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DIFFUSION COEFFICIENT OF CARBON DIOXIDE
THROUGH SEED BULKS

by

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ABSTRACT

The diffusion coefficients of carbon dioxide (CO_2) through rapeseed, wheat, corn and oats were determined. The effects of flow direction and porosity, moisture content and temperature of the grain on diffusion coefficient were studied in a specially designed cylindrical grain storage container in the laboratory.

One end of the grain column was exposed to a mixture of CO_2 and air of known concentrations of the component gases and the other was open to the atmospheric air. Decreases in CO_2 concentrations with time were measured and diffusion coefficients were calculated.

The diffusion coefficient was not affected significantly ($P > 0.05$) by the direction of CO_2 flow in relation to force of gravity. The effect on diffusion coefficient of the porosity of wheat (37.9 to 41.9%) was also statistically insignificant ($P > 0.05$). Coefficient of diffusion, however, decreased with increasing moisture content of wheat. The relationship of diffusion coefficient through wheat with temperature within a range of -10°C to 30°C was satisfactorily described by a quadratic function ($R^2 = 0.9431$). At 10°C the mean diffusion coefficients of CO_2 through stored seeds listed in order of increasing porosity were: rapeseed at 8% moisture content, 0.0284; wheat at 13% moisture content, 0.0346; corn at 14% moisture content, 0.0302; and oats at 14.5% moisture content, $0.0391 \text{ cm}^2/\text{s}$. Although porosity of the seeds appears to affect the diffusion

coefficient, there seems to be other differences among the seeds (such as shape and size of kernels) that affect the rate of diffusion. Thus, corn has a lower coefficient of diffusion than wheat.

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INTRODUCTION

Over 80 Mt of grain and oilseeds, worth more than 3 billion dollars, are stored in elevators and on farms in Canada with little or no equipment to detect any loss in quality or quantity due to deterioration. The presently employed monitoring method of detecting spoilage in bulks, whenever used, is to take point measurements of temperature in the bulk. Because of the low thermal diffusivity of grain a point temperature measurement must be within about 0.5 m of an active spoilage spot to detect the spoilage (Sinha and Wallace 1965). Measured temperatures can not be readily interpreted without prior knowledge of the temperature history of the grain bin. For example, a temperature of 30° C in a 6 m diameter bin in mid-winter may mean that there is an active hot spot or that the grain has not yet begun to cool at the center of the bin (Yaciuk et al. 1975).

The presence of a mouldy odour is a method frequently used by elevator managers to detect spoiled rapeseed. But the managers report that considerable spoilage has occurred before they are able to detect it by odour (Mills 1976).

Consequently there appears to be a need for a new monitoring system, that can warn the storage manager or farmer when his stored product begins to undergo unacceptable deterioration. Previous work (Muir et al. 1980) has shown that increased intergranular carbon dioxide (CO₂) concentrations, caused by spoiling grain and organisms, can be good indicators of incipient grain spoilage. The CO₂ concentrations

measured in a stored bulk can be readily compared with the CO_2 concentration of the ambient air (0.03%) as a standard to interpret the readings.

To develop a scientifically valid and commercially feasible monitoring system based on CO_2 measurements and to determine the required resolution and best location in the bin for such an instrument, the properties of CO_2 diffusion through grains and oilseeds are required. Henderson and Oxley (1944) determined the diffusion coefficient of CO_2 through wheat. Bailey (1959) studied the diffusion of oxygen through wheat, corn, barley and oats and indicated the dependence of the diffusion rate on temperature. There appears to be no studies on the rate of CO_2 diffusion through rapeseed, oats and corn, and also on the effect of moisture content, porosity or temperature of the grain on CO_2 diffusion coefficient. Therefore this project was initiated:

- (1) to determine the diffusion coefficient of CO_2 through wheat, rapeseed, oats and corn;
- (2) to determine the effect of direction of CO_2 flow relative to the force of gravity on diffusion coefficient; and
- (3) to determine the effect of porosity, moisture content and temperature of the seeds on the diffusion coefficient of CO_2 through seed bulks.

2. LITERATURE REVIEW

2.1 Basics of Diffusion:

2.1.1 Diffusion:

Mass transfer may occur by two modes (Jost 1960, Cunningham and Williams 1980):

- (1) molecular diffusion through a medium analogous to heat transfer by conduction and
- (2) bulk flow of the medium analogous to heat transfer by convection.

To define diffusion consider a fluid confined in a space of dimensions which are large compared to the mean free path of the fluid molecules. For gases at atmospheric pressure and room temperature, the mean free path is in the order of 10^{-4} mm (Weast 1981). Assume that one of the components of the fluid exists initially at different concentrations in two or more different locations in the confining space. At constant temperature, and in the absence of external forces, there will be a spontaneous movement, that is, diffusion of the component, in the direction of establishing a uniform concentration of that component in all parts of the enclosure.

In a qualitative way the cause of the spontaneous mixing may be interpreted as follows:

As a consequence of thermal agitation, molecules of a fluid are in constant motion in all directions. The number of molecules of a given kind moving in any given direction at a particular point in the fluid is proportional to the number of molecules present per unit volume. In the absence of a concentration gradient, on the average as many molecules per

unit time leave any hypothetical plane in a given direction as are returned to the plane from the opposite direction. However, if the number of molecules per unit volume decreases in a given direction, more molecules on the average move into the region of lower concentration than return from it. This results in a net transfer of molecules of that kind toward the region of lower concentration.

2.1.2 Concentration:

Concentration defines the quantitative relation of the components of a solution. It is the mass, volume or number of moles of solute present in proportion to the amount of solvent or total solution. The most commonly used ways of expressing concentration are: mass concentration, ρ_i , which is the mass of species i per unit volume of solution; the molar concentration, c_i , which is the number of moles of species i per unit volume of solution; the mass fraction, w_i , which is the mass of species i per unit mass of solution; and the mole fraction, x_i , which is the number of moles of species i per unit mole of solution. The word 'solution' here means a one-phase gaseous, liquid or solid mixture.

2.1.3 Concentration gradient:

Concentration gradient is the rate of change of concentration with distance.

2.1.4 Diffusion velocity:

In a diffusing mixture the various chemical species are moving at different velocities. Here the term velocity does

not mean the velocity of an individual molecule of the species i , rather it is the sum of the velocities of the molecules of the species i within a small volume element divided by the number of such molecules (Rosenberg 1977).

Let \bar{v}_i denote the velocity of the i^{th} species with respect to stationary coordinates. Then for a mixture of n species, the average mass velocity, \bar{v} , is defined as:

$$\bar{v} = \frac{\sum_{i=1}^n \rho_i \bar{v}_i}{\sum_{i=1}^n \rho_i} \quad \dots(2.1)$$

where: $\rho_i \bar{v}_i$ = local rate at which mass of species i passes through a unit cross section, placed perpendicular to velocity \bar{v} , $[ML^{-2}T^{-1}]$,

ρ_i = the mass of species i per unit volume of solution, $[ML^{-3}]$,

\bar{v} = the velocity at which the center of the mass of the gas moves, $[LT^{-1}]$,

n = number of species in the mixture,

M = dimension of mass,

L = dimension of length, and

T = dimension of time.

