

Improved Fumigation Process for Stored Foodstuffs by Using Phosphine in Sealed Chambers

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ABSTRACT: In this paper we present an innovative device designed and constructed to improve the fumigation process for stored foodstuffs with the use of phosphine gas in sealed chambers. The device allowed a considerable reduction in phosphine production time (from about 5 to 7 days for traditional systems to 2 days for the equipment considered), maintaining the system below the inflammability threshold, and at the same time achieving the total exhaustion of aluminum (or magnesium) phosphide so as to avoid toxic residues at the end of the process. With the standard device currently available on the market, after the normal 5–7 day fumigating period, the powder residue contains as much as 1–2% (w/w) of phosphide. Thus the residues, according to current legislation, have to be considered toxic and harmful. To overcome this disadvantage, appropriate modifications were made to the cylindrical tray used for the fumigation process: a nebulizer was installed, which has the function of increasing the moisture of the air spreading around the phosphide pellets and allowing a more rapid reaction with phosphide. Moreover, the cylindrical tray was also heated by means of an electrical resistance, and temperature was checked by a thermostat, so as to always obtain the same efficiency, independently of outside temperature, for both hot and cold periods, since reaction speed depends on the system temperature considered. In addition, a control device for air saturation allows condensation processes to be avoided. Using the modified cylindrical tray we performed tests to determine the best values of humidity and temperature for the process concerned, avoiding phosphine concentrations that might result in a fire hazard, and the remixing of phosphide pellets inside the cylindrical tray. Our experimental data allowed us to obtain a mathematical model used to gain an insight into the process in question.

KEYWORDS: fumigation, phosphine, foodstuffs, aluminum phosphide, magnesium phosphide

■ INTRODUCTION

Warehouse-stored agri-food products awaiting retail placement may undergo chemical, physical and microbiological changes and also be infected by insect pests. The latter is a very frequent event which, once started, may cause the total loss of quality of the food product. Once the infesting parasites proliferate inside the storage areas, the contaminated foodstuffs experience significant loss of value, due to loss of weight and nutritional content. Insects are also a vehicle for the propagation of molds and mycotoxins, insofar as, if allowed to proliferate inside food products, they contribute to a further increase in temperature, triggering oxidizing processes and microbiological contamination (molds and bacteria) that can give rise to the development of metabolites such as mycotoxins. Further, for the above reasons, the use of preventive measures to combat pests becomes of fundamental importance with a view to ensuring proper food storage.^{1–4} In such foods, each chemical process has to be documented and traceable, as required by recent regulations, to avoid the risk that there may be traces of potentially harmful chemicals for consumer health.⁵

In the case of the fumigation process with phosphine gas, it should be noted that inhalation of phosphine may cause severe pulmonary irritation leading to acute pulmonary edema, cardiovascular dysfunction, coma and death; gastrointestinal disorders, renal damage and leukopenia may also occur. Further, exposure to 1400 mg/m³ (1000 ppm) for 30 min may be fatal for animals and humans. Ingestion of phosphides, particularly aluminum and zinc phosphides, may induce severe gastrointestinal

irritation leading to hemorrhage, cardiovascular collapse, acute neuropsychiatric disorders, and respiratory and renal failure within a few hours.

Hydrogen phosphide or phosphine (PH₃) formulated in 0.6 or 3 g tablets or pellets of aluminum or magnesium phosphide are indifferently used in a ratio of 12 to 15 g per ton of foodstuff. This chemical is still one of the most widely used products for disinfestation during storage both in Italy and the rest of the world.^{6–11} This is thanks to a certain safety in usage (delayed development) and its physicochemical characteristics (smell threshold lower than the danger threshold, equilibrium in terms of air density), and its high effectiveness in combating insect pests.^{12,13}

Traditional fumigation techniques using phosphine gas still involve the manual introduction of tablets with the aid of probes by staff equipped with appropriate protective devices in storage areas. At the end of the fumigation process, the operators reopen the areas and start the recovery phase which lasts at least 48 h. The phosphine required for fumigation is generated slowly by the reaction of magnesium or aluminum phosphide with ambient humidity. As it is highly toxic, phosphine can easily kill eggs, larvae and insects by asphyxiation in low concentrations.^{14–16} Moreover, phosphide pellets contain delaying chemical compounds that develop inert gases like ammonia and

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carbon dioxide, which contribute to reduce the potential of phosphine autoignition or explosion. They also contain other chemicals (mostly mercaptans) in order to give a garlic odor to the phosphine gas (that has no color or smell), making it possible for operators in proximity of the gas to detect it organoleptically. Substances such as mercaptans are thus used to indicate the toxicity of phosphine and prevent gas inhalation over long periods. When fumigation takes place in small chambers (500–1000 m³), the pellets are simply placed in thin layers on a cylindrical tray;¹⁷ for large fumigation chambers (10,000–20,000 m³) the pellets are used in different ways.

