Studies of the ozonation process when drying grain

I V Baskakov, V I Orobinsky, V A Gulevsky, A M Gievsky and A V Chernyshov

Voronezh State Agrarian University named after Emperor Peter I, 1, Michurina str., Voronezh, 394087, Russia

E-mail: vasich2@yandex.ru

Abstract: The article presents the main results of studies on the influence of ozone concentration in the ozone-air mixture acting as a drying agent on the efficiency of the efficiency of grain dryers of various types. The positive effect of gas on shortening the duration of the process, increasing the speed of drying, reducing energy costs, increasing the productivity of grain dryers, has been revealed. An analysis based on the results of research conducted by leading scientists in this field and our own experiments made it possible to determine the feasibility of preliminary ozonization of a wet grain heap in metal buffer storage silos before feeding it to a grain dryer. In general, the advantages of using ozone during the drying of grain material before the traditional method are revealed. Agricultural producers are recommended to equip buffer silos for temporary storage of grain with an ozonization system, which, according to preliminary studies, will reduce the moisture content of the heap by one pass through the mine dryer by up to 8.3%. At the moment, the percentage of moisture removed for one drying cycle does not exceed 6%.

1. Introduction
In the 21st century, the search for non-polluting technologies is important. In this case, the use of ozone in various branches of the national economy is increasingly popular. Ozonization is already used in medicine, microbiology, cosmetology, housing and communal services, food and chemical industries. The increasing distribution of gas is also traced in agriculture. Different scientists conducted a number of studies using ozone in plant growing, horticulture, animal husbandry, poultry farming, beekeeping, and in during storage, drying and post-harvest grain processing as well [1-6].

2. Objects and methods of research
The objects of research were the grain heap, the process of grain drying, and also gas ozone. The possibility of using ozonization in agriculture was proposed in the 1980s. However, commercial implementation of gas in the industry has not been realized until the present. Initially, this was due to the complex design of ozonizers and the high cost of the process. In addition, in our country ozone refers to the highest class of hazardous substances, which also imposes a number of restrictions on its use. The modern level of technology development has allowed designing compact, relatively inexpensive ozonizers, which required reconsidering the attitude to ozone technologies. The works of leading Russian and foreign scientists and as well as own researches [1-6] in the field of grain drying of grain with the ozone-airixture were used as a theoretical and methodological basis for research. The purpose of the research was to improve the efficiency of modern grain dryers by using the ozonation process.
3. Results and their discussion

Harvesting of crops often takes place in unfavorable weather conditions, when the moisture content of grain and seeds exceeds the conditioning values. Due to the prolonged period of vegetation, some plants, for example maize, cannot be harvested on the larger territory of the country without further drying at all. To bring the grain material with humidity over 20% by pass through the majority of modern grain dryers is not possible until the condition is reached. The next loading of equipment through vertical noria will lead to additional grain damage in the range of 3.3...4.6%. Therefore, researches aimed at increasing the intensification of the drying process are relevant. In addition, the cost of post-harvest grain processing can be significantly decreased by reducing the energy consumption of modern grain dryers where an ozone-air mixture is used.

Scientists who laid the foundations for research on the efficiency of grain dryers by using the ozone-air mixture as a drying agent found out that the penetration of ozone into the grain occurs according to the law of gases diffusion. In this case, the oxidizer enters into a series of chemical reactions, which are accompanied by the release of heat. This reduces the energy consumption of the drying process, since it takes less time to heat the grain material to the optimum temperature. Ultimately, ozone promotes the heating of the grain from the inside, thereby increasing the diffusion coefficient of moisture and accelerating the vaporization. As a result, the amount of heat required to detach the water molecule during the drying process is reduced by 20...60%.

In general, the drying process by means of an ozone-air mixture is divided into three stages. First, ozone interacting with organic substances on the surface of the grain contributes to the removal of excessive moisture due to the orientation of water molecules around atomic oxygen, which facilitates their removal by air flow. Then, the gas improves the permeability of cell membranes and causes structural changes in the cover tissues. Due to this, the moisture from the inner layers moves more intensively to the surface of the grain. At the last drying stage, the sorption-bonded water molecules are eliminated due to the weakening of the dipole bonds.

According to D.A. Normov when drying grain, the concentration of ozone in the ozone-air mixture fluctuates between 2 ... 40 mg/m$^3$. A sufficiently large spread of the parameter is explained by the different conditions for carrying out the experiments.

