SORPTION OF CARBON DIOXIDE BY WHEAT

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ABSTRACT

Sorption of carbon dioxide (CO_2) by soft red winter wheat was tested in 1-L jars, each containing 700 g of grain with 12.9% moisture content and each filled to 93% of jar capacity. In one series of experiments, the jars of wheat were purged with CO_2 to obtain an initial concentration of 99.8%. The jars were sealed and pressure changes were recorded periodically. All tests were carried out at temperatures of 15, 20, 25 and 30°C. In a second series of experiments, different CO_2 partial pressures ranging between 30.6 and 98.6% were maintained at 25°C in the filled jars.

At the initial phase of sorption, the rate was proportional to the temperature of the wheat; the highest sorption was recorded at 30°C. As sorption progressed, the higher the temperature, the shorter the time required for the sorption to reach steady-state equilibrium. The times required to reach equilibrium varied inversely with temperature (65, 80, 95 and 120 h at temperatures of 30, 25, 20 and 15°C, respectively). The lowest pressure recorded was 520 mm Hg at 15°C. Maximum sorption also varied inversely with temperature (260, 297, 331 and 393 mg CO_2/kg of wheat at 30, 25, 20 and 15°C, respectively). A linear relationship was found between sorption of CO_2 and partial pressure at a constant temperature. This was in accordance with the classic adsorbtion isotherm of Freundlich. Using this equation, the sorption of wheat at 25°C for any given CO_2 concentration in the range included in the tests can be calculated.

INTRODUCTION

The effects of modified atmospheres (MA's) on stored-product insects involve altering the concentrations of the atmospheric gases normally present in a storage structure (Bailey and Banks, 1980; Navarro and Jay, 1987). One technique utilized to obtain a MA is the application of carbon dioxide (CO_2) to reach a concentration of $60 \pm 10\%$ (Jay, 1971). Using this technique, Jay (1980) found that sorption of CO_2 by grain makes the gas effective against those insect species whose immature stages feed inside the kernel.

The concentration of a gas in equilibrium with a solid is always greatest in the immediate vicinity of the solid. This phenomenon is termed adsorption, to be distinguished from absorption, which is the bulk penetration of gas by diffusion into the structure of a solid or liquid. In many cases where the two processes occur simultaneously, the term "sorption" is used (Monro, 1961; Young and Crowell, 1962). This term will be used in this paper.

Two processes contribute to the adsorption of a gas on a solid. The first is often called "physical adsorption" and is the result of molecular interaction forces called Van der Waal forces. In the case of physical adsorption, the gas forms a physically adsorbed layer on the solid, similar to the condensation of vapor to form a liquid film. The second process which contributes to adsorption is termed chemisorption and involves the transfer of electrons between the molecules of the solid and the gas. One way to distinguish between physical adsorption and chemisorption is to attempt to remove the adsorbed gas using reduced pressure. If the process is primarily physical adsorption, then desorption of the gas is easily accomplished; however, if the process is chemisorption, much more drastic methods are usually required to recover the gas. Both surface area and porosity (or pore volume) have been recognized as playing complementary parts in adsorption phenomena in a vast range of solids (Gregg and Sing, 1967). The adsorption mechanism of CO_2 into the grain has been found to be very similar to that observed in sorption of gases by charcoal and silica gel (Mitsuda et al., 1973). Sorption causes the removal of some molecules of the gas from the free space present in the treated enclosure; this in turn causes a progressive lowering of the concentration (partial pressure) of the gas in the free space.

