Quality of technological limestone quality as an important aspect of the efficiency of sugar beet factories

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Abstract. The authors studied 252 samples of limestone mined in 2014-2020 on the territory of 5 fields located in 2 regions of the Central Federal District of the Russian Federation. Limestone quality was assessed by the content of calcium carbonate and associated impurities. According to the results of the assessment, a number of deposits were formed in decreasing limestone quality. The highest quality was noted at the East-Bernikovskoe deposit (Tula region), containing on average 95.3% of calcium carbonate. Through the example of 10 beet sugar factories located in 5 regions of the Central Federal District, the influence of the quality of limestone on its consumption in sugar production was assessed. The authors studied the data on the consumption of limestone of the considered deposits at sugar beet factories, which was used in the period from 2014 to 2020. According to the results, a number of deposits were determined to increase the consumption of limestone in the production of sugar, which coincided with a number in terms of decreasing quality. A lower consumption of limestone was noted at beet sugar factories that used limestone from the East-Bernikovskoe (in average 3.81% during the studied period). Therefore, the choice of limestone of a certain deposit for the use in sugar production is a factor in enhancement of operating efficiency of beet sugar factories.

1. Introduction

The Russian Federation is becoming a self-sufficient country in sugar [1] and the world's largest sugar beet producer in the last few years. The annual volume of its production in the country is about 6 million tons, however in the 2020-2021 season it is expected to decrease to 5.2 million tons. For more than 200 years, the technology of sugar from sugar beet has been based on the use of special reagents for the purification of sugar-containing solutions: milk of lime and saturation gas. Lime milk is a suspension of calcium hydroxide with a density of 1.18-1.20 kg/dm$^3$, obtained by combining burnt lime with water. The demand for lime in the Russian Federation is almost completely satisfied by its own production and the share of its consumption by the sugar industry is about 6% of the total consumption [2]. The task of the supply of sugar industry with lime is solved by its own capacities directly at the sugar beet factories by burning limestone - an organic sedimentary rock consisting of calcite. Every year, Russian beet sugar factories consume about 1.5-1.7 million tons of limestone. Therefore, it is necessary to develop a rational approach to its use in order to organize the efficient operation of beet sugar factories.

The quality of lime milk and its activity determine the degree of purification of diffusion juice from non-sugars and affect the quality of white sugar [3]. In order to reduce costs in the production of sugar,
beet sugar factories strive to minimize the costs of the production of lime milk and reduce its consumption. Therefore, the consumption of limestone is one of the main technical and economic indicators characterizing the efficiency of the beet sugar factory. The consumption of limestone varies depending on many reasons: quality of sugar beet, technology of purification of diffusion juice [4], technical level of the beet sugar factory, level of automation of processes, duration of the production season, quality of limestone, etc. Many reasons of influence open up the possibility for an enterprise to manage these reasons [5, 6], especially taking into account the development of digitalization in economy [7]. In the Russian Federation, the consumption of limestone was more than 7% of the mass of processed beets until 2000. Over the past 20 years there has been a gradual decrease in consumption. During the last 5 years the consumption of limestone was less than 4% of the mass of processed beets. In the 2020-2021 production season seven beet sugar factories out of 68 had a limestone consumption of more than 5% to the mass of processed sugar beet. Seventeen factories had less than 3.5% to the weight of processed sugar beet. This confirmed the existence of reserves for its reduction in some beet sugar factories.

The leader in sugar production in Russia is the Central Federal District. In 2020, the gross harvest of sugar beets amounted to 18 million tons, and 39 beet sugar factories provided 2.9 million tons of sugar. At the same time, 6 factories had a limestone consumption of more than 5% to the mass of processed sugar beet, 12 factories were lower than 3.5%. On the territory of the Central Federal District there are more than 150 developed deposits of limestone, which is used in metallurgy, construction and chemical industry, the production of cement, rubber, glass, sugar and in agriculture. Limestone is supplied to the regional beet sugar factories from about 10 quarries, mainly located in the Lipetsk and Tula regions. The mined limestone can have a different composition and it have a positive or negative effect on consumption and affect the overall efficiency of sugar production when it is used in sugar beet factories. Therefore, it is relevant to consider the impurities in the composition of limestone from the standpoint of the influence on the process of its roasting, technological processes for the production of beet sugar, assessment of the quality of limestone in the context of deposits and its impact on consumption at beet sugar factories using the example of the Central Federal District.

2. Materials and methods
The influence of impurities in the composition of limestone on roasting and technological processes of sugar production was considered summarizing scientific and practical data. The quality assessment was carried out on 252 samples of limestone mined on the territory of 5 deposits located in 2 regions of the Central Federal District and supplied to beet sugar factories in the period from 2014 to 2020. The list of deposits, their location and the number of studied samples are shown in Table 1.