Similarly, average molar velocity \bar{v}^* is defined as:

$$\bar{v}^* = \frac{\sum_{i=1}^n c_i \bar{v}_i}{\sum_{i=1}^n c_i} \quad \dots(2.2)$$

where: $c_i \bar{v}_i$ = local rate at which moles of species i pass through a unit cross section, placed perpendicular to the velocity \bar{v}^* , $[L^{-2}T^{-1}]$,

c_i = the number of moles of species i
per unit volume of solution, $[L^{-3}]$

\bar{v}^* = the average velocity of the molecules
of the gas, $[LT^{-1}]$

In a single component system, these two velocities \bar{v} and \bar{v}^* are the same, but in a multicomponent system they can differ. In a multicomponent system the conditions may be such that the molecular flux vector of the whole system is in the direction in which lighter molecules diffuse, while the center of mass of the whole system moves in the direction in which heavier molecules diffuse (Cunningham and Williams 1980).

In a flow system, the velocity of a given species with respect to \bar{v} or \bar{v}^* rather than with respect to stationary coordinates, leads to the definition of the diffusion velocities, which indicate the motion of the component i relative to the local motion of the fluid stream:

$\bar{v}_i - \bar{v}$ = diffusion velocity of species i with
respect to \bar{v} ,

$\bar{v}_i - \bar{v}^*$ = diffusion velocity of species i with
respect to \bar{v}^* .

2.1.5 Diffusion coefficient:

According to Jost (1960), diffusion coefficient is "the flow or current of a substance which passes perpendicularly through a reference plane of unit area, during a unit time, under unit concentration gradient." The unit chosen for the quantity of the substance is not specified since it can be mole, mass or volume of the substance. Most literature cite the values of diffusion coefficient in the units of cm^2/s .

In other words the dimensions of diffusion coefficient are $[L^2T^{-1}]$.

2.2 Laws of Diffusion:

2.2.1 Fick's first law of diffusion:

Using a consistent set of units of measurement, let x be the co-ordinate axis chosen perpendicular to the reference plane and c the concentration of the diffusing substance given as an amount of the substance per unit volume, Fick's first law may be stated as (Bird et al. 1960):

$$J = -D \frac{dc}{dx} \quad \dots(2.3)$$

where: D = diffusion coefficient for system under consideration, $[L^2T^{-1}]$,

J = diffusion flux, $[ML^{-2}T^{-1}]$ and,

$\frac{dc}{dx}$ = concentration gradient, $[ML^{-4}]$.

The negative sign indicates that the flow direction is opposite to the direction of the concentration gradient. This law is applicable to steady state conditions.

2.2.2 Fick's second law of diffusion:

Fick's second law of diffusion is defined as (Jost 1960),

$$\frac{\partial J}{\partial x} = \frac{\partial}{\partial x}(-D \frac{dc}{dx}) = -\nabla \cdot (DVC) = \frac{\partial c}{\partial t} \quad \dots(2.4)$$

where: c = concentration of diffusing gas, $[ML^{-3}]$, and

t = time interval, $[T]$

For homogeneous materials, the material property, coefficient of diffusion is independent of position, thus Eq. 2.4 is simplified to:

$$\nabla^2 c = -\frac{1}{D} \frac{\partial c}{\partial t} \quad \dots(2.5)$$

Depending on the need of a particular problem Eq. 2.5 can be expanded in cartesian, cylindrical or spherical coordinate systems.

2.2.3 Graham's law of diffusion of gases:

Graham's law of diffusion of gases states that under comparable conditions, "the relative speeds of the diffusion of the gases are inversely proportional to the square roots of their relative densities" (Rosenberg 1977).

2.2.4 Ideal gas law:

This law is not a diffusion law but is useful when gases are involved. The ideal gas law is:

$$\begin{aligned} P v &= R T' \\ \text{or} \quad P V &= n R T' \end{aligned} \quad \dots(2.6)$$

where: P = the pressure, $[ML^{-1}T^{-2}]$,

V = total volume, $[L^3]$,

T' = absolute temperature, $[K]$,

R = the universal gas constant, $[ML^2T^{-2}K^{-1}Mol^{-1}]$

n = the number of moles and

v = the volume per mole (V/n), $[L^3]$.

The value of the universal gas constant (R) is $0.0083 \text{ m}^3 \text{ kPa} \cdot K^{-1} \cdot \text{mol}^{-1}$.

The ideal gas law, like other gas laws is only an approximation. At ordinary pressure, however, the predicted values derived from the ideal gas law agree with the experimental

values within $\pm 1\%$ (Rosenberg 1977).

2.3 Work Related to Diffusion of Gases through Bulk Grain:

Henderson and Oxley (1944) reported the diffusion coefficient of CO_2 through wheat (12% moisture content, 38% porosity) at room temperature to be about one third of the value of the diffusion coefficient of CO_2 through open air. The value of diffusion coefficient of CO_2 through wheat was $0.0415 \text{ cm}^2/\text{s}$. In their experiments a known mixture of air and carbon dioxide was delivered to the top of the grain column contained in a cylindrical container of galvanized iron, 0.62 m long and 0.078 m^2 in cross-sectional area. The diffused CO_2 was absorbed by caustic soda (NaOH) solution, kept at the bottom of the diffusion tower. The NaOH solution was continuously and gently stirred to ensure proper absorption of CO_2 . The amount of diffused CO_2 was found by drawing samples of the NaOH solution at intervals throughout a test. After addition of an excess of barium chloride (BaCl_2) the samples were titrated against hydrochloric acid (HCl) of known concentration. The samples were drawn until an equilibrium condition was established. It is not clear whether the time used in calculating the diffusion coefficient is the time during which an equilibrium condition was established or the time for which the test was run after equilibrium was established.

Robertson (1948) tried to determine the diffusion coefficient of CO_2 through wheat but discontinued his experiments after the receipt of the publication of Henderson and Oxley. However, he has indicated that there was no significant

difference in the diffusion rate when the flow of CO_2 was vertically upward, horizontal or vertically downward.

Bailey (1959) determined the coefficients of diffusion of oxygen (O_2) through bulk corn, wheat, barley and oats. At 23°C the mean coefficients of diffusion of O_2 through corn, wheat, barley and oats (in order of increasing porosity) were 0.0558, 0.0670, 0.0642, and $0.0721 \text{ cm}^2/\text{s}$ respectively. His diffusion tower was similar to that of Henderson and Oxley (1944). The diffused oxygen was absorbed by a stirred solution of pyrogallol in aqueous caustic soda (NaOH) kept at the bottom of the diffusion tower. The amount of oxygen diffusing through the grain was determined from the change of conditions at the top of the grain column because samples of alkaline pyrogallol solution could not be quantitatively analysed for O_2 . He has indicated that the dependence of the diffusion coefficient on temperature is satisfactorily described by a quadratic relationship. Bailey also indicated that the diffusion rate was dependent on the porosity of the grain but no mathematical relationship was worked out.

Adamczyk et al. (1978a, 1978b, 1978c) have reported the method and the results of the measurements of the diffusion velocity of helium (He), neon (Ne), argon (Ar), xenon (Xe), hydrogen (H_2) and carbon dioxide through a layer of dry wheat. The details of the apparatus and grain are not given in the papers. They modelled the gas exchange in the grains by a resistance-capacitance model. Capacitance (C) represented the gaseous capacity of the basic cells among the grains and resistance (R) represented the gaseous resistance

between the cells. Their work is qualitative and comparative in nature giving no quantitative measurement of the diffusion coefficient.

No other work has been found in the literature on the diffusion of gases through grains. Work related to the diffusion of gases through some other porous materials is reviewed in the next section.