In the application of CO_2 into large bins containing wheat, an initial rapid decay of concentration shortly after purging was observed by Banks et al. (1980). This initial rapid decay seems to be associated with sorption of the CO_2 by the grain. Despite much interest in CO_2 treatment, little information has been published on the sorption mechanism of wheat (Donahaye and Navarro, 1983). The most detailed work on the mechanism of CO_2 sorption by different commodities has been reported by Mitsuda et al. (1973) in relation to skin-packaging. They found that when grain was confined in a bag made of flexible laminated plastic film containing a CO_2 atmosphere, both the bag and its contents became as rigid after sealing as if packed in vacuo. The adsorption responsible for this rigidity has led to the development of skin-packaging, the "carbon dioxide exchange method" (CEM), for the preservation of rice in storage (Mitsuda and Yamamoto, 1980). Although Mitsuda et al. (1973) were able to demonstrate that wheat at 20°C adsorbs 75 ml CO_2/kg in 3 h, the sorption mechanism of the CO_2 on wheat was not fully investigated. Cofie-Agblor et al. (1993, 1995) have examined the characteristics of CO_2 sorption by wheat at four temperatures and four moisture contents (m.c.). The maximum mass of CO_2 sorbed in 60 h was 0.510 g/kg wheat at 18% m.c. and 0°C. The present work was initiated to obtain additional and comparative information on both the sorption mechanism of CO_2 in relation to temperature and the maximum reduced pressures that can be obtained when wheat is maintained in gastight containers.

MATERIALS AND METHODS

Wheat

Soft red winter wheat harvested in 1983 and having an average m.c. of 12.97% (SE ± 0.0609) was used in the tests. This wheat contained foreign material of different particle sizes, as would be present in actual storage. The foreign material was composed of 0.15% (w/w) large particles retained by a 5-mesh sieve, 0.27% particles retained by a 30-mesh sieve and 0.04% smaller particles (dust). The remaining 99.54% of the tested material was wheat.

Manometry

The sorption of CO_2 was measured using a transducer type manometer (Hastings Vacuum Gauge, Model DNNV-800) connected to a 960-ml container. Prior to each experiment, the transducer was calibrated against a Fortin type barometer (US Signal Corps model 02-380) and against the very low absolute pressure of <2 mm Hg obtained from a high vacuum pump. The amount of CO_2 adsorbed by wheat created a negative pressure in the container which was recorded for periods of up to 8 d.

CO_2 concentration

The gas concentration in the headspace of the container was measured by a gas chromatograph (Fisher Model 1200) equipped with a thermal conductivity detector and two columns, one packed with molecular sieve 13X (60/80 mesh) and the other with Columpak PQ (80/100 mesh). An integrator (Hewlett-Packard Model 3390A) was used to measure the areas under the peaks.

Experimental procedure

The volume occupied by a predetermined weight (686 g) of wheat grain was measured using the manometric technique described by Day (1964). The grain m.c. was determined using a capacitance moisture meter (Motomco Model 919). The grain was then poured into containers having a predetermined volume (960 ml), and the metal screw-on lid was tightly closed. The 68-mm diameter lid was equipped with two 1.15-mm i.d. copper tubes. One tube extended 160 mm and the other 35 mm into the container. They extended 45 mm above the outside edge of the lid and were used for the gas inlet and outlet.

The containers were submerged in constant-temperature water baths equipped during the experiments with refrigeration and heating systems so that the temperature could be adjusted to both below and above room temperature. The grain temperature was measured daily by a thermistor placed in the center of a container of the same volume which also held 686 g of wheat. This method of temperature measurement in a separate container was adopted in order to avoid leaks from the container lids. The containers were purged with CO_2. Prior to the CO_2 purge, the wheat was maintained for 24 h in the baths to ensure temperature stabilization.

Each experiment began with an initial purge of CO_2 supplied from pressurized cylinders at a flow rate of approximately 200 ml/min for 9 min. During this purge phase, gas

samples were taken for CO_2 analysis. At the end of the purge, the transducer was immediately connected to the gas inlet tube, the container was sealed and both the initial container pressure and the barometric pressure were recorded.

Two sets of experiments were conducted. In the first set, an initial average CO_2 concentration of 99.8% was attained immediately after purge and the pressure changes due to adsorption were periodically measured. Since the containers were maintained without additional CO_2 supply, in this set of experiments the pressure drop due to adsorption decreased the partial pressure of CO_2. These experiments were replicated three times at temperatures of 15, 20, 25 and 30°C. In the second set of experiments, a constant CO_2 concentration was periodically supplied from CO_2 cylinders so that a constant partial pressure was maintained in the containers. The pressure in the containers was subsequently brought to the original pressure, determined by daily observations, by supplying CO_2 at the tested concentration; 30-ml or 1-ml gastight syringes equipped with a three-way Luer-lock attachment were used for this. In these experiments five different CO_2 concentrations ranging from 30.64% to 99.81% were tested at 25°C. Sorption of CO_2 in mg CO_2 sorbed/kg of grain was calculated after corrections had been made for STP conditions.