The parameters of quality assessment included the determination of the content of the following main and accompanying components of limestone: calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), silicates (SiO₂), aluminum and iron oxides (Al₂O₃ + Fe₂O₃), calcium sulfate (CaSO₄).

| Deposit number, location | Deposit name        | Number of studied samples |
|--------------------------|---------------------|---------------------------|
| Lipetsk region           |                     |                           |
| 1                        | Olshanetskoe        | 71                        |
| 2                        | Khmelnetskoe        | 39                        |
| 3                        | Rozhdественское     | 25                        |
| 4                        | Argamachskoye       | 37                        |
| Tula region               |                     |                           |
| 5                        | East-Bernikovskoe   | 80                        |

A limestone sample was crushed mechanically, ground in a mortar to a finely dispersed state and sieved through a sieve with a diameter of 0.2 mm. The sequence of the determination of the
components by analytical chemistry methods is as follows: silicates, oxides of aluminum and iron, calcium sulfate are determined by gravimetry, calcium carbonate and magnesium carbonate is determined by titrimetry.

During the determination of silicates, an insoluble residue was precipitated after the sample was treated with hydrochloric and nitric acids and the residue were calcined to constant weight. In order to determine the oxides of aluminum and iron, they were precipitated in the form of hydroxides with a solution of aqueous ammonia from the filtrate obtained after the separation of the insoluble precipitate of silicates. The hydroxide precipitate was calcined to constant weight. The content of calcium sulfate was determined by the method of precipitation of sulfate anions with barium chloride from the filtrate obtained after the separation of the insoluble silicate residue. The residue of barium sulfate was calcined to constant weight. The recalculation for the content of calcium sulfate was carried out using the coefficient 0.5832.

The total content of calcium carbonate and magnesium was determined by complexometric titration with Trilon B in the presence of a dark blue chromium indicator in an alkaline medium of an aliquot part of the solution obtained after separating the residue of aluminum and iron hydroxides. In an aliquot part of the same solution, the content of calcium carbonate in the presence of the indicator murexide was determined in a similar way. The content of magnesium carbonate was determined by the difference between the total content of components and the content of calcium carbonate.

According to the results of the content of the main and accompanying components of limestones from various deposits, they were ranked in descending order of quality.

In order to assess the impact of the quality of limestone on its consumption at beet sugar factories, a sample of factories was carried out, which in the period from 2014 to 2020 used limestone of one deposit from the list given in Table 1. The sample included nine sugar beet factories from five regions of the district, which met the specified requirements. One factory was included additionally due to a unique situation: 3 years of using limestone from one of the considered deposits and 3 years of using limestone from another studied deposit. Thus, the sample included two factories for four limestone deposits, and three factories for one deposit. For each factory, the average consumption of limestone for the studied period and the average for the deposit were calculated.

3. Results and Discussion

The chemical composition of limestone is directly related to the quality of calcium oxide and furnace gas formed during roasting, as well as the resulting lime milk, since the roasting technology largely determines the physicochemical properties of lime (calcium oxide), and then the properties of milk of lime (calcium hydroxide) during its slaking.

The main component of limestone is calcium carbonate. Due to it limestone is mined and used in sugar beet production. However in any rock of limestone there are always accompanying impurities. For example macro impurities in the form of magnesium carbonate, calcium sulphate, oxides of silicon, aluminum, iron. Microimpurities include other inorganic substances that are in small quantities: sodium, potassium, phosphorus, copper, fluorine, chlorides, etc., as well as bituminous substances. Many of them, mainly sodium and potassium compounds, bituminous substances, sublime during roasting and pass into the furnace gas.

Magnesium carbonate is considered an undesirable impurity because, having a lower melting temperature, it lowers the melting point and dissolves itself in the liquid phase. The resulting magnesium oxide is recrystallized and is present in a coarse-crystalline form in the burnt furnace lime. The high content of magnesium oxide in furnace lime significantly increases the loss of contaminated calcium oxide during the clarification of lime milk. In the process of roasting of limestones with a high content of magnesium carbonate, some of the magnesium oxide always enters the semi-finished products of the process stream, causing a decrease in the cleaning effect, rapid ignition of filter cloths and heating surfaces of evaporators.

There is controversial information about the required content of magnesium carbonate in limestones for sugar industry. Some researchers believe that its content should not exceed 1.5%, others
- 2%, as already at a content of 3%, the adjustments should be made to the modes of purification of diffusion juice. Others note that in the range of magnesium carbonate content in limestone up to 3%, there is no need to make adjustments to the roasting parameters, only limestone with a magnesium carbonate content of more than 5% is unsuitable for sugar industry.