2.4 Work Related to Diffusion of Gases through some Engineering Porous Materials:

Ray (1976) has described methods for measuring the flow or diffusion of a gas through a porous solid of undefined pore characteristics. For flow measurement under a pressure gradient, a porous cylinder was sealed between two glass tubes and the curved surface coated with a sealant. The outer end of one glass tube was connected to a vacuum or gas line and the end of the other was connected to a manometer. In the diffusion experiments equal pressures were maintained on both sides of the porous sample through which hydrogen was diffused unidirectionally under a gradient in the partial pressure of the hydrogen. One face of the sample was connected to a hydrogen gas line and the other to an argon gas line. The porous samples were of reduced hematite and of reduced cobalt oxide. The samples were 6.66 mm in length and 57.6 mm^2 in cross-sectional area. The reduced cobalt oxide had a pore radius of 10^{-3} mm and a porosity of 65%. The hydrogen concentrations were measured with a hydrogen concentration cell. At the reference electrode of the cell hydrogen was continuously bubbled at one atmospheric pressure

(101.325 kPa), and at the other electrode a mixture of hydrogen and argon was bubbled. Based on the flow rate of argon and the electromotive force of the cell the concentration of hydrogen in the argon stream was calculated.

Chester et al. (1974) have discussed multicomponent diffusion experiments for a system of helium, nitrogen and methane in γ -alumina catalyst pellets over a wide range of pressures, temperatures and composition gradients. The pellets were cylindrical, 0.3175 mm in length and diameter, with a particle density of 1360 kg/m^3 .

Chen et al. (1977) measured the diffusion rates of nitrogen and methane across ten porous solids at 35°C and 101.325 kPa pressure by steady state flow method. The porous samples were cylindrical in shape and diffusion occurred in the direction of the axis. Six of the specimens were 50 mm in length and 25 mm^2 in cross-sectional area filled with glass beads or sand. The beads and sand were secured in position by removable screens. The other four units were designed with a 38 mm diameter hole into which a sandstone core 13.8 mm long was fitted and cemented with epoxy. They reported that diffusion coefficient was exponentially related to the porosity in the porosity range 11.7% (for sandstone) to 46.7% (for 5 mm cubic glass beads).

The diffusion cells of both Chester et al. (1974) and Chen et al. (1977) were similar in principle except for certain modifications to accommodate the different sample sizes.

Verma (1973) has conducted the flux measurements for forced flow, diffusion and forced flow combined with diffusion for gases through four varieties of natural and impregnated stones. Diffusion fluxes were measured for two different binary gas systems: nitrogen-carbon dioxide and nitrogen-helium.

Yang et al. (1977) have discussed a transient technique to determine diffusion coefficients of gases through porous materials in the range of 0 to 10^{-6} mm²/s. The main component of the experimental setup was a spherical chamber 25.4 mm in diameter. The chamber was supported by three small posts. The spherical samples of nuclear graphite and bituminous coal 20 mm in diameter were placed inside the chamber. The sample was soaked in gas A at 102.66 kPa pressure for 20 h to produce the initial concentration (C_{A0}) in the solid. Gas B was then swept at a known rate through the chamber for a certain period of time, during which gas A diffused from the sample to gas B. The gas chamber was then closed and equilibrated for 20 h to determine the final concentration of gas A at the end of test period. The diffusion equation given by Fick's second law of diffusion was solved under imposed initial and boundary conditions in spherical coordinates. Using three terms of the infinite converging series solution and measured concentrations of gas A at the start and at the end of the time period, the diffusion coefficient was calculated. The diffusion coefficient was dependent on temperature but no functional relationship was reported.

2.5 Diffusion of Isotopic Materials:

Ney and Armistead (1947) have discussed a method of finding the self-diffusion coefficient of a vapor by observing with a mass spectrometer the rate at which a material rich in one isotope diffuses into normal material. The main components of the diffusion apparatus were two cylindrical copper bulbs of volumes 925 and 259 ml connected by a copper tubing 68 mm in length and 32.15 mm^2 in cross-sectional area. Diffusion coefficients were calculated by the steady state method based on the following assumptions:

- (A) the concentration gradient in the connecting tube was linear, and
- (B) the concentration in the bulbs was uniform.

Weller et al. (1972a, 1972b) conducted their experiments with a diffusion apparatus similar in principle to the two-bulb, capillary tube cell described by Ney and Armistead (1947). They measured the diffusion of krypton-85 through a mixture of 25% krypton and 75% xenon in a porous graphite at a pressure of 20.84 kPa.

2.6 Work Related to Binary Gaseous Diffusion:

Watts (1964, 1965) measured the diffusion coefficient of trace amounts of xenon-133 in binary mixtures of xenon with helium, neon, argon and krypton. His apparatus was similar in principle to that described by Ney and Armistead (1947). The self diffusion coefficient of xenon was $0.06 \text{ cm}^2/\text{s}$ and the binary diffusion coefficients for systems Xe-He, Xe-Ne, Xe-Ar and Xe-Kr were 0.535, 0.23, 0.127 and $0.0823 \text{ cm}^2/\text{s}$ respectively at one atmospheric pressure (101.325 kPa). The

reciprocal of diffusion coefficient of xenon-133 in various mixtures was linearly related to the mole fraction of xenon.

By measuring the rate of evaporation Watts (1971) determined the diffusion coefficients of carbon tetrachloride (CCl_4), chloroform (CHCl_3) and methylene chloride (CH_2Cl_2) in air. The liquid was filled in a bulb of volume 5 ml and was allowed to diffuse through capillaries 2 and 3 mm in diameter and 30 - 60 mm in length. The reported results were corrected for the effect of impurities in the diffusing material. There was no significant effect of capillary diameter and length on diffusion coefficient.

Fuller and Giddings (1965) have presented a critical review of the methods for predicting binary gaseous diffusion coefficients. Nine models were compared theoretically as well as numerically. These prediction equations are applicable to pure binary diffusion and can not be applied to the diffusion of gases through grains. However, this work indicates that the rate of diffusion is dependent on the temperature, molecular weights and partial pressures of the diffusing gases.

3. MATHEMATICS OF DIFFUSION

3.1 Steady State Method of Finding Diffusion Coefficient:

The steady state method is applied to determine the diffusion coefficient when the flow conditions are independent of time. In the steady state method elaborate equipment is required and a lot of diffusing substance is wasted before steady state is established. When steady state is reached the amount of material diffused during a measured time across a known cross-sectional area under a known concentration gradient is measured. Fick's first law of diffusion (Eq. 2.3) in its finite difference form is used to calculate the diffusion coefficient:

$$N = DA \frac{\Delta c}{\Delta x} \quad \dots(3.1)$$

where: N is the diffused mass, g/s,

D is the diffusion coefficient, cm^2/s ,

A is the cross sectional area perpendicular to the diffusion path, cm^2 and

Δc is the concentration difference between two planes located Δx cm apart, g/cm^3 .

3.2 Transient Method of Finding Diffusion Coefficient:

The transient method is applied to determine the diffusion coefficient when the flow conditions are dependent on time. In this method the equipment can be simplified and also the wastage of diffusing material is less. But the mathematical analysis becomes more complicated than the steady state case. To determine the diffusion coefficient under transient or unsteady state conditions the diffusion equation given by

Fick's second law of diffusion for unsteady state must be solved for the imposed boundary and initial conditions:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \dots(3.2)$$

subject to

$$C(0,t) = \phi(t)$$

$$C(\ell,t) = \psi(t)$$

$$C(x,0) = F(x)$$

where:

$c(x,t)$ is the concentration of CO_2 in the grain column at a distance x from the inlet of the cylindrical grain chamber and at time t , $[ML^{-3}]$

ℓ is the length of diffusion path in the direction of x , $[L]$

ϕ is a time dependent concentration function at the inlet of the grain column,

ψ is a time dependent concentration function at the outlet of the grain column, and

F is a position dependent concentration function at $t=0$ in the grain column.

