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CARBON DIOXIDE GAS SORPTION BY STORED WHEAT

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ABSTRACT

Sorption of carbon dioxide gas (CO_2) by stored wheat was measured in flasks at 0, 10, 20, and 30°C at moisture contents (m.c.s) of 12, 14, 16, and 18% (wet basis). The gas concentrations were measured by gas chromatography and the vacuum created by sorption at constant volume and temperature was determined with a mercury manometer. The amount of CO_2 sorbed increased exponentially with time. Generally, sorption of CO_2 decreased with increasing temperatures from 0-30°C at all m.c.s. The amount of gas sorbed, however, increased with increasing moisture contents at 0, 10, and 20°C but decreased at 30°C. The maximum amount of the gas sorbed in 24 hr was 0.42 g (CO_2)/kg wheat and the least amount was 0.18 g (CO_2)/kg of wheat at test combinations of 0°C and 18% m.c. and 30°C and 18% m.c., respectively. A high positive correlation existed between initial CO_2 concentration and the concentration at 24 hr between the range of 6-95% (v/v) at 20°C and 14% m.c., with the regression analysis yielding an R^2 of 0.99.

INTRODUCTION

The presence of insect pests and microorganisms is one of the major problems facing the grain storage industry. The traditional approach to controlling insect infestations in stored-grain has been the application of chemical insecticides and fumigants. The development of resistance to insecticides by insects and consumer concern over the use of pesticides in food have, however, resulted in the search for alternative measures of insect control. Controlled and modified atmospheres of elevated carbon dioxide (CO_2) and depleted oxygen (O_2) levels, control insects in stored-grain with various degrees of success (Jay and Pearman, 1973; Bailey and Banks, 1980; Jay, 1980; White *et al.*, 1988; Rameshbabu *et al.*, 1991). White *et al.* (1988) indicated that CO_2 levels in flasks decreased after 24 and 168 hr, but did not mention whether this was caused by leakage from the flasks or sorption by the grain. Navarro *et al.* (1986) observed a cyclic pressure increase and decrease in a grain bin caused by sorption and desorption of CO_2 during recirculation. They noted that when a high concentration of CO_2 remained layered for a sufficient time, sorption occurred leading to the development of a negative pressure in the bin. Desorption and a positive pressure occurred when a low CO_2 level moved into the layer during recirculation.

The rate of CO_2 production has been used as an indicator of insect and microbial activity in stored grain (Bailey, 1940; Robertson, 1948; Steele *et al.*, 1969; White *et al.*, 1982; Fernandez *et al.*, 1985). The possibility of CO_2 sorption by the grain was not considered in these studies.

The physical mechanism of gaseous uptake by solids involves two processes, namely, adsorption and absorption. In adsorption, the surface of a solid attracts and holds an atom, molecule, or ion from a solution or gas with which it is in contact. In absorption, however, the molecules of the gas penetrate into the mass and internal structure of the solid. According to Brunauer (1946) the two processes often occur simultaneously during gaseous uptake by a solid. The term sorption includes both the adsorption and absorption.

Mitsuda *et al.* (1973), studying CO_2 gas sorption by cereal grains and oilseeds, found that rice, wheat, corn, peanuts, soybeans, and their flours sorb significant amounts of CO_2. Desorption curves indicated that the CO_2 gas sorbed by the grains was released completely when the grain was allowed to stand in air. For wheat, 75 (mL CO_2)/(kg wheat wet basis) was sorbed within 3 hr at 20°C. No values were given for wheat at other temperatures and moisture contents (m.c.s). The effective use of CO_2 as an indicator of biological activity in stored-grain, and the maintenance of lethal concentrations of the gas under controlled-atmosphere storage, will require detailed knowledge of CO_2 sorption under various storage conditions. Therefore, the objective of our research was to measure the sorption of CO_2 by wheat at 12-18% m.c.s (wet basis) and 0-30°C, covering the main range of stored-grain conditions occurring in Canada.

MATERIALS AND METHODS

Equipment and materials

Glass Erlenmeyer, thick-walled flasks (500 mL), fitted with rubber stoppers having two holes drilled through them were used. The holes were fitted with plastic tubing (4 mm i.d.): one, 140 mm long and pushed to near the bottom of the flask, and the other, 50 mm long above the rubber stopper. Both tubings were capped with tight-fitting rubber sleeve stoppers. The volume of each flask was determined by filling with distilled water at 20°C to the stoppered level.