RESULTS AND DISCUSSION

Effect of sorption on changes in pressure

Typical reduced pressures created by sorption in the gastight containers are shown in Fig. 1. Since the amount of CO_2 sorbed is proportional to the amount of grain in the container at a given partial pressure of CO_2 and temperature, the resulting reduced pressure will also be proportional to the void space of the system. Therefore, the drop in pressure shown in Fig. 1 can only represent the experimental conditions when the grain bulk volume occupied 93% of the total container capacity. Under these conditions, the lowest pressure recorded was 520 mm Hg at 15°C. The sorption rate changed inversely with the temperature of the wheat, and the highest absolute pressure of 606 mm Hg was obtained at 30°C. Mitsuda and Yamamota (1980) reported that a 0.8-L container filled with grain (apparently rice) developed a negative pressure of 0.27 kg/cm² after 7 d. This negative pressure in terms of absolute pressure at STP conditions was calculated to be approximately 555 mm Hg. This pressure falls in the range obtained in our experiments (close to the 25°C line in Fig. 1). However, since the commodity and the temperature were not mentioned in this paper, the results can not be compared quantitatively.

Sorption rate of CO_2

The initial sorption rate of CO_2 by wheat was found to follow a linear relationship during the first 3 h of the process when results were plotted on a log-log scale (Fig. 2). In these experiments, the containers in which the sorption process took place were maintained without addition of CO_2 to compensate for the changing partial pressure conditions. Therefore, the sorption rate in these experiments does not follow the conventional kinetic laws (Daniels and Alberty, 1963) and the rates shown in Fig. 2 have the restriction of
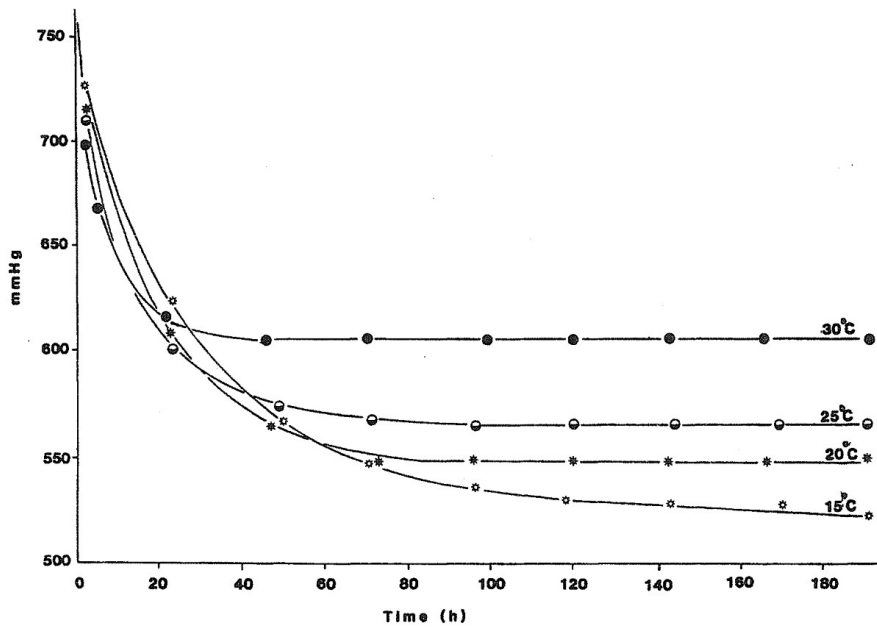
Fig. 1. Pressure decay due to sorption of CO_2 in gastight containers filled to 93% capacity with wheat (bulk volume to container) at four different temperatures, with an initial CO_2 concentration of 99.8% and an initial pressure of 768 mm Hg.