To solve eq. 3.2 to determine the concentration of CO_2 at any time t and distance x , a solution in the form of a Fourier series is assumed (Mollison 1881).

$$C(x,t) = \sum_{n=1}^{\infty} A_n(t) \sin \frac{n\pi x}{\ell} \quad \dots(3.3)$$

where the Fourier coefficients are:

$$A_n = \frac{2}{\ell} \int_0^{\ell} c(x,t) \sin \frac{n\pi x}{\ell} dx \quad \dots(3.4)$$

By integrating Eq. 3.4 by parts, A_n is found to be:

$$A_n = \frac{2}{\ell} \left[\left\{ C(x,t) \left(-\frac{\ell}{n\pi} \cos \frac{n\pi x}{\ell} \right) \right\}_0^{\ell} + \frac{\ell}{n\pi} \int_0^{\ell} \frac{\partial c}{\partial x} \cos \frac{n\pi x}{\ell} dx \right]$$

$$\begin{aligned}
&= \frac{2}{\ell} \frac{\ell}{n\pi} \left[\{-c(\ell, t)(-1)^n + c(0, t)\} + \frac{\ell}{n\pi} \left\{ \frac{\partial c}{\partial x} \sin \frac{n\pi x}{\ell} \right\}_0^\ell \right. \\
&\quad \left. - \frac{\ell}{n\pi} \int_0^\ell \frac{\partial^2 c}{\partial x^2} \cos \frac{n\pi x}{\ell} dx \right] \quad \dots (3.5)
\end{aligned}$$

Substituting Eq. 3.2 into Eq. 3.5,

$$\begin{aligned}
A_n &= \frac{2}{\ell} \left[\frac{\ell}{n\pi} \{\phi(t) - (-1)^n \psi(t)\} - \frac{\ell^2}{n^2 \pi^2} \frac{1}{D} \int_0^\ell \frac{\partial c}{\partial t} \sin \frac{n\pi x}{\ell} dx \right. \\
&= \frac{2}{\ell} \left[\frac{\ell}{n\pi} \{\phi(t) - (-1)^n \psi(t)\} - \frac{\ell^2}{D n^2 \pi^2} \frac{\ell}{2} \frac{\partial A_n}{\partial t} \right] \quad \dots (3.6)
\end{aligned}$$

Multiplying Eq. 3.6 by $\frac{D n^2 \pi^2}{\ell^2}$ and rearranging for A_n ,

$$\frac{\partial A_n}{\partial t} + \frac{D n^2 \pi^2}{\ell^2} A_n = \frac{2 D n \pi}{\ell^2} \{\phi(t) - (-1)^n \psi(t)\} \quad \dots (3.7)$$

Multiplying eq. 3.7 by $e^{D n^2 \pi^2 t / \ell^2}$,

$$\begin{aligned}
e^{D n^2 \pi^2 t / \ell^2} \frac{\partial A_n}{\partial t} + \frac{D n^2 \pi^2}{\ell^2} e^{D n^2 \pi^2 t / \ell^2} A_n &= \frac{2 D n \pi}{\ell^2} e^{D n^2 \pi^2 t / \ell^2} \\
&\quad \{\phi(t) - (-1)^n \psi(t)\}
\end{aligned}$$

or

$$\begin{aligned}
\frac{\partial}{\partial t} \{e^{D n^2 \pi^2 t / \ell^2} A_n\} &= \frac{2 D n \pi}{\ell^2} e^{D n^2 \pi^2 t / \ell^2} \{\phi(t) - (-1)^n \psi(t)\} \\
&\quad \dots (3.8)
\end{aligned}$$

Integrating Eq. 3.8 with respect to time results in:

$$\begin{aligned}
(e^{D n^2 \pi^2 t / \ell^2})_{A_n=0} \int_0^t \frac{2 D n \pi}{\ell^2} e^{-D n^2 \pi^2 t / \ell^2} \{\phi(t) - (-1)^n \psi(t)\} dt &+ C_n \\
&\quad \dots (3.9)
\end{aligned}$$

where C_n are coefficients of integration.

Dividing Eq. 3.9 by $e^{D n^2 \pi^2 t / \ell^2}$,

$$A_n(t) = C_n e^{-Dn^2 \pi^2 t / \ell^2} + \frac{2Dn\pi}{\ell^2} e^{-Dn^2 \pi^2 t / \ell^2} \left[\int_0^t e^{Dn^2 \pi^2 \tau / \ell^2} \{\phi(\tau) - (-1)^n \psi(\tau)\} d\tau \right]$$

...(3.10)

To determine C_n considering Eq. 3.3 at time $t=0$ and substituting from Eq. 3.2 for initial condition,

$$C(x, 0) = \sum_{n=1}^{\infty} C_n \sin \frac{n\pi x}{\ell} = F(x) \quad \dots(3.11)$$

From Eq. 3.4,

$$C_n = \frac{2}{\ell} \int_0^{\ell} F(x) \sin \frac{n\pi x}{\ell} dx \quad \dots(3.12)$$

Therefore,

$$C(x, t) = \sum_{n=1}^{\infty} C_n e^{-Dn^2 \pi^2 t / \ell^2} \sin \frac{n\pi x}{\ell} + \frac{2D\pi}{\ell^2} \sum_{n=1}^{\infty} e^{-Dn^2 \pi^2 t / \ell^2} \sin \frac{n\pi x}{\ell} \int_0^t e^{Dn^2 \pi^2 \tau / \ell^2} \{\phi(\tau) - (-1)^n \psi(\tau)\} d\tau$$

...(3.13)

For the assumptions that at the outer end the CO_2 is instantly lost to the atmosphere ($\psi(t)=0$) and that initial distribution of CO_2 in the grain column is uniform and constant at ambient air CO_2 concentration ($F(x) = K$),

Eq. 3.13 is simplified to:

$$C(x, t) = \sum_{n=1}^{\infty} C_n e^{-Dn^2 \pi^2 t / \ell^2} \sin \frac{n\pi x}{\ell} + \frac{2D\pi}{\ell^2} \sum_{n=1}^{\infty} e^{-Dn^2 \pi^2 t / \ell^2} \sin \frac{n\pi x}{\ell} \int_0^t e^{Dn^2 \pi^2 \tau / \ell^2} \phi(\tau) d\tau$$

...(3.14)

where:

$$C_n = \frac{2}{\ell} \int_0^{\ell} K \sin \frac{n\pi x}{\ell} dx \quad \dots(3.15)$$

The function $\phi(t)$ could be determined by measuring CO_2 concentration at the inlet of the grain column with time. Decrease in concentration generally is of the form of exponential decay, so assuming $\phi(t) = e^{-pt}$, Eq. 3.14 is reduced to,

$$C(x,t) = \sum_{n=1}^{\infty} C_n e^{-Dn^2\pi^2 t/\ell^2} \sin \frac{n\pi x}{\ell} + \frac{2D\pi}{\ell^2} \sum_{n=1}^{\infty} n e^{-Dn^2\pi^2 t/\ell^2} \sin \frac{n\pi x}{\ell} \int_0^t e^{(Dn^2\pi^2/\ell^2 - p^2)t} dt$$

or

$$C(x,t) = \sum_{n=1}^{\infty} C_n e^{-Dn^2\pi^2 t/\ell^2} \sin \frac{n\pi x}{\ell} + 2\pi D \sum_{n=1}^{\infty} \frac{n}{Dn^2\pi^2 - p\ell^2} [e^{-pt} - e^{-Dn^2\pi^2 t/\ell^2}] \cdot \sin \frac{n\pi x}{\ell} \quad \dots(3.16)$$

Eq. 3.16 has been solved for the assumption that the inlet of the grain column is instantly exposed to the time dependent function $\phi(t)$. In practical situations this instantaneous change is difficult to achieve, so this equation is invalid as x approaches the inner or outer ends of the grain column. End functions $\phi(t)$ and $\psi(t)$ are already known so this equation describes the concentration of CO_2 for $0 < x < \ell$ and $t > 0$.