In general, drying the grain by using an ozone-air mixture helps to reduce the time of the process. However, this effect varies from plant to plant. Analysis of the studies’ results by various authors showed that the highest grain drying rate is observed in oats and barley, and the smallest in wheat and rye in the ozone concentration range of 2 ... 11 mg/m$^3$. This is explained by the peculiarities of the seed structure of these plants and the different rates of ozone penetration of ozone into the interior of particular caryopsis. For the same reason, at the beginning of the experiments, the influence of the ozone-air mixture on the moisture content of the grain is not traced and is within the range of the measurement error. A significant reduction in the percentage of moisture removed is observed only after the grain is saturated with the ozone. Since the internal structure of the grains and the conditions for carrying out the experiments directly affect the diffusion of the gas inside the seed, the effectiveness of the ozonation process depends on the initial state of the heap and the process regimes. In general, the processing of grain by the ozone-air mixture reduced the time of bringing to the standard condition in all the investigated cereal crops from 1.3 to 2.5 times (Figure 1).

The analysis of the studies’ results on the reduction in the of grain moisture content of grain crops with the time of ventilation is described with sufficient accuracy by a polynomial dependence of the second degree:

$$W = -k_1 \cdot t^2 - k_2 \cdot t + k_3,$$  \hspace{1cm} (1)

where $W$ – the moisture content of the grain,%;
$t$ – the drying time, $h$;
$k_1, k_2, k_3$ – the coefficients.
Figure 1. Results of grain seeds ventilation with ozone-air mixture and air.

The values of coefficients are $k_1$, $k_2$, $k_3$ presented in Table 1. In general, there is a certain tendency in changing their value from exposure to ozone-air mixture as a drying agent. Coefficient an ozone-air mixture exposed $k_1$ for drying grain with the use of heated air varies in the range -0.043... -0.001. The use of the ozone-air mixture as a drying agent reduces this factor by 0.004...0.48 times. The coefficient $k_2$, on the contrary, increases when drying the grain using ozone as compared to the control samples. The free term of the equation, when the ozonation process is used, as a rule, decreases or practically does not change. Determination of the dependence of the decrease in grain moisture on the time of ventilation in standard active storage bins and the use of recommendations for correcting the corresponding coefficients will allow predicting the effectiveness of the introduction of ozone technologies.

Table 1. Coefficients variation under condition of decreasing moisture content of grain in dependence on ventilation time

| Crop | Ventilation with using | Coefficients Value | The reliability coefficient of the approximation $R^2$ |
|------|------------------------|--------------------|---------------------------------------------------|
|      |                        | $k_1$ | $k_2$ | $k_3$ | |
| Wheat| Air                    | -0.0346 | -0.3217 | 30.107 | 0.9864 |
|      | Ozone-air mixture      | -0.0714 | -0.2802 | 30.366 | 0.9810 |
| Rye  | Air                    | -0.0381 | -0.3465 | 29.879 | 0.9961 |
|      | Ozone-air mixture      | -0.1110 | -0.1209 | 29.308 | 0.9912 |
| Barley| Air                  | -0.0422 | -0.3139 | 29.810 | 0.9962 |
|      | Ozone-air mixture      | -0.6405 | 2.7167  | 26.614 | 0.9959 |
| Oats | Air                    | -0.0019 | -1.2744 | 31.752 | 0.9946 |
|      | Ozone-air mixture      | -0.4464 | 0.9036  | 29.429 | 0.9892 |
When drying grain in grain dryers, the process proceeds more rapidly (Figure 2), since the temperature of the drying agent in them is much higher than in the case of ventilation. The experiment was carried out on triticale. The initial moisture content of 29% was brought to the condition in a standard grain dryer in six hours. Using an ozone-air mixture allowed reducing the time of drying by 2 hours.

![Figure 2. The results of drying the triticale grain with an ozone-air mixture and air.](image)

In this case, the drying process in a standard grain dryer can also all be described by polynomial dependence (1) of the second degree. However, the coefficients $k_1$, $k_2$, $k_3$ acquire other values (Table 2).

| Crop | Drying with using | Coefficients value | The reliability coefficient of the approximation $R^2$ |
|------|-------------------|--------------------|------------------------------------------------------|
| Triticale | Air | $k_1$ | $k_2$ | $k_3$ | 0.94 |
| | Ozone-air mixture | 0.3106 | -4.6594 | 32.05 | |

To increase the accuracy of calculations, it is necessary to continue further studies on the effect of the ozone-air agent on the efficiency of the drying process, as well as to expand the range of factors considered.