For such silos, phosphine is produced by equipment located outside, and it is introduced through pipelines inside the silos and fed into a recirculation system. The recirculation system for these types of silos is fitted with steel ducting, a 25 kW aeration fan and a 1.5 kW phosphine fan. At full silo loading and using fans, the 10,000-ton silos can achieve an air change in less than one hour.

That said, at the end of fumigation, it is necessary to remove the residual powders, which contain about 1–2% (w/w) of aluminum or magnesium phosphide that will not have reacted with the humidity. Due to their high toxicity, such residues are considered special waste. It is therefore necessary to avoid accidental dispersion in the environment of the dust residues, and to ensure proper treatment in compliance with the laws in force. Moreover, there is ever-increasing demand to remove the residual powders of magnesium and aluminum phosphide at the end of fumigation due to the increasing volumes of food treated worldwide.

Many food industry regulations require foodstuffs suppliers to take care in treating residues from the fumigation process which is based on the use of formulated chemical compounds in porous bags placed on the surface in question and removed at the end of fumigation. For this procedure, highly skilled staff, able and authorized to manage the fumigation process, are required in all its stages: from initial preparation and sealing to the most delicate stages of delivery and monitoring of the gas concentration inside the structure, through to environmental impact management at the end of treatment.^{18,19} Phosphine gas begins to rise and then spreads, in a time range of 1–4 h, depending on ambient humidity and temperature. Production of phosphine is complete within five days if the temperature is above 20 °C, while it requires longer at lower temperatures. Phosphine does not chemically interact with the fumigated products, which is why it does not alter their characteristics. In addition, it can be easily removed and does not confer particular smells to treated foodstuffs.^{20–22} For all these reasons phosphine may be considered a phytosanitary product and is still today the most widely used product worldwide for disinfection during storage, above all due to its safety in use (delayed development, olfactory threshold less than the danger threshold, equilibrium as regards air density) and its efficacy.²³

In the past decade, several studies^{24–29} were carried out to improve the fumigation process with phosphine. These chiefly concerned the following: optimizing the action of phosphine, improving and accelerating its penetration in the gaseous phase into the deep layers of the mass; creating a uniform gaseous concentration in the product mass to achieve high fumigation efficacy; avoiding handling of foodstuffs; totally eliminating the residual powder produced by the reaction of the phosphine which, contained in removable trays, would be removed in the fumigated foodstuffs at the end of treatment. Therefore, in this paper a device was designed and produced for small fumigation

chambers (500–1000 m³) to improve the phosphine production process by timely management of pellet remixing, and by humidity and temperature control of the fumigation environment.

MATERIALS AND METHODS

Equipment for Phosphine Production. Equipment was set up to improve the production process of phosphine gas (Figure 1 and

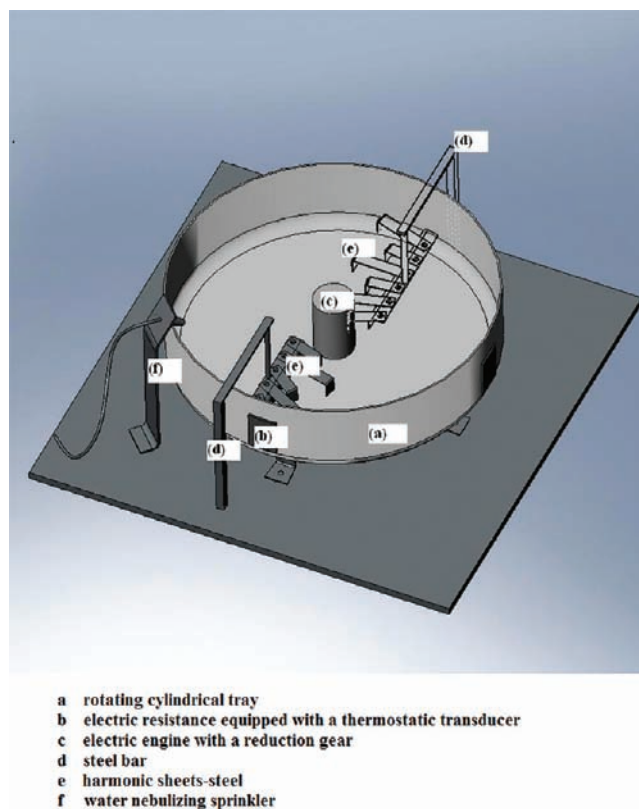


Figure 1. Equipment used in the fumigation process (lateral view).