The silicates in limestones can occur in the form of individual inclusions with a crystalline structure, or in the form of an amorphous substance distributed throughout the rock. Their harmfulness is manifested both during the roasting of limestone and during further processes up to the crystallization of sucrose. In particular, the presence of silicates leads to the formation of melts in the furnace and has a negative effect on the durability of its lining. The transition of silicon oxide to lime and its incomplete removal during the purification of lime milk from impurities leads to the damage of the working parts of the pumps. It also clogs the valves and pipelines, increasing the number of blowdowns of the purification devices of diffusion juice.

When lime milk is obtained, silicates partially pass into solution in a colloidal form, migrating into the purified diffusion juice. Their presence in the semi-finished products of the process stream leads to the formation of scale on the surface of the evaporators during evaporation and also contributes to the corrosion of the pipes of the evaporators. Ultimately, the presence of silicates in the juice and then in the syrup, determines the presence of turbidity in the solution. Moreover it creates a risk of sugar inclusion in crystals. Such sugar can give muddy solutions.

The oxides of aluminum and iron are considered the most dangerous impurity in limestones, which lead to the formation of melts in the furnace. Moreover, they have a negative effect on the durability of the furnace lining. It is connected with the fact that the compounds of calcium oxide with aluminum and iron oxides are the most fusible. They form the first portions of the liquid phase in the furnace and play a more important role in lime reflows than silicates. In case of insufficient purification of lime milk, aluminum and iron oxides get into the semi-finished products of the process stream, being deposited on the filter cloth in the form of amorphous sediments containing up to 5% of oxide hydrates. Therefore, it is believed that the total content of aluminum and iron oxides should not exceed 1.5%.

The main purpose of the effect of the impurities of calcium sulfate on the limestone roasting process is to lower the temperature of formation of the liquid phase, as well as to participate in the formation of this phase. When slaking lime, the increased content of calcium sulfate significantly inhibits this process. At the stage of defecation, a part of calcium sulfate passes into juice due to its increased solubility in sugar solutions. Subsequently its small crystals can clog the pores of filter fabrics. When it gets into the evaporator with juice, calcium sulfate is deposited in the form of scale on the heating surface of the apparatus. Some authors believe that the content of calcium sulfate in limestone should not exceed 0.2%, others give a value of 0.4%.

In general, the main requirements for the composition of limestone for sugar production in the Russian Federation are as follows: the content of calcium carbonate not less than 93.0%; magnesium carbonate not more than 3.0%; silicates not more than 3.0%, aluminum and iron oxides in total not more than 1.5%, calcium sulfate not more than 0.2%; natural moisture. They differ from the requirements of other European countries (Table 2) downwards.

| Component name, component content, % | Ukraine | Countries of European Community | Russia |
|--------------------------------------|---------|---------------------------------|--------|
| CaCO₃, not less                      | 93.0    | 96.0                            | 93.0   |
| MgCO₃, not more                      | 2.5     | 1.0                             | 3.0    |
| SiO₂, not more                       | 3.0     | 1.0                             | 3.0    |
The presence of limestone impurities in the form of magnesium carbonate and silicates worsens the purification of diffusion juice and leads to a decrease in the quality of sugar, which necessitates the use of various methods of the improvement of the quality of lime milk \[8, 9\].

The results of the assessment of the quality of limestones are presented in Table 3. The numerator in Table 3 shows the ranges of variation of indicators, the denominator shows the average value. To exclude the influence of possible gross deviations of the values, mathematical processing of the research results was carried out using the algorithms of variance analysis.

| Deposit number | CaCO\(_3\) | MgCO\(_3\) | SiO\(_2\) | Al\(_2\)O\(_3\) + Fe\(_2\)O\(_3\) | CaSO\(_4\) |
|----------------|------------|------------|-----------|-------------------------------|-----------|
| 1              | 90.2...93.7| 1.5...3.9  | 1.6...4.9 | 0.1...1.5                     | 0.1...0.2 |
| 2              | 92.5...95.4| 1.6...2.9  | 1.5...2.5 | 0.3...0.7                     | 0.1...0.2 |
| 3              | 91.6...93.9| 1.4...3.3  | 1.7...3.4 | 0.2...0.7                     | 0.1...0.2 |
| 4              | 91.1...94.2| 1.5...3.5  | 1.7...3.5 | 0.3...0.7                     | 0.1...0.1 |
| 5              | 94.1...96.6| 1.1...2.4  | 0.2...1.4 | 0.1...0.5                     | 0.1...0.2 |
| Average        | 93.4±0.2   | 2.4±0.1    | 2.1±0.2   | 0.5±0.04                      | 0.2±0.02  |

The highest quality of limestone was in deposit No. 5. The average content of calcium carbonate was 95.3%, respectively, the content of associated impurities was lower in relation to the average values according to the assessment results, while the number of analyzed samples for this deposit was the largest - 80. In further analysis we will study the composition of this limestone as a reference.