The efficiency of the drying process is influenced by the concentration of ozone in the ozone-air mixture. The trend can be traced on all the investigated cereal crops. However, the most obvious effect of ozone is observed on oats and barley, and least on wheat and rye. Analysis of the studies’ results on the change in the rate of grain seeds drying depending on ozone concentration in the ozone-air mixture is described with sufficient accuracy by a polynomial dependence of the third degree:

$$V = -m_1 \cdot C^3 + m_2 \cdot C^2 + m_3 \cdot C + m_4,$$

where $V$ – the rate of drying of the grain of a given crop, %/hour;  
$C$ – ozone concentration in the ozone-air mixture, mg/m$^3$;  
$m_1$, $m_2$, $m_3$, $m_4$ – coefficients (Table 3).
Table 3. Coefficients values with variation in the drying speed in dependence on ozone concentration

| Crop   | $m_1$  | $m_2$  | $m_3$  | $m_4$  | $R^2$    |
|--------|--------|--------|--------|--------|----------|
| Oats   | -0.0111| 0.0890 | 0.1359 | 0.2086 | 0.9541   |
| Barley | -0.0172| 0.1856 | -0.2986| 0.4086 | 0.9868   |
| Barley | -0.0183| 0.2201 | -0.5437| 0.4829 | 0.9935   |
| Wheat  | -0.0167| 0.2033 | -0.5471| 0.5686 | 0.9809   |
| On the average | -0.0158 | 0.1745 | -0.3134| 0.4167 |

The coefficients obtained are sufficiently close. Consequently, the determining factor for drying the grain is the ozone concentration in the ozone-air mixture, and less significant - the crop. Using even the averaged coefficients, it is possible to predict the drying speed with sufficient accuracy, having the initial point. It can be obtained in a standard grain dryer as in the beginning of the process the effect of ozone is practically not traced, since it did not have time to penetrate inside the grains. In this case, an additional factor must be introduced into the equation, which would take into account the characteristics of a particular crop. But to achieve this it is necessary to carry out a series of experiments.

Analyzing the results of these experiments, scientists at Azov-Chernomorskaya State Agroengineering Academy came to the conclusion that an increase in the gas concentration above 8 mg/m$^3$ is not advisable, since the efficiency of the process remains practically unchanged for large values (Figure 3).

![Figure 3. Effect of ozone concentration in the drying agent on the drying speed of grain seeds.](image)

In most modern grain dryers in one pass, you can remove no more than 6% moisture. The longer the presence of grain material in the drying column leads to a loss of quality indicators of grain because of its overheating. At the same time, the permissible drying temperature of commercial and feed raw materials is determined by the preserving condition of the consumer and technological properties, and when treating seeds, the maximum heating is assigned taking into account the conservation of germination energy and germination. The use of an ozone-air mixture as a drying agent will increase the percentage of moisture removed in one pass through the grain dryer.

Similar studies were conducted at Scientific and Practical Center of the National Belarus Academy of Sciences for Food and Drink. Grain with initial moisture of 24...25% was dried on a column drier SZK-15. Moreover, both conventional air and an ozone-air mixture were used as a drying agent. To bring the grain to the condition in a standard grain dryer was only possible in two cycles. By doing so, after the first pass the humidity of the product was varied in the range of 19...22%, and after the second – 11...13%. The time spent per cycle was 2.0...2.8 hours. The use of an ozone-air mixture as a
drying agent allowed to dry the grain to a humidity of 12...13% in a pass through a grain dryer. As a result, the productivity of equipment has increased by 35.7...50%, and the specific fuel consumption has decreased. Thus, in one drying cycle, using an ozone-air mixture, it was possible to remove up to 12% of grain moisture and exclude from the production line an additional lifting of the material with a vertical noria, which would reduce the injury of seeds during the preparation of the seed material.

The increase in productivity was also noted in other types of grain dryers. Thus, Zernograd scientists dried barley grain with an initial moisture content of 26.2% in a tower dryer SBVS-5. At the same time, the increase in the capacity of the equipment when using the ozone-air mixture heated to 48°C as a drying agent was in 1.9 times compared to that of a standard grain dryer. The duration of the process was reduced by 53%.

Studies to determine the drying speed by means of an ozone-air mixture and air, depending on the time of the operation, showed that the ozone action positively affects this parameter at the initial stages of the process. The difference between standard and experimental treatment in the first hour of the experiment was 23%, and then decreased to 13% and after five hours was practically equalized.

Based on the analysis, a hypothesis that it is not possible to ozonize the entire drying process was put forward. In this case, the processing of grain by ozone must be carried out in buffer metal storage silos by their ventilation with an ozone-air mixture. This will reduce the moisture content of the grain heap even before drying and saturate the grain material with gas. And with small grain moisture values, ventilation with an ozone-air mixture will allow it to be brought to a condition without the use of a grain dryer. In the case of excessive moisture content in the grain material, the drying of the previously proozonized heap will proceed more efficiently and with lower energy costs.