Figure 2) consisting of a 600 mm diameter stainless steel (AISI 304) cylindrical tray (a), with a capacity of about 1 kg of magnesium or aluminum phosphide pellets with a mean diameter of 3 mm. The lower part of the tray surface is able to contain 1 kg of pellets, with no pellets overlapping. The tray is connected to an electric resistance (b) equipped with a thermostatic transducer for checking temperature, and thus can be heated up to temperatures between 30 and 80 °C; electric engine (c) with a reduction gear, which allows the cylindrical tray to rotate at velocities between 0.5 and 5 revolutions per minute; two steel bars (d) that each support five harmonic steel sheets (e). The steel sheet is 15 mm wide, spaced 15 mm apart, with one end folded downward at an angle of 90°, 0.5 mm thick and between 30 and 60 mm long. Due to its elasticity, it perfectly follows the bottom of the tray and scrapes it lightly. This is an important effect when the pellets begin to be converted into powder, due to the reaction with the air moisture. Besides, they are of different lengths, which facilitates remixing of the pellets and the powder. The steel sheet on the two bars is offset, such that each pellet on the tray bottom during rotation is sure to interact with at least one steel sheet. A nebulized water sprinkler (f), located at 30 cm above the rotating tray, and connected to an electric valve, managed by a PLC, that allows hygrometric control of the process in question, sprinkling nebulized water drops of about 50 mg, at regular time intervals, for each 90° rotation of the cylindrical tray, in this way to increase the air moisture value. Indeed, as the quantity of nebulized water sprinkled can be regulated according

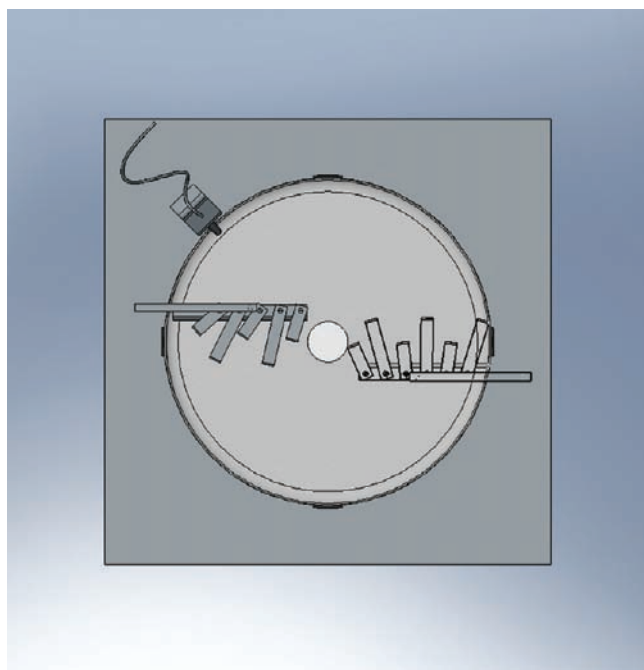


Figure 2. Equipment used in the fumigating process (top view).

to the tray's rotation speed, the increase of the air moisture value depends on the rotation speed.

It is to be noticed that, with the nebulized water's quantities introduced, only an increasing of the air moisture in contact with the pellets is performed. To avoid condensation phenomena, a thermometer, a pressure transducer and a hygrometer connected to a PLC have been used, so that, before the air moisture value is equal to 90% of the moisture value necessary for condensation (according to the Mollier diagram), the nebulized water sprinkling is stopped. In this way condensation conditions are avoided and dangerous contact with liquid water is avoided.

The tray and the frame are in AISI 304 Inox steel, which is inert when interacting with phosphine and hence increases its durability.

Measurement of Phosphine Gas Concentrations. To measure the phosphine gas concentration developing during fumigation tests, we used an iTX multigas monitor gas detector (Industrial Scientific, Oakdale, PA, USA) to evaluate the concentration of the gas produced and to signal the presence of dangerous gas concentrations at the precise instant in which samples were taken. This gas monitor detects phosphine gas concentrations from 0 to 3000 ppm with an alarm threshold of 0.2 ppm as the minimum sensitivity value.

We used aluminum phosphide produced by the Shenyang's pesticide factory (Shenyang, People's Republic of China), available to specialized technicians of a Naples-based firm (Italy) which fumigates stored foodstuffs.

