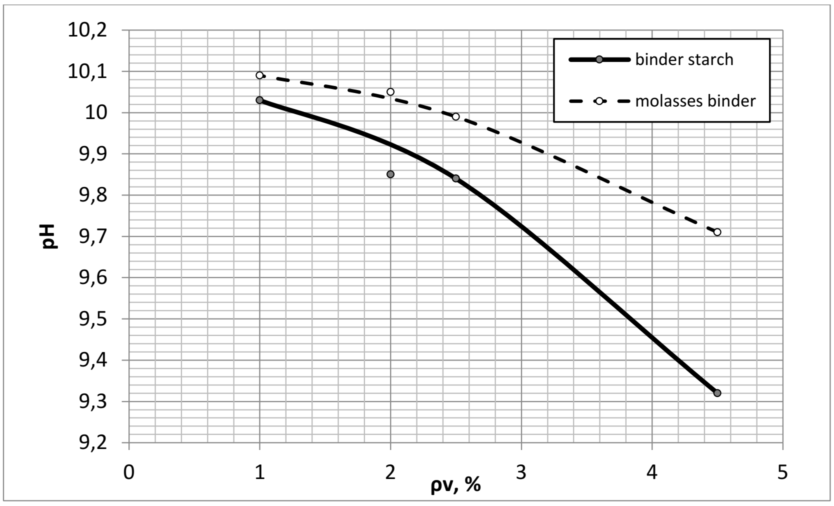

Figure 5. The value of the pH factor of the pellets depends on the type and concentration of the binder (ρv)

From the diagram, it can be seen that with an increase in the amount of added binder, the boiling point of the pH factor decreases, especially in the area above the concentration of both types of the binder of 2.5%. It is also clearly observed that the chosen type of binder has a significant impact on this indicator. Pellets using molasses as a binder give better pH factor results.

6. CONCLUSIONS

As a result of this research, the following claims can be made:

The biggest influence on the strength of the pellets is the amount and type of binder used. As the amount of binder increases, so does the strength of the pellets. In this regard, the limiting factor in the production of pellets and the choice of binder concentration is primarily the required strength value conditioned by their application and the economical parameters of such production.

On the hardness ie. the wear resistance of pellets and the type and amount of binder have a significant impact. It is reflected in the value of the wear resistance of pellets up to a certain concentration of binder in the pellet, beyond which the value of this indicator cannot be equalized by adding binder. In the case of demanding higher values of wear resistance with the optimal amount of added binder (which in this research was established with about 2.5% binder in the pellet), the only way to fix this parameter should be sought through the technological parameters of the pelletizing device (speed of rotation and tilt disc).

The type and amount of binder have a significant influence on the value of the pH factor of the pellets. More favourable results in this research were obtained for pellets in which molasses binder was applied. In the case of both types of binders, increasing the amount of added binder decreased the value of the pellet's pH factor.

Both types of binders are favourable in terms of water solubility, i.e. required results.

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