Wheat, (cv. Katepwa) registered No. 1 seed (United Grain Growers, Winnipeg, Manitoba) and harvested in the autumn (August-September) of

1990 was used. The initial m.c. of the wheat was determined by the oven method using the ASAE Standard S352.1 (ASAE, 1990). The wheat samples wetted to the desired m.c.s were kept at 2°C. The volume of the wheat was determined by the pycnometer method described by Mohsenin (1986) using toluene.

An environmental chamber controlling the temperature to within ±1.0°C of the set temperature provided the required experimental temperatures.

Gas composition analyses were performed using a gas chromatograph (Hewlett-Packard model HP 5890A, Avondale, PA, USA) with a 1-mL fixed-volume sample injector loop, a thermal conductivity detector, and a porapak Q column in series with a molecular sieve (13X). The gas chromatograph was operated at an oven temperature of 70°C, a detector temperature of 150°C, and a 30 mL/min flow rate of the carrier gas, helium. The gas analysis was computed by an HP3396 integrator.

Experimental design

The sorption of CO_2 by wheat within a 24 hr period was measured at 4 m.c.s (12, 14, 16, and 18% wet basis) and 4 temperatures (0, 10, 20, and 30°C). The uptake of CO_2 with time was determined at 4 temperatures (0, 10, 20, and 30°C) in wheat of 14% m.c. and at 4 m.c.s (12, 14, 16, and 18% wet basis) and 20°C. To measure the effect of sorption on the relationship between the initial gas concentration and the concentration after 24 hr, different initial gas concentrations were used at 20°C and 14% m.c.

Experimental procedure

Wheat samples of 250 g were placed in moisture-proof polyethylene bags and conditioned to the experimental temperature in the environmental chamber for 24 hr. At the start of each test, the wheat samples were transferred into the flasks that were sealed tightly with the rubber stoppers.

The flask contents were then flushed with CO_2 of 99.995% purity (research grade, Welders Supply, Winnipeg) for 40 s at atmospheric pressure, and the tubings were immediately plugged with sleeve stoppers. A 2 mL sample was then drawn into a gas-tight syringe for analysis.

For determination of sorption rates, the vacuum of three replicate flasks was measured using a mercury U-tube manometer at 1, 2, 3, 5, 7, 12, and 24 hr. In tests involving different initial concentrations, 2 mL samples were taken and analyzed for gaseous composition at the initial 0 hr, and 24 hr.

Data analysis

The ideal gas equation and Dalton's law of partial pressures were used in the analysis of the data. It was assumed that the amount (in moles) of O_2, nitrogen (N_2), and water vapour remained constant throughout each test period.

RESULTS AND DISCUSSION

Effect of temperature

The mean of the initial CO_2 concentrations for all the tests was 98.20±0.61% (volume basis [v/v]). The amount of CO_2 gas sorbed decreased with increasing temperature from 0-30°C at 14% m.c. (wet basis) (Fig. 1). There are two possible explanations for the above observation: 1) Because adsorption is exothermic (Brunauer, 1946), the amount of gas adsorbed at equilibrium must decrease with increasing temperature in accordance with Le Chatelier's principle, and 2) As temperature increases, the random molecular motion of the gas molecules increases, thereby reducing the forces of attraction between the grain and gas molecules. No significant differences were observed between the amounts of CO_2 sorbed in 24 hr at 10 and 20°C, but were significantly different from the amount sorbed at 0 and 30°C (μ=0.05). Sorption was highest at 0°C with a value of 0.30 g (CO_2)/kg wheat, and was lowest at 30°C with 0.24 g (CO_2)/kg wheat within 24 hr. Mitsuda *et al.* (1973) observed that maximum sorption of CO_2 by brown, polished, and paddy rice decreased with increasing temperatures from 10-25 and 35°C.

The rate of sorption decreased with time, but equilibrium was not reached within 24 hr (Fig. 1). The amount of gas sorbed in relation to the total gas sorbed within 24 hr was not influenced by temperature during the first 5 hr of exposure, but was highest at 10°C after 12 hr of exposure (Table 1). Mitsuda *et al.* (1973) also observed that 50 - 60% of the maximum adsorption occurred within the first 6 hr for rice and red beans, and within approximately 4 hr for peanuts. They also found that equilibrium was not attained in 24 hr.

Table 1: Amount of CO_2 sorbed (expressed as percentage of amount sorbed within 24 hr) by wheat of 14% m.c.