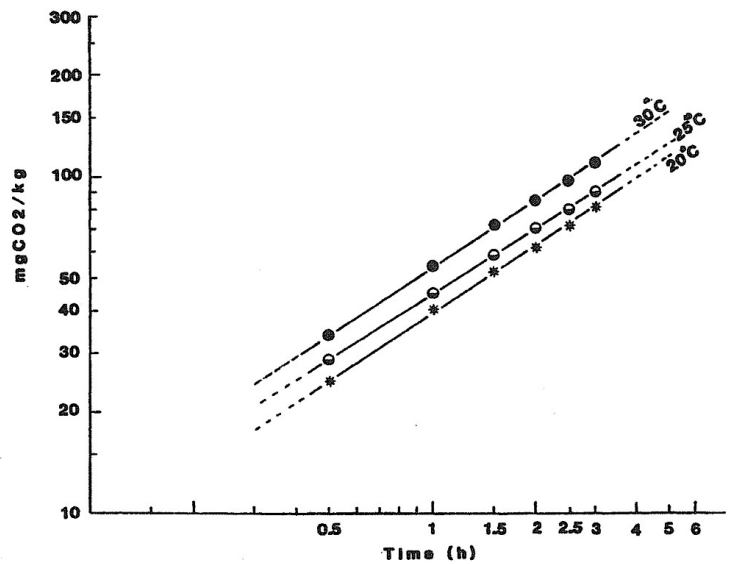Fig. 2. Sorption rate of CO_2 by wheat during the first 3 h of the process at three different temperatures with an initial CO_2 concentration of 99.8% in containers filled to 93% capacity with wheat.

being dependent on the intensity of the changing CO_2 partial pressures throughout the sorption process. Since the grain comprised 93% of the container volume, the sorption rates shown in Fig. 2 could be considered similar to pressure changes that may occur in practice in grain bulks.

The slopes for the time–sorption curves were almost parallel with values of 0.664, 0.635 and 0.659 for 20, 25 and 30°C, respectively. A similar analysis was performed at 15°C, but the initial CO_2 purge probably caused a temperature change in the container; therefore during the first hour a sorption rate near the value of that found for 20°C was obtained. The calculated slope at 15°C was 0.512, which was markedly different from the slope obtained at the higher temperatures. The correlation factors calculated for the relationship with the sorption rate were $r^2 = 0.9994$, 0.9994, 0.9995 and 0.9982 for 15, 20, 25 and 30°C, respectively. Results obtained by Yamamoto and Mitsuda (1980) indicate that at 20°C, wheat adsorbed 75 ml CO_2/kg in 3 h. This amount of CO_2 is equivalent to 147.2 mg CO_2/kg wheat. Cofie-Agblor *et al.* (1995) also showed that sorption of CO_2 was about 135 mg/kg at 20°C after 3 h for wheat at 14% m.c. In contrast our results indicate that at 20°C only 81.6 mg CO_2/kg was sorbed after 3 h.

The sorption rate in our experiments was calculated under decreasing partial pressure. In practice, when a commodity is kept in a container a decrease in the partial pressure due to the sorption process would be expected, and in a completely sealed container the drop in pressure would cause a decrease in the partial pressure of CO_2. Similarly, in a container with leaks sorption would cause air to enter the system as the pressure decreases, although the total pressure would be maintained close to that of the surrounding atmosphere. Therefore, the partial pressure of CO_2 would decrease, resulting in further lowering the sorption rate. Our results clearly show that at the initial phase of sorption the higher the temperature the higher is the sorption rate (Fig. 2).