Then, deposit No. 2, where the content of calcium carbonate was 93.7%. At the same time, the content of magnesium impurities in this deposit was 1.2 times higher than the reference; the content of silicates was 3.3 times higher. Further, there was deposit No. 3 with an average content of calcium carbonate of 93.1%. At the same time, the content of magnesium impurities in this deposit was 1.6 times higher than the reference; the content of silicates was 4.5 times higher. The deposits No.1 and No.4, on average, had a content of calcium carbonate below the standard adopted in the Russian Federation.

The leaders in the high content of accompanying components were deposits No. 1 and No. 4 with the content of magnesium carbonate (on average 2.8%, some samples - up to 3.9%); deposits No. 1 and No. 3 with the content of silicates (on average 2.8%, some samples - up to 4.9%); deposit No. 1 with the content of oxides of aluminum and iron, where some samples contain 1.5%; deposits No. 1, 2, 3 with the content of calcium sulfate (on average 0.2%).

Taking into account the number of studied samples, the proportion of samples meeting the requirements for each deposit, which varied from 100% (deposit No. 5) to 40% (deposit No. 1), it is possible to compose a number of deposits in decreasing limestone quality in the following order (according to the numbering of table 1): 5 > 2 > 3 > 4 > 1. The highest quality was in the East-Bernikovskoe deposit (Tula region), the lowest quality was in the Olshanetskoe deposit (Lipetsk region).

The results of the assessment of the impact of the quality of limestone on its consumption at beet sugar factories are presented in Table 4.

As we can see, the list of limestone deposits in terms of its consumption at beet sugar factories is arranged in an ascending order: 5 > 2 > 3 > 4 > 1 and coincides with the list in decreasing order of limestone quality. This indicates the existence of an inverse relation between the consumption of limestone in beet sugar factories and its quality. At the same time, the Elan-Kolenovsky factory in the
period from 2014 to 2016 used limestone from deposit No. 3; the consumption of limestone during this period was 4.21% of the mass of processed beets. In 2017-2019 the factory changed its supplier and used the limestone from deposit No. 5 of the highest quality. During this period the consumption of limestone decreased to 3.94% of the mass of processed beets. The Dmitro-Taranovskiy beet sugar factory, which used for the entire studied period the limestone of deposit No. 5 had a lower limestone consumption - 3.67% to the mass of processed sugar beet.

Therefore, the choice of limestone of a certain deposit for use in sugar production is one of the factors in increasing the efficiency of beet sugar factories.

Table 4. Limestone consumption in sugar beet factories depending on its deposit

| Beet sugar factory           | Limestone consumption, % to the mass of processed sugar beet | Limestone deposit number |
|-----------------------------|-------------------------------------------------------------|--------------------------|
| Pereleshinsky               | 4.20                                                        | 1                        |
| Zalegoschensky              | 4.39                                                        |                          |
| Khokholsky                   | 3.94                                                        | 2                        |
| Liskinsky                   | 3.75                                                        |                          |
| Lebedyansky                 | 3.54                                                        |                          |
| Elan-Kolomovsky             | 4.21                                                        |                          |
| Olymsky                     | 3.94                                                        |                          |
| Lgovsky                     | 3.95                                                        |                          |
| Krivetsky                   | 3.87                                                        | 4                        |
| Dmitrotaranovsky            | 3.67                                                        |                          |
| Elan-Kolomovsky             | 3.94                                                        | 5                        |

4. Conclusion
The authors studied the influence of the main admixtures of limestone on the processes of its roasting and technological processes of sugar production from sugar beet, as well as the requirements for the composition of limestone for sugar production in Europe and the Russian Federation. During the research the quality assessment of limestone of 5 deposits of the Central Federal District of the Russian Federation for the period from 2014 to 2020 was carried out. A list of deposits were drawn in decreasing quality of limestone, the highest quality was in the East-Bernikovskoe deposit in the Tula region.

The influence of the quality of limestone on its consumption at beet sugar factories was assessed using the example of 10 beet sugar factories of the Central Federal District for the period from 2014 to 2020. The relation of a decrease in the consumption of limestone with an increase in its quality was revealed. The lowest consumption of limestone at beet sugar factories was observed when using limestone from the East-Bernikovskoe deposit. Consequently, one of the factors in the increase of the efficiency of beet sugar factories is the choice of limestone of a certain deposit for the purposes of sugar production.

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