To determine the diffusion coefficient D using Eq. 3.16 the concentration of CO_2 in the grain column has to be measured at a fixed value of x , such as $\ell/2$ at time t_1 and t_2 . Assuming

that the first term of the infinite series solution of Eq. 3.16 gives a good approximation (in general a minimum of three terms are considered) then:

$$C(\frac{\ell}{2}, t_1) = \frac{2K}{\pi} e^{-D\pi^2 t_1 / \ell^2} + \frac{2\pi D}{D\pi^2 - p\ell^2} [e^{-pt_1} - e^{-D\pi^2 t_1 / \ell^2}] \quad \dots(3.17)$$

and

$$C(\frac{\ell}{2}, t_2) = \frac{2K}{\pi} e^{-D\pi^2 t_2 / \ell^2} + \frac{2\pi D}{D\pi^2 - p\ell^2} [e^{-pt_2} - e^{-D\pi^2 t_2 / \ell^2}] \quad \dots(3.18)$$

Using Eqs. 3.17 and 3.18 the value of D could only be determined by a trial and error method. If three terms of the series are used to approximate the solution it would be too time consuming to determine D by this technique.

3.3 Cowie and Watts Method:

Another method to solve a similar type of problem has been given by Cowie and Watts (1971). They measured the diffusion of methane and chloromethanes in air. In deriving the solution they made the following assumptions for the apparatus shown in Fig. 3.1.

1. The concentration gradient in the capillary tube is linear.
2. The concentration in the bulb is uniform.
3. The concentration outside the bulb is zero.
4. At all times the conditions approximate a steady state condition, i.e. the concentration gradient in the tube and the diffusion flux at any instant are those that would be found if the concentration in the bulb was maintained constant at the instantaneous value.

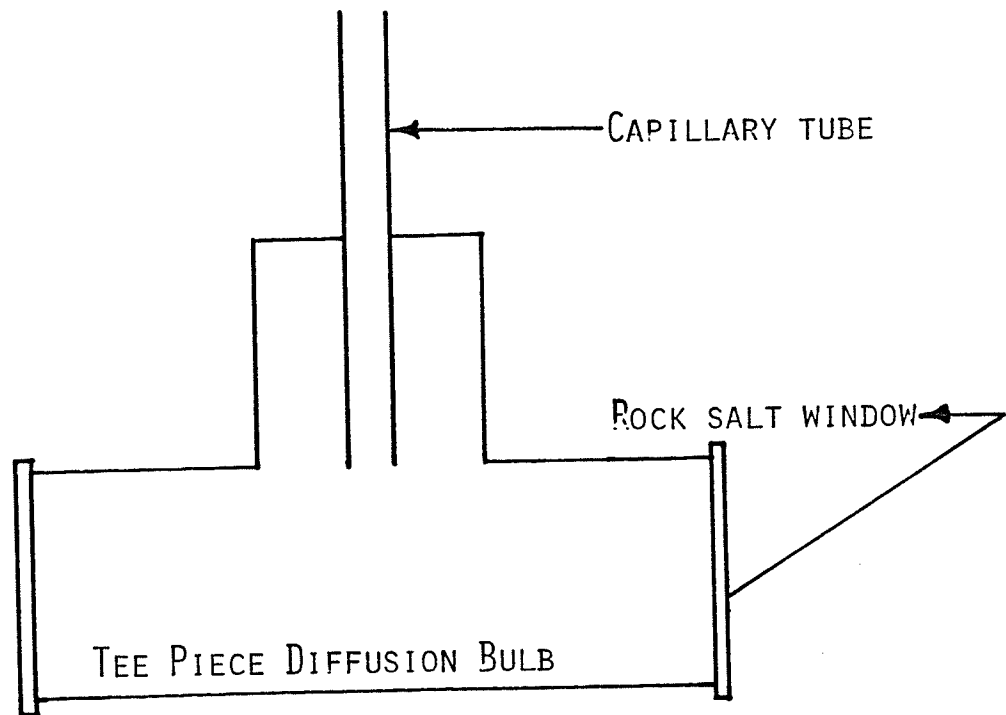


FIG. 3.1: SCHEMATIC DIAGRAM OF DIFFUSION CELL. (COWIE AND WATTS 1971).

Now if c is the concentration in the bulb in kg/m^3 and ℓ and A are the length and cross-sectional area in m and m^2 respectively of the tube,

$$J = -D \frac{\partial c}{\partial x} = - \frac{Dc}{\ell} \quad \dots(3.19)$$

and also:

$$J = \frac{V}{A} \frac{\partial c}{\partial t} \quad \dots(3.20)$$

where V is the cell volume and ∂c is the infinitesimal change of the concentration in the cell during the time interval ∂t . Thus,

$$\frac{\partial c}{\partial t} = - \frac{DAc}{\ell V} \quad \dots(3.21)$$

For limit $\partial t \rightarrow 0$ and integrating Eq. 3.21,

$$\ln(c) = - \frac{DA t}{\ell V} + \beta \quad \dots(3.22)$$

where β is a constant of integration.

Thus a plot of $\ln(c)$ against time t is linear with slope being $-DA/\ell V$. The diffusion coefficient, D , is calculated from the slope of the best fit straight line through the experimental points.

4. MATERIALS AND METHODS

4.1 Diffusion Apparatus:

The main components of the diffusion apparatus (Fig. 4.1) are a gas chamber, 350 x 350 x 350 mm inside dimensions and a cylindrical grain chamber of 164 mm inside diameter and 500 mm in length. The gas chamber was fabricated from a 9 mm thick Plexiglas acrylic sheet and the cylindrical grain chamber was cut from a Plexiglas acrylic tube of 6 mm wall thickness. On one face of the gas chamber a 176 mm diameter hole was drilled and the cylindrical grain chamber was joined to it by using 3M adhesives (3M Canada Ltd. London Canada). On the inner end of the cylinder a fixed screen and on the outer end a detachable screen were attached to hold the grain in the cylinder. The screens had 1.702 mm diameter holes with 35% open area. To hold rapeseed in the cylinder another square hole (0.85 x 0.85 mm) plastic wire mesh with 45% open area was used in addition to the circular-hole steel mesh. A (225 x 225 mm) door was hinged from the inside of the gas chamber. A copper wire 1.5 mm in diameter was used to open and to tightly close the door. This door was used to attain uniform concentration in the gas chamber while closed and to allow diffusion of CO_2 through seed bulks while open. On one side of the gas chamber a 100 mm diameter hole was drilled to permit entry of a person's hand. This hole was closed by a detachable cover during experiments. Three Plexiglas acrylic tubes of 6.2 mm inside diameter and 20 mm in length were fitted to three faces of the gas chamber. About 10 mm of the tube length projected out of the faces. The