Sorption at equilibrium

The length of time needed for the sorption process to reach steady-state equilibrium at varying pressures, due to adsorption at different temperatures, is shown in Fig. 3. These data demonstrate that the higher the temperature, the shorter the time required to reach equilibrium. Figure 3 shows that the time required to reach equilibrium was 65, 80, 95 and 120 h at 30, 25, 20 and 15°C, respectively. This is in contrast to the initial sorption process, which showed a higher initial rate at higher temperatures (Fig. 2). In the study by Cofie-Agblor *et al.* (1995) the longest duration was 60 h which was not sufficient to reach equilibrium, as they also indicated. The amount of CO_2 sorbed at equilibrium could only be calculated from their equations, whereas in our work the values were the times recorded until equilibrium was reached, and for the experiments at 15°C this lasted up to 120 h.

Calculations of pressure drop or air entry into a CO_2-treated wheat container could be made from the results shown in Figs. 2 and 3, provided the initial CO_2 concentration is 99.8% and the filling ratio is 93%. Since a higher sorption was found at 15°C than at 30°C, it would be advantageous to apply MA's at high temperatures with subsequent reduction of a substantial amount of the CO_2 concentration.
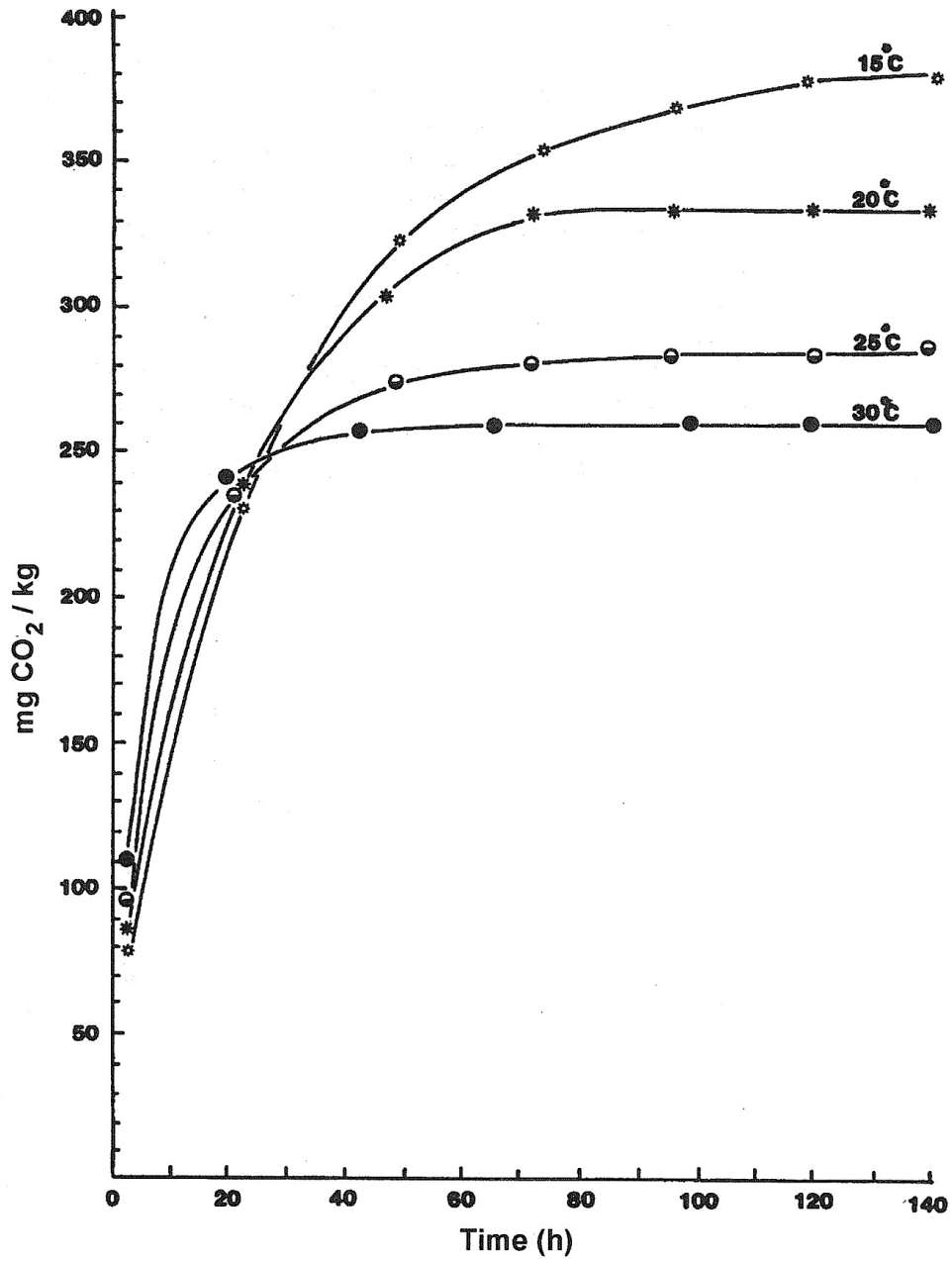
Fig. 3. Time to reach sorption equilibrium between CO_2 and wheat at four different temperatures, with an initial CO_2 concentration of 99.8% in containers filled to 93% capacity with wheat.