Choice of the Best Temperature and Rotation Speed Values for the Tray. Initially, experiments were carried out with the device in question to determine the humidity produced by the nebulized water sprinkler that allows maximum phosphine production, avoiding hazardous conditions due to phosphine gas concentrations over the inflammability threshold. Since the water quantity sprinkled depends on the tray's rotation speed, we performed tests at different rotation speeds, corresponding to different nebulized water quantities sprinkled in the air above the phosphide, and we measured the gas quantity produced during the test period, other conditions being equal. The tests were stopped when the concentration of phosphine gas detected was close to the alarm threshold value detected by the gas concentration measuring instrument. The kinetics of the phosphine production was examined for 12 h, which proved sufficient to determine the maximum phosphine gas concentration produced in all the examined conditions. While monitoring the rotation speed and hence the quantity of nebulized water, we performed tests starting

from a temperature of 20 °C, to determine the temperature of the tray that allows maximum phosphine production of gas, yet avoiding flame triggering conditions. All the experimental tests were performed in real environmental conditions with pressure of 0.99×10^5 Pa. Temperature value ranged between 15 and 20 °C, and air moisture value ranged between 20% and 25%.

Numerical Simulation of Pellet Remixing Inside the Tray. Subsequently, we studied the remixing process performed by the folded steel sheet and sustained by two bars. The steel sheet, dipped in a rotating flow field, allow continuous remixing of the pellets, which are quasi-spherical in shape. During the remixing, the pellet surface exposed to the action of air moisture continuously changes, giving a good performance of reaction between the air moisture and phosphide. Therefore the remixing and, then, the efficiency of the fumigation process depend on the tray's rotation speed and on the shape and number of the folded steel sheet used for remixing the pellets, and improvements can be made by studying the geometric and kinematic parameters of the process considered. Therefore we realized a 3D model of the device considered by means of the program code SolidWorks 7, that allowed the geometries of the system setup to be defined. To better understand the remixing process, we used the computational code ANSYS + Flotran to perform a numerical simulation of the interaction phenomenon of the pellets with the steel sheet. We ascertained that the remixing process occurs, given that at the beginning of the process about 1 kg of pellets is scattered on the bottom of the cylindrical tray. In particular, we used the *Particle Transport Model* available in the ANSYS program code. This allowed us to model the interaction between the solid particles of pellets scattered on the bottom of the cylindrical tray with the folded steel sheet. In this case we modeled the folded steel sheet used to remix the pellets which, due to the tray's rotation, interacts with the pellets. The pellets were considered as small spheres with a diameter of 3 mm.

Fumigation Tests. The equipment was finally tested on a 900 m³ silo (fumigation chamber) (Figure 3), about 10 m high, with a base

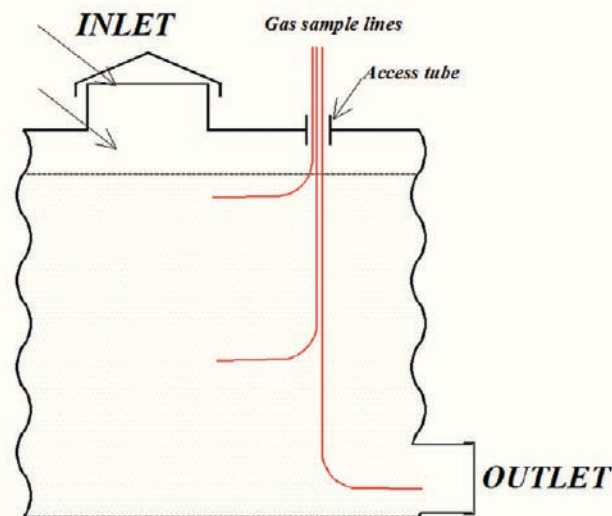


Figure 3. Fumigation chamber scheme, with phosphine gas sampling lines.

surface area of 90 m², suitably sealed, and appropriately modified for insertion of a pipeline for sampling the phosphine gas produced. For this purpose, three sampling lines were set up with an inlet section at the base of the silos (0.5 m from the ground), at mid height (4.5 m from the ground) and at the top (8.5 m from the ground). The fumigation process was performed by the considered device, using previously determined rotation speeds and temperatures for phosphine gas production. Fumigation was carried out using 1 kg of aluminum phosphide pellets, normally used for fumigating chambers of this size.