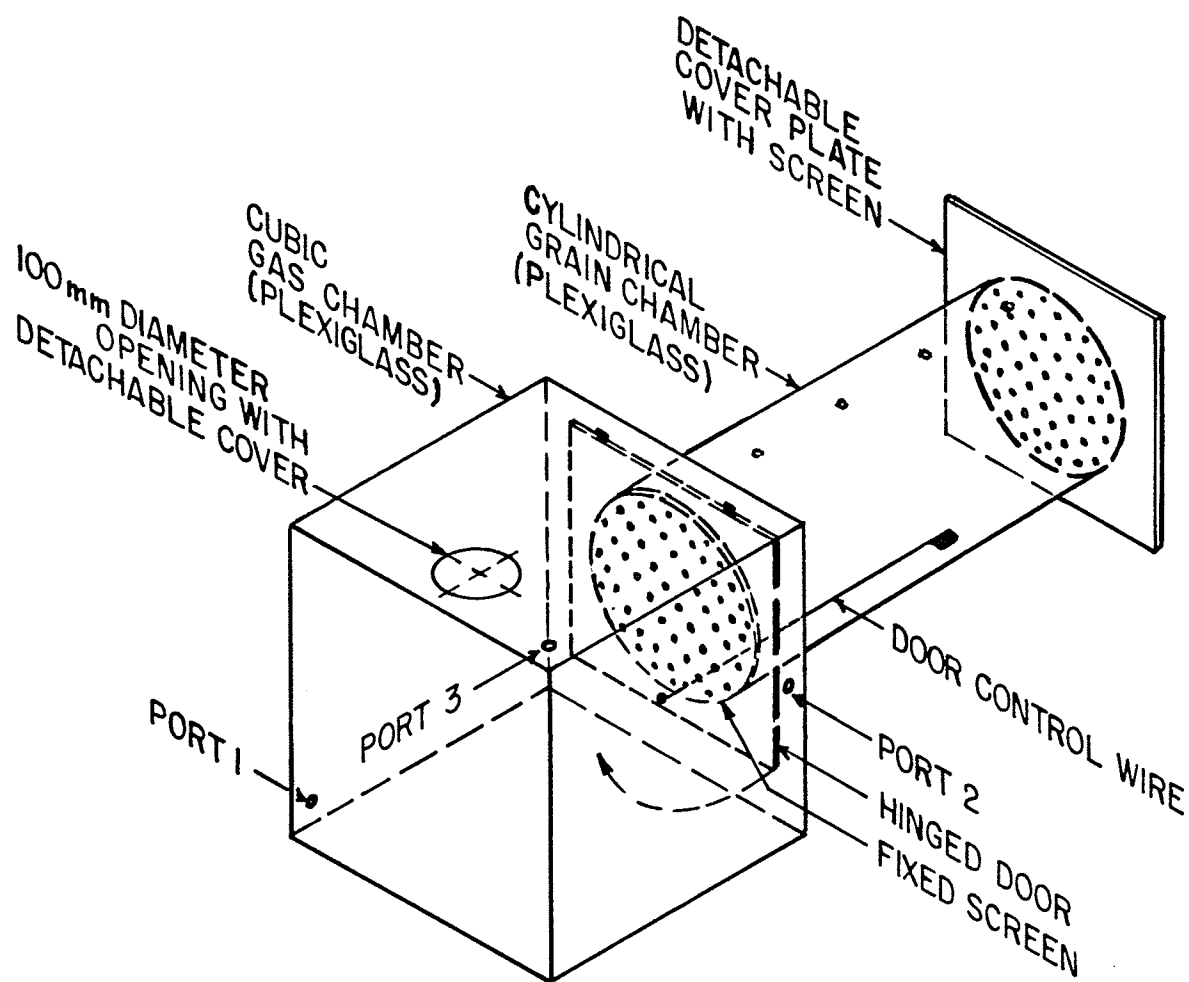


FIG. 4.1 : DIFFUSION APPARATUS

projected length of tube was cut to a 9.5 mm outside diameter so that a rubber septum, 9.5 mm inside diameter, could be tightly fitted to close the ports during experiments. One of these ports was used to inject carbon dioxide to the gas chamber at the start of the experiment and all three ports were used to sample the gas in the gas chamber during experiments. Similar four ports 10 cm apart were located along the length of grain chamber. Plastic syringes with needles 203 mm in length (Chromatographic Specialities Limited, Brockville, Ont.) were used to sample the gas in the diffusion box. The apparatus was tested for air tightness up to 138 kPa gauge pressure by filling the apparatus with air and applying soap solutions to all the joints.

4.2 Seeds:

Wheat (cv. Neepawa, graded No. 2 Canada Western Red Spring harvested September 1980, having an initial moisture content of 14.8%) was used to determine the diffusion coefficient of CO_2 through wheat at 13%, 15% and 18% wet basis moisture contents.

Rapeseed (cv. Regent, Canada Certified No. 1 seed, harvested September 1980) was used to determine the diffusion coefficient through rapeseed at 8% moisture content. The initial moisture content of the rapeseed was 7.8%.

Hybrid seed corn (cv. Asgrow RX17, about 1 year old) was used to determine the diffusion coefficient at its initial moisture content of 14.1%.

Oats (cv. Harmon, No. 2 Canada Western, about 1 year old) was used to determine the diffusion coefficient at its initial

moisture content of 14.5%.

All four seeds; wheat, rapeseed, corn and oats were certified and commercially cleaned seed.

4.3 Moisture Determination:

To determine moisture contents, triplicate samples of about 10 g each were dried at 130°C in an air oven for 4 h, 19 h, 22 h, and 72 h for rapeseed, wheat, oats and corn, respectively (Anon. 1975). The wet basis moisture content was determined by dividing the mass of moisture evaporated by the mass of the wet sample, multiplying by 100% and then averaging the three replicate samples. All grain moisture contents are expressed on a wet mass basis in the thesis.

4.4 Conditioning of Grain:

To increase the moisture content of the grain to a desired level, the grain was conditioned in a rotary mixer. A predetermined quantity of water was added to the grain sample, and the grain sample was mixed for 2 h at constant speed. The grain was then stored in a sealed polythelene bag for 48 ± 2 h at 2.5°C to allow for uniform distribution of the added moisture (Milner and Geddes 1954).

The moisture content of the grain was reduced to a desired level by drying the samples in an air oven. A pre-calculated amount of water was removed by heating the grain at 70°C . The moisture levels of the grain thus obtained were lower by 1% from the desired moisture content of the grain. Moisture content of grain was raised to the desired level by following the above procedure.

To condition the grain to the test temperature the grain was stored in a sealed polythelene bag for 2 days at the test temperatures.

4.5 Porosity Measurement:

Kernel volumes of a known mass of seed were determined using an air comparison Pycnometer, (Model 930, Beckman Instruments, Inc., Fullerton, California, USA). Kernel densities were calculated by dividing sample mass by the measured volume of the sample and porosities were determined by (Mohsemin 1970):

$$\epsilon = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 \quad \dots(4.1)$$

where:

ρ_b = bulk density, (g.cm^{-3}),

ρ_t = kernel density, (g.cm^{-3}) and

ϵ = porosity, %.

4.6 Experimental Procedure:

The diffusion apparatus was set vertical, resting on one of the faces of the gas chamber inside the laboratory. The detachable cover plate with screen was removed from the cylindrical grain chamber. A known quantity of grain was poured into the cylindrical grain chamber using a glass beaker. When the grain was filled to the top level of the grain chamber a brass rod 25.3 mm in diameter was thrice inserted into the grain to a depth of about 400 mm and pulled out. More grain was then added to bring the grain to the level of the edge of the cylindrical grain chamber.