Sorption isotherm

An attempt was made in these experiments to simulate field conditions where, after an initial CO_2 purge, sorption would create a partial pressure differential. The amount of CO_2 sorbed to reach equilibrium was measured at 25°C in order to demonstrate the relationship between sorption and constant partial pressures. This relationship was tested for linearity using the classic adsorption isotherm of Freundlich (Daniels and Alberty, 1963). The calculated correlation factor was $r^2 = 0.9890$ for the tested CO_2 concentrations varying between 30.64% and 99.81%. This relationship was described by the equation: log mg CO_2/kg = 2.643 + 1.719 log P CO_2. A plot of our data and the calculated line are shown in Fig. 4. Using this equation, the adsorption of wheat at 25°C for any given CO_2 concentration in the range of our tests can be calculated. A similar relationship for rice has been described by Mitsuda *et al.* (1973).

The expected amount of CO_2 sorbed at a constant CO_2 partial pressure may well describe a specific situation in which the supply of CO_2 to the commodity is almost constant. However, since in a field situation (or even in a small container) there is always a changing CO_2 partial pressure, the rate at which sorption takes place needs further investigation.
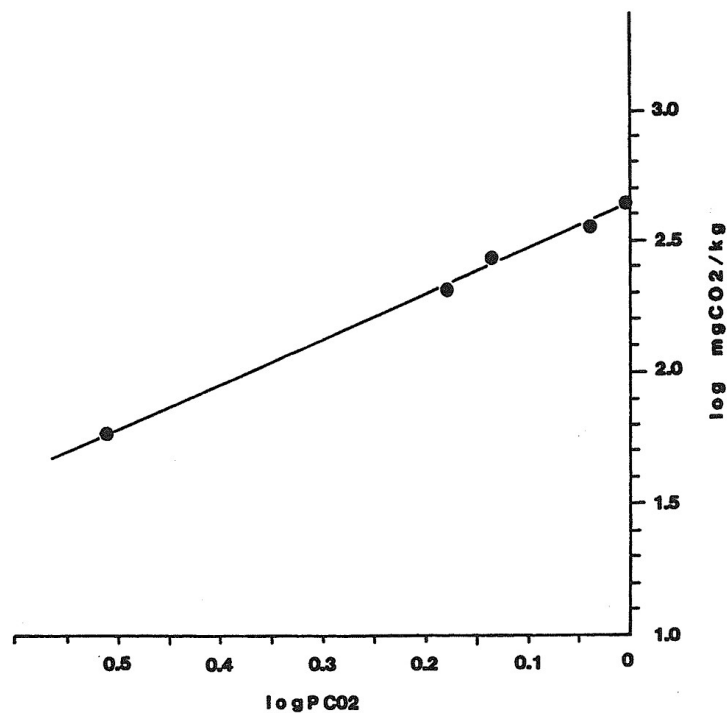

Fig. 4. Relation between the amount of CO_2 sorbed and the partial pressure of CO_2 at 25°C until equilibrium is reached between the CO_2 and the wheat.

Once the sorption rates at different temperatures and varying partial pressures are known, it may be possible to formulate an equation to describe the CO_2 concentration for any given ratio of the volume occupied by commodity to the total volume of the container.

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