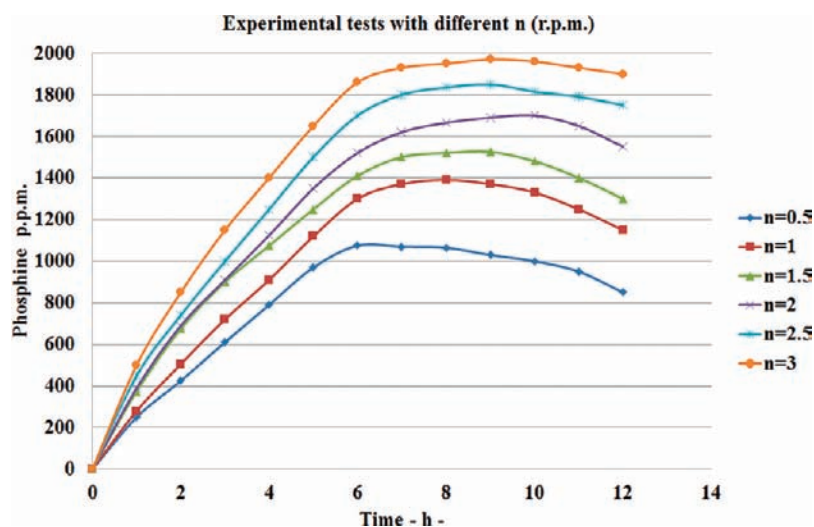


Figure 4. Phosphine production plotted against number of tray rotations (rpm).

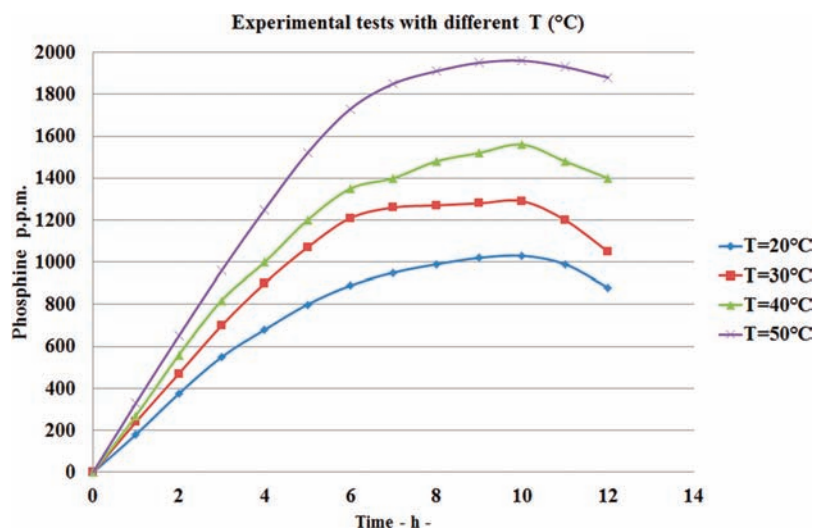


Figure 5. Phosphine production as a function of temperature at 3 rpm.

All the experimental tests were performed in real environmental conditions with pressure of 0.99×10^5 Pa; temperature values ranged between 15 and 20 °C and air moisture between 20% and 25%.

The tests were repeated three times to be able to perform statistical analysis; the experimental data were handled by using the Statgraphics Plus 5 program code.

RESULTS AND DISCUSSION

Parameter Determination for Phosphine Production.

Figure 4 and Figure 5 show the average values of three repetitions of tests by using different numbers of revolutions per minute (n) and temperature values (°C); the concentration was an average of three repetitions.

In Figure 4 phosphine gas concentration is plotted as a function of n considered, which is related to the quantity of nebulized sprinkled water. The nebulized water sprinkler is managed by a PLC that allows 50 mg of water to be nebulized and sprinkled in the air above the cylindrical tray, every 1/4 of a round, to increase air moisture (with this system, direct contact of the liquid water with the pellets is avoided). It was observed that, with a rotation speed of three revolutions per minute, the maximum production of phosphine gas was obtained, other

conditions being equal, avoiding the hazard threshold value being attained, and in all cases without exceeding it. This is due to the fact that as the humidity increases, phosphine gas production increases. In this case 600 mg of H_2O/min is the quantity of nebulized water considered. Indeed, for the considered equipment, the increase in the rotation speed leads to an increase in air humidification and an increase in remixing. Hence the probability of air humidity coming into contact with active material rises.