	Temperature (^{o}C)			
Time (hr)	0	10	20	30
5	57	59	57	58
12	73	82	79	70

Effect of moisture

At a constant temperature of 20°C, sorption of CO_2 gas increased with increased m.c. from 12-18% (wet basis) (Fig. 2). Sorption was greatest at 18% m.c. with a value of 0.31g/kg of wheat (at the indicated m.c.) within 24 hr. This value was 14.3, 10.6, and 7.0% greater than the amount of CO_2 sorbed at 12, 14, and 16% m.c., respectively. Mitsuda *et al.*, (1973)

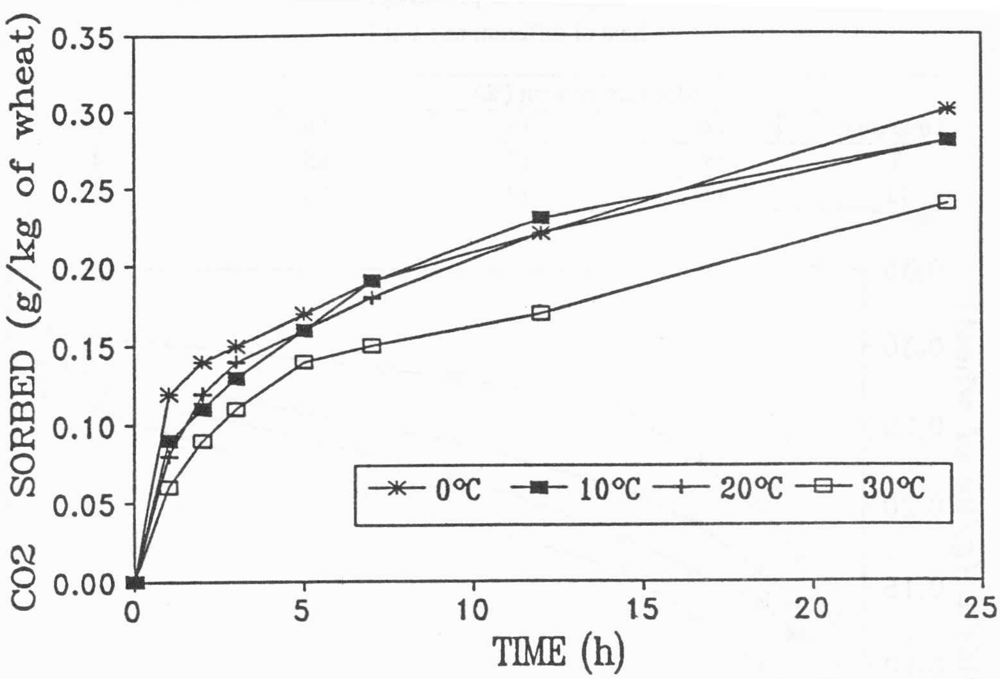


Fig. 1: Carbon dioxide uptake by wheat of 14% m.c. (wet basis) at different temperatures.

observed increased sorption with increased m.c. in brown rice and showed from the calculated line using the Bunsen absorption coefficient that solubility of the gas in water plays a minor role in CO_2 sorption. Increased sorption with increased m.c. was probably due largely to increased kernel volume and porosity. When a grain kernel absorbs water, it increases in volume and becomes more porous (for example, the volume determined for test wheat of 18% m.c. [wet basis] was 4.38% more than at 12% m.c. [wet basis]). This means that kernel resistance to diffusion is decreased and therefore more gas is diffused into the kernel at higher m.c.s than at lower m.c.s when the kernel is more compact in structure. Also, the increased volume and moisture enable more sorption of the gas per unit wet mass at high m.c.s.

The amount of sorption in relation to the total amount sorbed within 24 hr was also influenced by m.c. as shown in Table 2. At 12% m.c., 67% of the total gas sorbed in 24 hr was reached within 12 hr, while at 18% m.c., it was 90%.

Effect of temperature and m.c. interaction

At 12-18% m.c., the amount of CO_2 gas sorbed decreased generally or remained near constant with increasing temperatures (Fig. 3a). Sorption at

Table 2: Amount of CO_2 sorbed (expressed as percentage of amount sorbed within 24 hr) by wheat of different m.c.s at 20°C.