In order to confirm this hypothesis, an experiment was conducted. Grain of winter wheat with a total mass of 30 kg and a moisture content of 27.3% was vented for one hour in a closed loop with an ozone-air mixture. Agent flow rate was 1 m³/h and an ozone concentration – 8 mg/m³. At the same time, the technological process of the complex for grain heaps ozonizing proceeded as follows. Atmospheric air without oil-laden compressor 1 (Figure 4) was fed into the refrigerator air dryer 2 and further into the ozonator 3 of the Water Ozonator series. The ozone-air mixture obtained was fed through the aeration system to a metal container 5 with a capacity of 50 liters. Ozone concentration was monitored with the “Sigma-0.3” system, one of which indicators was located inside the ozonation chamber, and another – outside to observe the MPC level in the human working place.

As a control sample, the same batch of grain with an initial moisture content of 27.3%, located in a heated room at a temperature of 25°C, was used.

As a result, the vented grain after processing with an ozone-air mixture reduced the humidity to 25%. In this case, this parameter was 26.3% in the control sample.

Both batches of grain were loaded in equal proportions into a laboratory column dryer, in which the inner column 10 (Figure 5) was divided by partitions 2 into two independent compartments.
eliminating the possibility of mixing the drying products. Loading and unloading of the samples was carried out at identical intervals of half an hour in equal portions. The drying conditions of the previously proozoneized grain and the control sample were exactly the same.

Figure 5. Diagram of laboratory column grain dryers: 1 – charging hopper; 2 – partitions; 3 – charging flaps; 4 – supply ducts for hot air; 5 – exhaust ducts of exhaust air; 6 – discharge flaps; 7 – draining pipes for dried grain; 8 – the suction fan; 9 – moist air chamber; 10 – column divided into two separate grain streams; 11 – the chamber of hot air; 12 – heating element.

During the experiment the temperature of the drying agent into the hot air chamber 11 (Figure 5) averaged 55°C with a short-term range of variation 49.1…59.9°C. After passing through the grain layer, this parameter was reduced to 23.1 ± 0.5°C. Moist air was removed from the chamber 9 by means of the suction fan 8. The results of the experiment to determine the effect of ozonation process on the effectiveness of grain drying of winter wheat are represented in Table 4.

Table 4. Results of the experiment to determine the effect of preliminary treatment of winter wheat grain with an ozone-air mixture on the drying efficiency

| Time of drying, min | Control untreated sample of grain | Experimental lot of grain after hour ventilation with ozone-air mixture |
|---------------------|----------------------------------|---------------------------------------------------------------|
| Moisture, %         | Temperature, °C                  | Moisture, % | Temperature, °C |
| 0                   | 26.3                             | 25.4        | 25.0 | 26.0 |
| 30                  | 23.6                             | 26.7        | 21.8 | 26.8 |
| 60                  | 22.5                             | 24.0        | 20.9 | 23.7 |
| 90                  | 18.0                             | 23.8        | 17.5 | 23.8 |
| 120                 | 16.2                             | 24.5        | 16.2 | 23.9 |
| 150                 | 15.6                             | 23.8        | 15.5 | 24.5 |
| 180                 | 14.4                             | 21.1        | 14.8 | 24.3 |
| 210                 | 14.3                             | 24.4        | 14.4 | 25.1 |

The analysis of the experiment results proves that the effect of ozone is mainly traced during the first 30 minutes. For a given period, the moisture content in the experimental grain consignment decreased by 3.8%, which is 12.8% relative to the initial value. In the control sample, within 30 minutes of drying, it was possible to reduce the presence of moisture by 2.7% or 10.3% relative to the start of the experiment. This indicates that the preliminary ozonation of a damp heap to accelerate water yielding capacity in the initial drying period by 1.1% under given conditions or 2.5% relative to the initial value. Subsequently, the ozone decomposed and the process proceeded with similar
parameters. In general, the positive effect of preliminary ozonization of the grain before drying was traced during the first two hours (Figure 6).

![Grain drying results of winter wheat in laboratory grain dryers.](image)

**Figure 6.** Grain drying results of winter wheat in laboratory grain dryers.

The drying process in the laboratory grain dryer can also be described by the polynomial dependence (1) of the second degree. The coefficients \( k_1, k_2, k_3 \) are presented in Table 5.