In Figure 5 phosphine gas concentration is plotted against the temperature of the cylindrical tray. Using test measurements, we observed that, after a few minutes, the pellets assumed the same temperature as the tray, insofar as the thickness of the layer of pellets is about 2–3 mm and the pellets have good thermal conductivity. As may be seen in the graph, maximum phosphine production is obtained at 50 °C, after only eight hours of reaction, other conditions being equal. At this temperature phosphine gas production reaches values that are closer to the danger threshold, without actually exceeding it. All this is explained by the fact that the chemical reaction for phosphine production increases with a rise in temperature because it is an endothermic reaction.

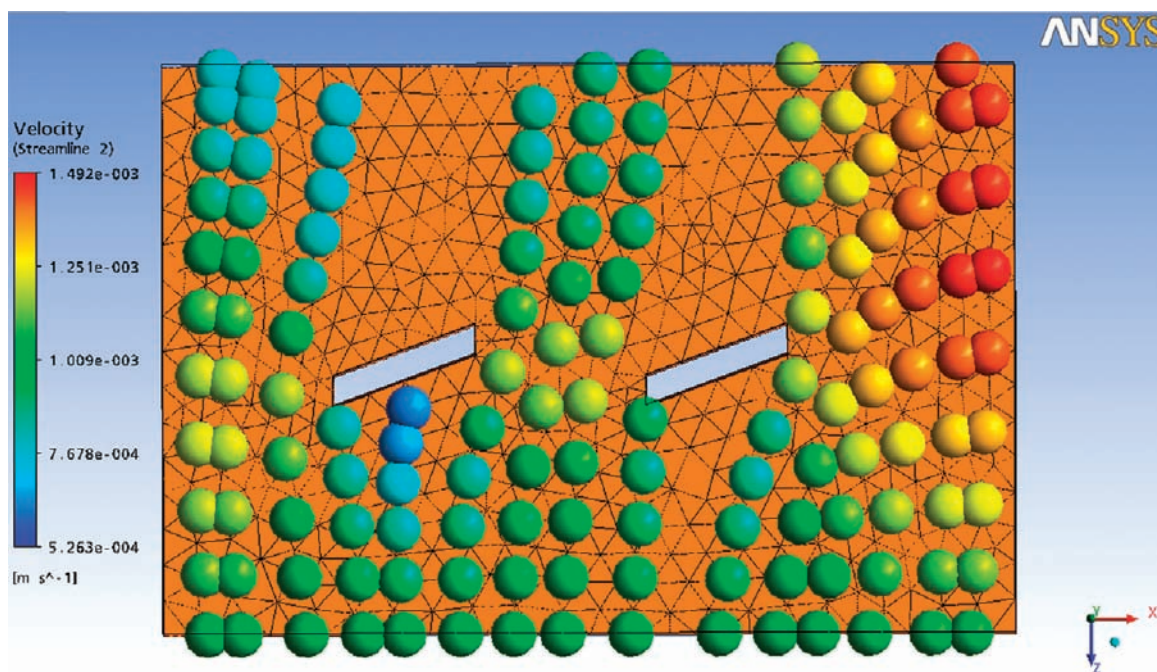


Figure 6. Remixing numerical simulation (top view).

Numerical Simulation of Pellets Remixed Inside the Tray. Numerical simulation of the pellet–steel sheet interaction phenomenon revealed that the pellets located on the bottom of the rotating cylindrical tray, when they interact with steel sheets, divert from their circular path, as is shown in Figures 6, Figure 7a and Figure 7b, and tend to occupy the position of adjacent pellets, thereby leading to remixing. All this happens thanks to the slope of the steel sheets with respect to the radial direction, and the speed of rotation. It should also be borne in mind that the offset geometric configuration of the steel sheets is such that, during rotation, the pellets that do not collide with the steel sheets of one bar will bump into the steel sheets of the other bar.

Therefore the pellets that do not collide against the steel sheets of a bar (and which lie on the flow line that the pellets should follow after a collision) interact with those diverted from the steel sheets.

Thus interaction occurs between two types of pellets (those that interact with the steel sheets and those that do not). This causes the pellets to rise and pile up on one another. In Figure 7b the colors represent the velocities of pellets assumed to be spheres.

The aim of simulation was to show that remixing really happens (in general there is no guarantee that remixing succeeds). Remixing of pellets (assumed as spheres) ensures that a new surface portion of phosphide pellets is continuously in contact with air humidity; in other words the surface of the spheres in contact with humidity changes in time (during remixing); last the surface of pellets in contact with humidity is not always the same as occurs in the case of traditional devices. Indeed, in the case of traditional devices, without pellet remixing, after the portion of the pellets in contact with air moisture exhausts the reaction, there remains an inactive thin dust that prevents the underlying parts reacting with the air moisture. Hence there is a portion of pellets which can make no contact with the air moisture, and therefore does not react throughout the fumigating process. This is avoided if the pellets are remixed.

the Fumigation Process. The fumigation process was finally performed with the equipment considered, using the determined optimal values, and a comparison with data from a traditional process was performed. For this purpose, we used the equipment for fumigating legumes, applying 1 kg of aluminum phosphide in pellets. The chamber was about 1000 m³ and about 75% filled in volume, as is common practice.