	Moisture content (%)			
Time (hr)	12	14	16	18
5	48	57	85	74
12	87	79	83	90

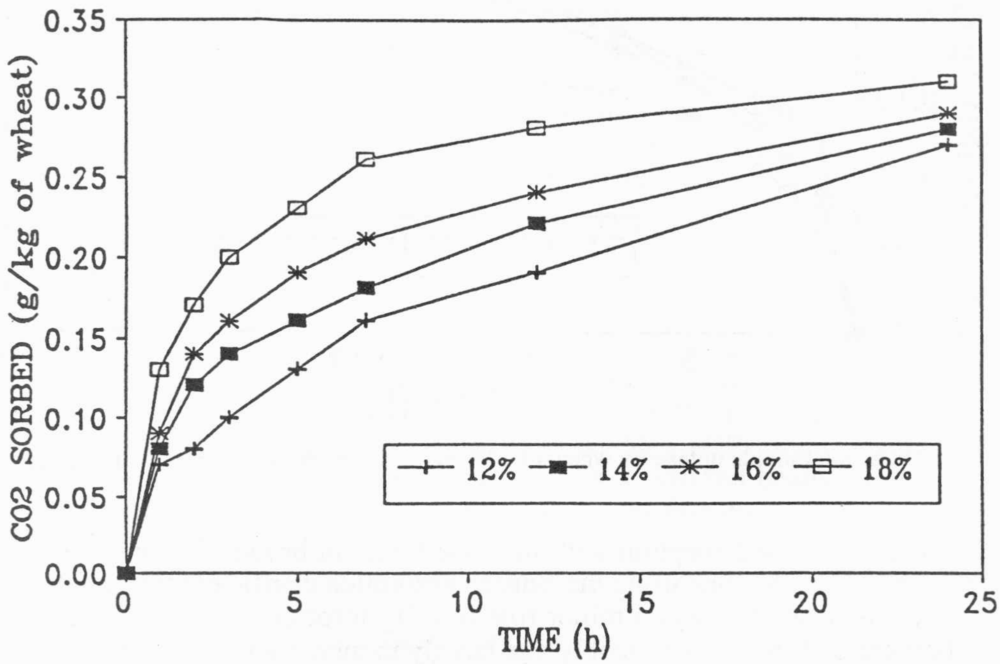
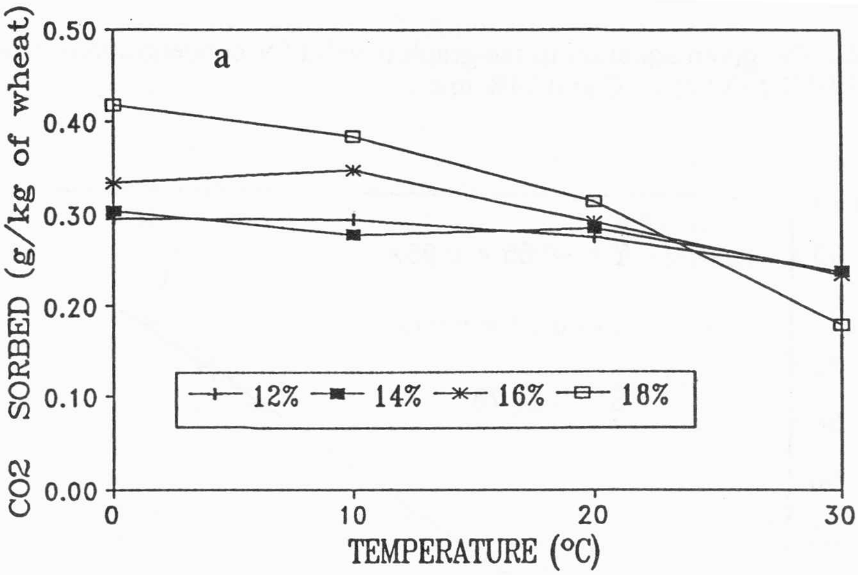


Fig. 2: Carbon dioxide uptake by wheat of different m.c.s at 20°C.

0-20°C increased generally with increasing m.c., but at 30°C, sorption remained nearly constant with increasing m.c. from 12-16%, and then decreased from 16-18% (Fig. 3b).

Sorption was greatest at 0°C and 18% m.c. (0.42 g/kg wheat). This is 40% greater than at 0°C and 12% m.c., and more than twice as much as sorption at 30°C and 18% m.c., where sorption was lowest. In addition to the reasons given earlier for decreasing sorption with increasing temperature, the reduction in the amount of gas sorbed at 30°C and 18% within 24 hr may be due to the production of CO_2 by seeds and microorganisms. This factor will have to be checked in the near future. There were no significant differences in sorption at 30°C for 12, 14, and 16% m.c. (μ=0.05).