The diffusion apparatus was then set in the desired orientation on a wooden stand. The hinged door and opening for the entry of a person's hand were closed. Through one of the ports carbon dioxide gas from a high pressure cylinder was injected at 169.0 kPa for 20 s into the gas chamber. During injection of CO₂ the displaced air escaped through the other two ports. All three ports were closed with rubber septums. The apparatus was left undisturbed for about 1.5 h to obtain a uniform distribution of CO₂ throughout the gas chamber. Initial CO₂ concentration was determined by sampling the gas chamber at the three ports. Because of variation in the gas cylinder pressure and manual control of the valve opening the initial concentration in the gas chamber was not a constant value. But the diffusion coefficient is independent of initial concentration (Cunningham and Williams 1980) and therefore the variation in initial concentration was acceptable. After initial sampling in the gas chamber, the hinged door was opened to allow the diffusion of CO₂ through the cylinder of the grain at atmospheric pressure. After opening the door an initial period of 21 ± 1 h was allowed for flow to develop. Gas samples (6 mL each) were withdrawn from the gas chamber through the three ports and at the outer end of the grain cylinder at 21 h, 27 h, 33 h, and 45 h after the opening of the hinged door. Samples from the gas chamber were divided in half for analysis.

4.7 Analysis of Gas Samples:

A Perkin-Elmer, Sigma 3B, gas chromatograph with a thermal conductivity detector was used to analyse all the gas samples.

The carrier gas was Helium (He), the detector temperature was 150°C and the oven was held at 45°C . Carbon dioxide was separated from the other gases by a 1.8 m column packed with Porapak N (50/80 mesh). A 1 ml fixed volume gas sampling valve was connected to the column to standardize the volume of the injected samples. The gas chromatograph was regularly calibrated with a series of commercially prepared high purity mixtures of CO_2 in He of specified concentrations (Alltech Assoc., Arlington Heights, Ill. USA). The amounts of CO_2 separated from other components of the gas samples were recorded on a strip chart recorder (Fisher Recordall Series 5000, Houston Instruments, Austin, Texas, USA). The peak heights for CO_2 (Fig. 4.2) were used to calculate the percent CO_2 in the gas samples. The analysed CO_2 concentrations were corrected to standard temperature and pressure (STP) using measured atmospheric pressure and temperature.

4.8 Calculation of Diffusion Coefficient:

The method of calculating the diffusion coefficient is similar to that used by Cowie and Watts (1971) except that in their experiments the logarithm of concentration was linearly related to time whereas in this research the concentration was linearly related to time. The correlation coefficients, R^2 , were greater than 0.99 for 49 experiments out of 51 experiments and were 0.985 and 0.989 for two remaining experiments (Appendix A, B and C). This is because of retarded flow of CO_2 through seed bulks in the present study.

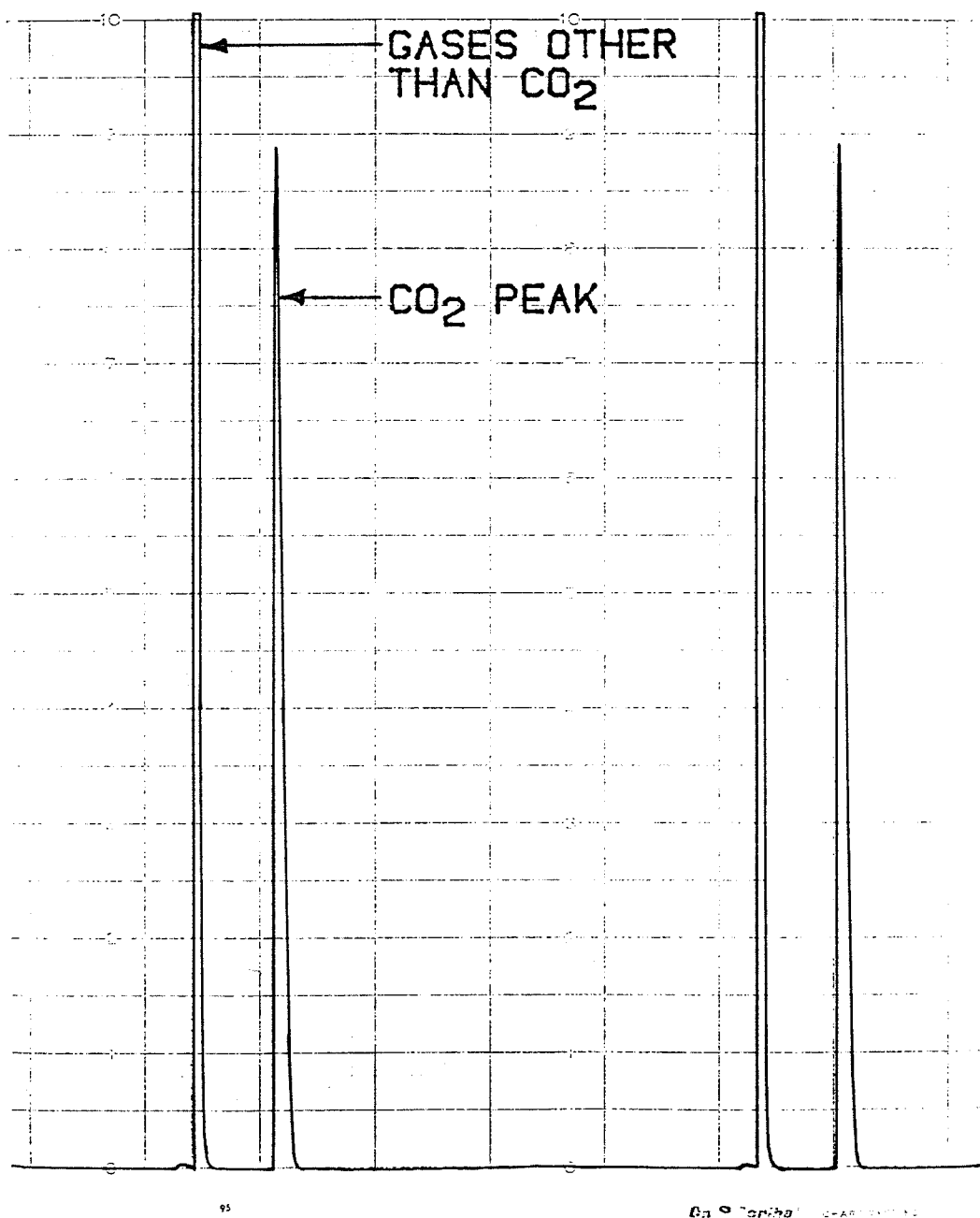


Fig. 4.2: Typical gas chromatogram for CO₂ measurement by Perkin Elmer Sigma 3B chromatograph (chart speed 1.25 cm/min).

A linear regression analysis was done on the measured CO_2 concentrations in the gas chamber for 24 h using the GLM procedure of Statistical Analysis Systems (Anon. 1979). For all experiments the correlation coefficients (R^2) were more than 0.98. Carbon dioxide concentrations in the gas chamber were predicted at 21 h, 27 h, 33 h and 45 h from the opening of the hinged door. The CO_2 concentration at which CO_2 diffused during the 27 h to 33 h period was assumed constant at the average value of the predicted concentrations at 27 h and 33 h. During the 6 h time period the measured CO_2 concentrations at the outer end of the grain column were averaged for a particular experiment. The concentration difference between the inlet and outlet of the grain column was determined by subtracting atmospheric air CO_2 concentration from the average value of the predicted concentrations in the gas chamber at 27 h and 33 h. The amount of CO_2 diffused during this 6 h period was calculated by subtracting the amount of CO_2 present in the gas chamber at 33 h from the amount of CO_2 present in the gas chamber at 27 h based on predicted CO_2 concentrations in the gas chamber. The diffusion coefficient was then calculated by:

$$D = \frac{Q \cdot \Delta l}{A \cdot \Delta c \cdot t} \quad \dots (4.2)$$

where:

D = diffusion coefficient, cm^2/s ,

Q = the amount of CO_2 diffused through
the grain during 6 h, mg,

A = cross-sectional area of the grain
column, cm^2 ,

t = time during which the amount Q was
diffused, s,

Δc = concentration difference between inlet
and outlet of the grain column, mg/cm^3 , and

Δl = length of the grain column, cm.