Gas concentrations within the tanks were recorded once every hour using a gas phosphine meter. Measurements of phosphine gas concentrations were plotted against time. It should be noted that the meter had an upper limit of 2000 ppm; readings of 2000 ppm on the following graphs of concentrations over time should be read as “in excess of 2000 ppm”. Three tests were repeated with traditional equipment, and the minimum exposure period for phosphine for Italian climates was considered, that is normally 5–7 days.

The maximum concentrations detected during the three repeated tests, for a traditional fumigation process, are shown in Figure 8. In the residual powder obtained a 1–2% amount of active phosphide was detected.

Further, three tests were repeated with the considered equipment, and two days were required to completely exhaust the phosphide, against the 5–7 days currently required using standard equipment. The maximum concentrations detected during the three repeated tests are reported in Figure 9. At the end of fumigation, with the equipment in question, the powder residue was analyzed to determine the aluminum phosphide residue, which did not prove significant.

The obtained kinetic curve was fitted in its initial part (until 8 h) by a logarithmic curve with the following expression:

$$C = 798.27 \times \ln(t)$$

for $t \neq 0$ until the maximum value of 2000 is reached, where C is the phosphine concentration and t is the time in hours. This equation allowed a mathematical model of the phenomenon to be obtained.

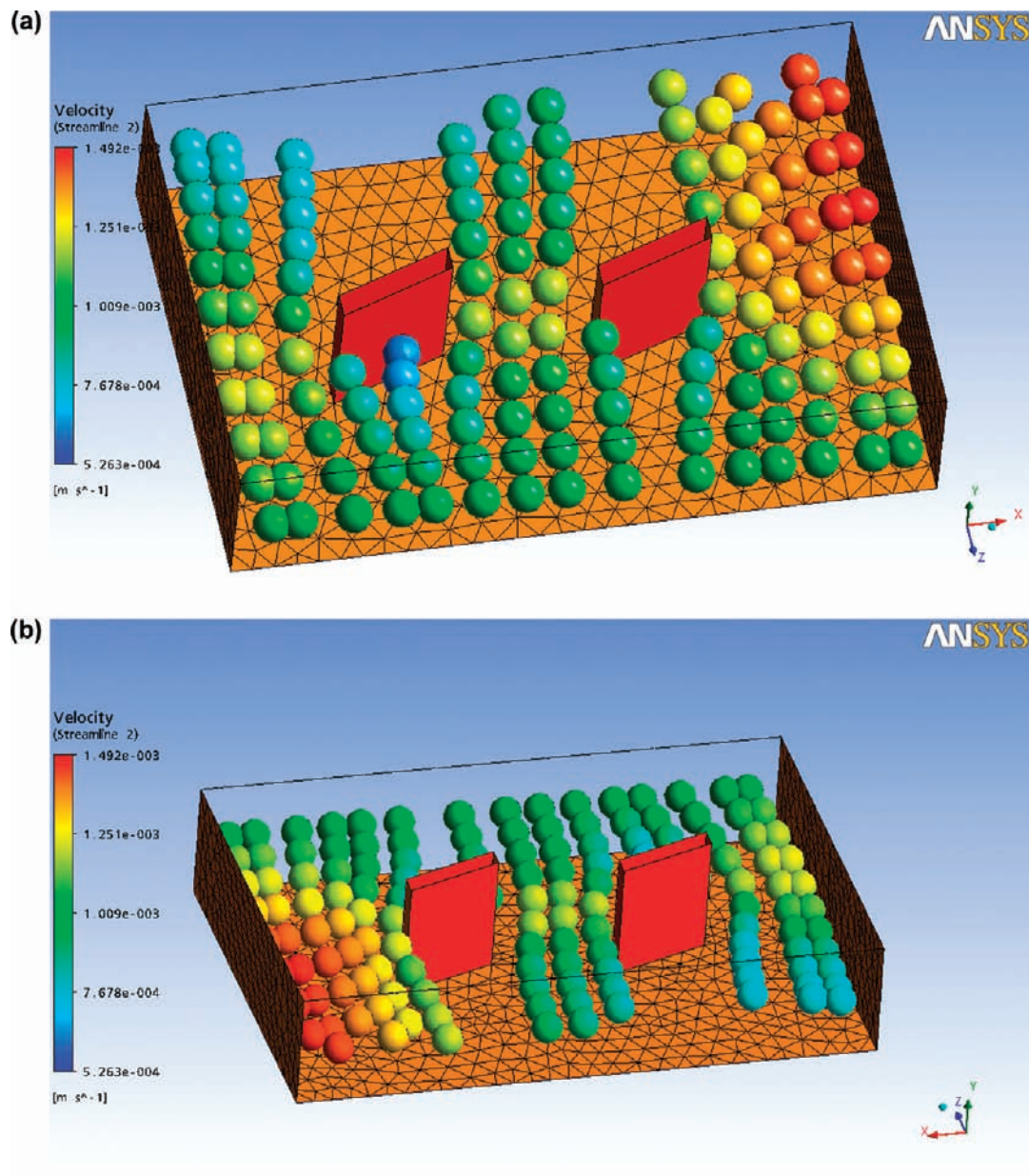


Figure 7. (a) Isometric view of the numerical simulation (scrolling upward). (b) Isometric view of the numerical simulation (scrolling downward).

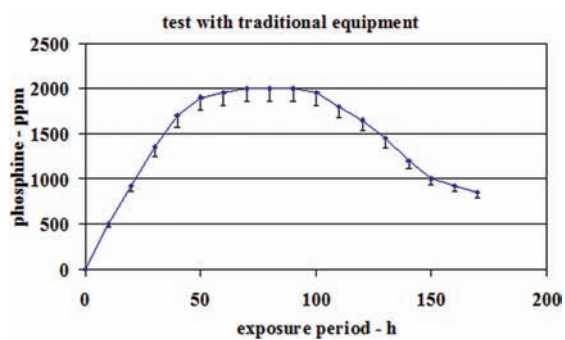


Figure 8. Phosphine production (concentration) vs exposure time, inside the fumigation chamber, obtained by using the traditional equipment.

Finally, statistical analysis of the data showed that the maximum percentage error detected, for all the tests performed,

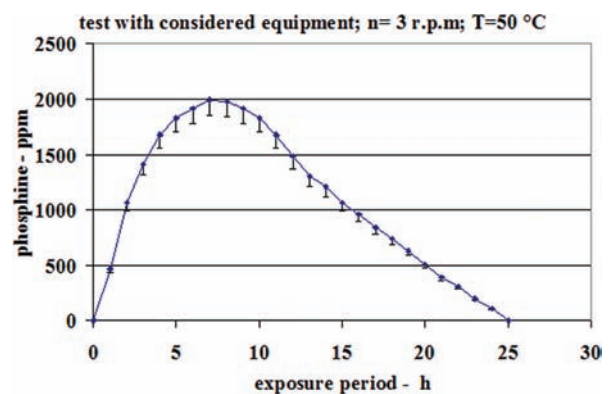