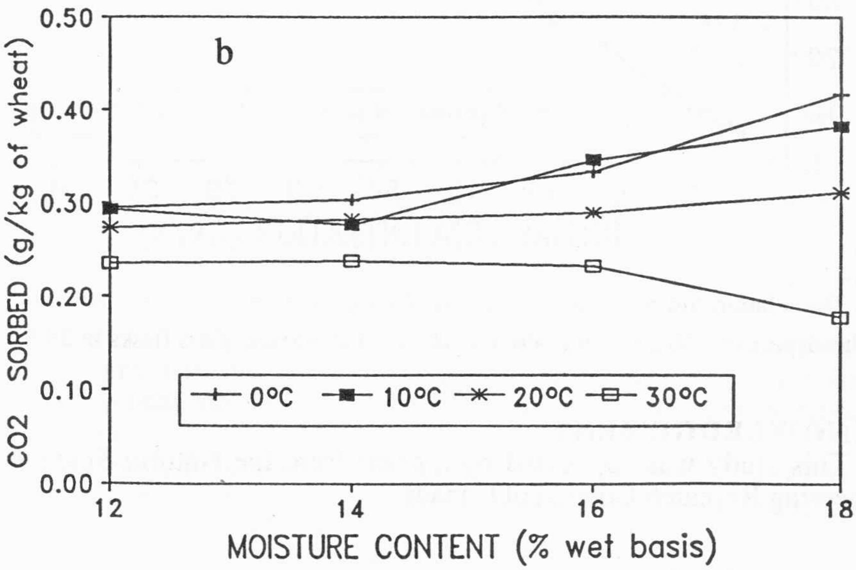


Fig. 3 (a and b): Trends in CO_2 gas sorption at various combinations of temperature (a) and m.c. (b).

Relationship between initial concentration and concentration after 24 hr

Regression analysis indicates that the concentration of CO_2 after 24 hr can be predicted accurately if the initial concentration of the gas is known

(Fig. 4). The given equation in the graph is valid for concentrations ranging from 6-95% (v/v) at 20°C and 14% m.c.

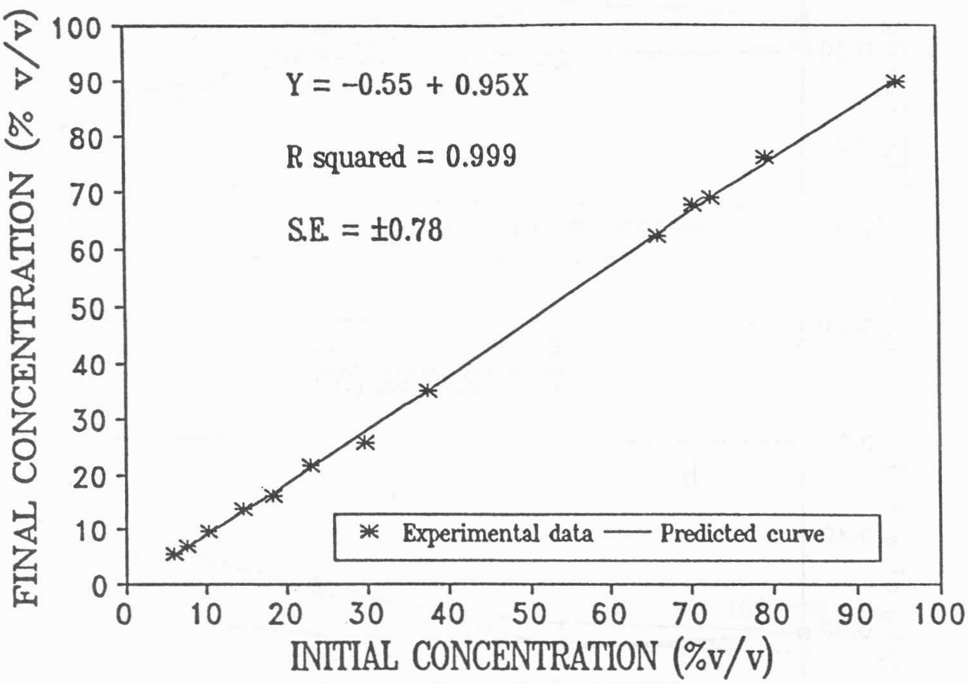


Fig. 4: The relationship between initial and final concentration of CO_2 gas in the voids and headspace of 250 g wheat (14% m.c. at 20°C) in 500 mL glass flasks in 24 hr.

ACKNOWLEDGEMENT

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