**Table 5.** Polynomial dependence coefficients of the second degree when drying winter wheat grain in a laboratory mine grain dryer

| Crop            | Drying with Using | Coefficients value | The reliability coefficient of the approximation \( R^2 \) |
|-----------------|-------------------|--------------------|-------------------------------------------------|
| Triticale       | Air               | \( 0.2196 \)       | \( -3.7923 \)                                   |
|                 |                   | \( 30.320 \)       | \( 0.9756 \)                                   |
| Ozone-air mixture | 0.2065            | \( -3.3673 \)       | \( 28.148 \)                                   |
|                 |                   |                     | \( 0.9854 \)                                   |

In general, if we compare the use of an ozone-air mixture in the ventilation of a wet grain heap and in the grain dryer, the first one has several advantages over the temporary storage of grain in buffer metal silos, which is currently used in most modern grain cleaning aggregates and mini elevators. Firstly, hour ozonization contributes to a decrease in the moisture content of grain crops by 2.3% from the initial value of 27.3%. In this case, the presence of grain under natural conditions reduced this parameter by 1%. This indicates that the ventilation of the ozone-air mixture under the given conditions is more effective by 1.3%. Secondly, preliminary hour ozonization contributes to the absorption of ozone in the grain, which in the initial period of standard drying allowed removing moisture by 1.1% more than in the control sample. Thirdly, treating the heap with an ozone-air mixture disinfects and deodorizes grain and the equipment used. As a whole, the use of the ozone-air mixture in the ventilation of the buffer silo will remove up to 8.3% of the grain moisture in one drying cycle.
Thus, the expediency of metal silos ozonizing of wet grain before drying on standard grain dryers is traced. However, in order to increase the efficiency of the process, it is necessary to carry out a number of studies to determine the effect of ozone concentration and processing time needed the grain heap to absorb the gas. Perhaps, the temperature reduction of the drying agent will also intensify the drying. A similar conclusion is made on the basis of the assumption that exceeding this parameter at 38 °C causes acceleration of ozone decay. Another important thing is the fact that a decrease in the temperature of a dry agent will lead to significant energy savings. By means of a series of experiments it is necessary to determine how much the drying process on stationary column and louver-type dryers in advance of ozonized grain in silos will be less energy-intensive. At the same time, to ensure the safety of research, it is necessary to equip the system with sensors to exceed the maximum permissible ozone concentration in the work place, and to mount appropriate catalysts in possible leakage areas. Simultaneously, silos and grain loading and unloading mechanisms should be hermetically sealed as much as possible.

4. Conclusions
Agricultural producers are recommended to equip buffer silos for temporary storage of grain with an ozonization system, which, according to preliminary studies, will reduce the moisture content of the heap by one pass through the column grain dryer by up to 8.3%. At the moment, the percentage of moisture removed for one drying cycle does not exceed 6%. The use of silos equipped with aeration system and ozonation plant would allow keeping semi-dry grain without additional drying operation, since the ventilation of silos by ozone-air mixture allows reducing the heap moisture by 2.3% at the initial value of 27.3%. When coming a raw grain material in the grain cleaning unit, its saturation with ozone would promote not only an increase in the period of safe buffer storage, but also significantly reduced the cost of bringing the product to the standard condition.

References
[1] Akbas M Y and Ozdemir M 2006 Effect of different ozone treatments on aflatoxin degradation and physicochemical properties of pistachios *Journal of Science of Food and Agriculture* **86** 2090-2104
[2] Fernández L A, Bataller M, Rey R P, Véliz E, Hernández C and Alvarez C 2006 Use of ozone in the decolorization of sugar industry liquors *Science and Engineering* **28** 261–267
[3] Faroni L R D, Pereira A M, Sousa A H, Silva M T C and Urrichi W I 2007 Influence of corn grain mass temperature on ozone toxicity to *Sitophilus zeamais* (Coleoptera: Curculionidae) and quality of oil extracted from ozonized grains *IOA Conference and Exhibition* **1** 1-6
[4] László Z, Hovorka-Horvath Z, Beszedes S, Kertesz S, Gyimes E and Hodur C 2008 Comparison of the effects of ozone UV and combined ozone/UV treatment on the color and microbial counts of wheat flour *Ozone: Science and Engineering* **30** 413-417
[5] Orobinsky V I, Tarasenko A P, Gievsky A M, Chernyshov A V and Baskakov I V 2018 Improving the mechanization of high-quality seed production *Advances in Engineering Research* **151** 849-852
[6] Orobinsky V I, Gievsky A M, Baskakov I V and Chernyshov A V 2018 Seed refinement in the harvesting and post-harvesting process *Advances in Engineering Research* **151** 870-874