Figure 9. Phosphine production (concentration) vs exposure time, inside the fumigating chamber, obtained by using the equipment in question.

was 7%, a good value given that we were working with gas and very large volumes in fumigation chambers. In Figure 8 and Figure 9 the related error bars are reported.

It should be pointed out that, even if the pellets exhaust their active principle in only about 20 h, that does not mean that the fumigation process should be interrupted. Indeed, as the silo is closed and hermetically sealed, phosphine acts inside the silo until it is removed. Hence it is very probable that the fumigation process, by using the equipment considered, could be shortened because the action of phosphine gas on foodstuffs is more efficient according to microbiological analysis.

Conclusions. This paper considered new equipment that can be used in the process of fumigating stored foodstuffs with phosphine. Currently, traditional fumigation equipment does not ensure complete transformation of the phosphide into phosphine gas due to the formation of aluminum oxide powder which reduces contact of the active material with air moisture. By contrast, our innovative device allows the reaction between the phosphide pellets with air moisture to be completely exhausted, thanks to the heated cylindrical tray and the remixing of the pellets subjected to contemporaneous nebulized water sprinkling. This means that the reaction residues obtained with the equipment considered do not have to be digested with the same procedures as those obtained with traditional equipment, which requires special costly digestion techniques as their powder residues always contain at least 1–2% (w/w) of phosphide. Further, of great importance was the decrease in fumigation time, which is also economically important, insofar as it allows the stored foodstuffs to be made available on the market in less time, irrespective of outside temperature, using a heated tray. Indeed, the fumigation process can be carried out efficiently even under low outside temperatures.

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