5. RESULTS AND DISCUSSIONS

5.1 Calibration of the Diffusion Apparatus:

As the experimental procedure to determine diffusion coefficient was similar to that of Cowie and Watts (1971) and was based on their assumptions listed in section 3.3, these assumptions were validated experimentally.

The concentration gradient in the grain column was linear during the test period (Fig. 5.1) The concentration was uniform throughout the gas chamber but was not the same for every experiment. The maximum deviation from the mean carbon dioxide concentration in the gas chamber was 2.5% of the mean reading (Appendix A). The concentration of CO₂ at the outer end of the grain column was equal to the ambient air CO₂ concentration.

5.2 Effect of the Direction of CO₂ Diffusion on the Diffusion Coefficient:

Carbon dioxide was allowed to diffuse at 10⁰ C through bulks of wheat and rapeseed in three directions viz vertically up, horizontal and vertically down. It was expected that CO₂ would diffuse downward under the force of gravity more rapidly than it would diffuse upward because the density of CO₂ (1.963 kg/m³) at standard temperature and pressure (STP) is 1.472 times greater than the density of air (1.334 kg/m³). This phenomenon was observed during some preliminary experiments when CO₂ was diffused through air. The reduction in the CO₂ concentration in the gas chamber during 1 h was more when CO₂ was diffused vertically downward through air than when it was diffused vertically upward. But when CO₂ was

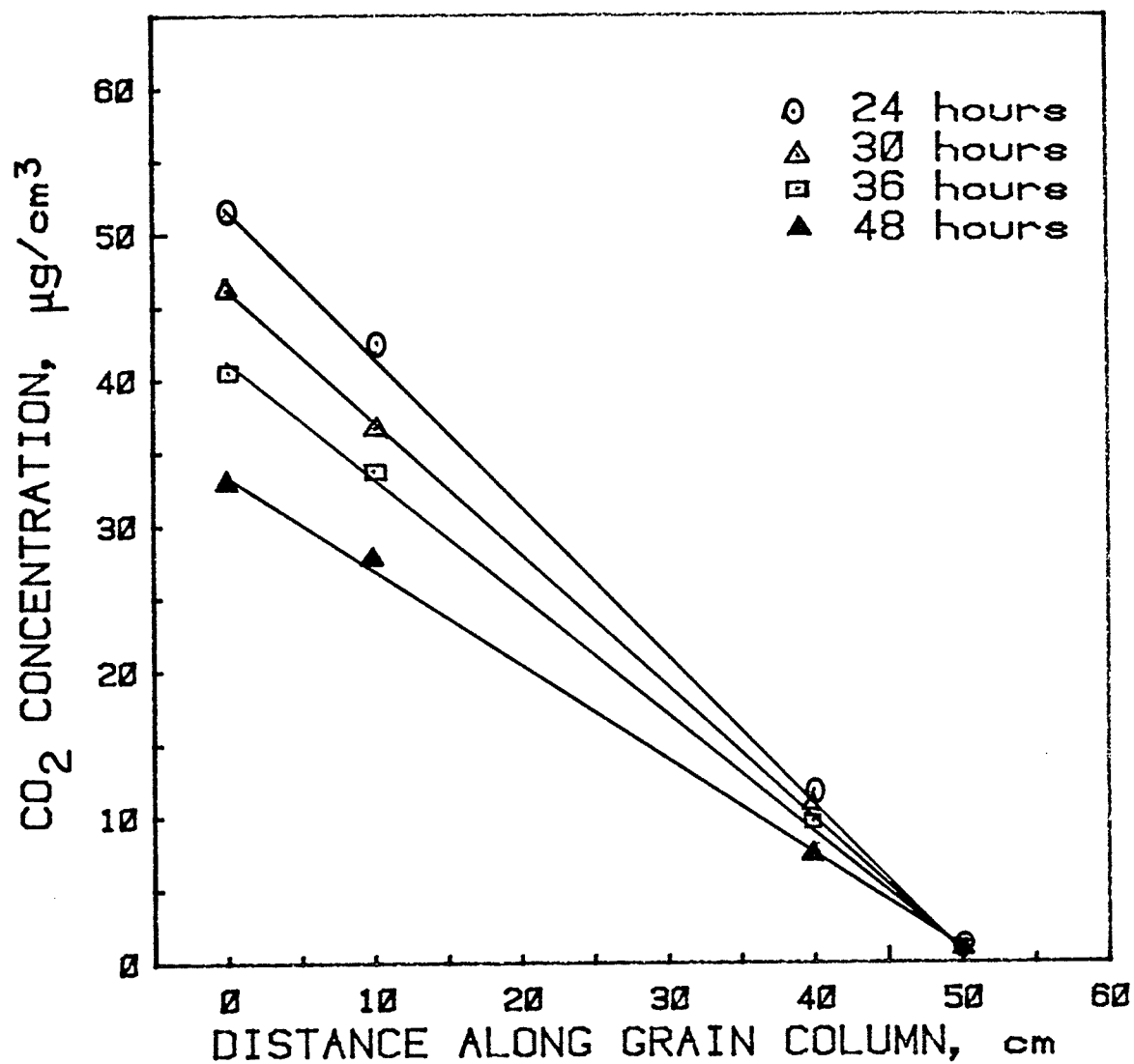


Fig. 5.1: Carbon dioxide concentration along the length of grain column at different time intervals.

diffused through wheat and rapeseed the change in CO_2 concentration in the gas chamber was directionally independent and considerably slower (Table 5.1).

The values of the diffusion coefficient of CO_2 through wheat (13% moisture content) were 0.0338, 0.0347 and 0.0346 cm^2/s and for rapeseed (8% moisture content) were 0.0269, 0.0290 and 0.0284 cm^2/s respectively for CO_2 diffusing vertically up, horizontal and vertically down at 10°C . The variation in the diffusion coefficient of CO_2 through both wheat and rapeseed was statistically insignificant ($P > 0.05$) with CO_2 flow direction (Fig. 5.2). A similar phenomenon was also observed by Robertson (1959) when he conducted experiments on CO_2 diffusion through wheat. Because by definition the process of diffusion is dependent only on the partial pressure or concentrations of the diffusing material, the diffusion coefficient should be constant and independent of the direction of diffusion. When CO_2 is introduced at the top of the diffusion column and is allowed to diffuse through a less dense gas like air, the combined effect of gaseous diffusion and gravitational bulk flow of the denser gas through the less dense gas can cause direction-dependent flow. But when CO_2 is introduced at the top of a grain column the gravitational bulk flow is retarded and evidently becomes relatively unimportant. Thus flow by diffusion prevails, which is the same in all directions.

Based on the laboratory observations that diffusion coefficient is independent of flow direction, the effects on diffusion coefficient of porosity, moisture content, temperature

Table 5.1: The Effect of Direction of CO₂ Diffusion on the CO₂ Concentration in the Gas Chamber for CO₂ Diffusion through Air, Wheat and Rapeseed.

Media	Direction of CO ₂ diffusion	Concentration in the gas chamber (µg/cm ³)		
		0 h	1 h	6 h
air	↓	103.2	38.7	
air	→	87.7	30.7	
air	↑	108.7	102.2	
wheat	↓	95.5		87.8
wheat	→	102.3		96.6
wheat	↑	101.1	-	93.7
rapeseed	↓	158.1		146.8
rapeseed	→	176.3		165.8
rapeseed	↑	192.9		183.0

↓ Vertically downward

→ Horizontal

↑ Vertically upward

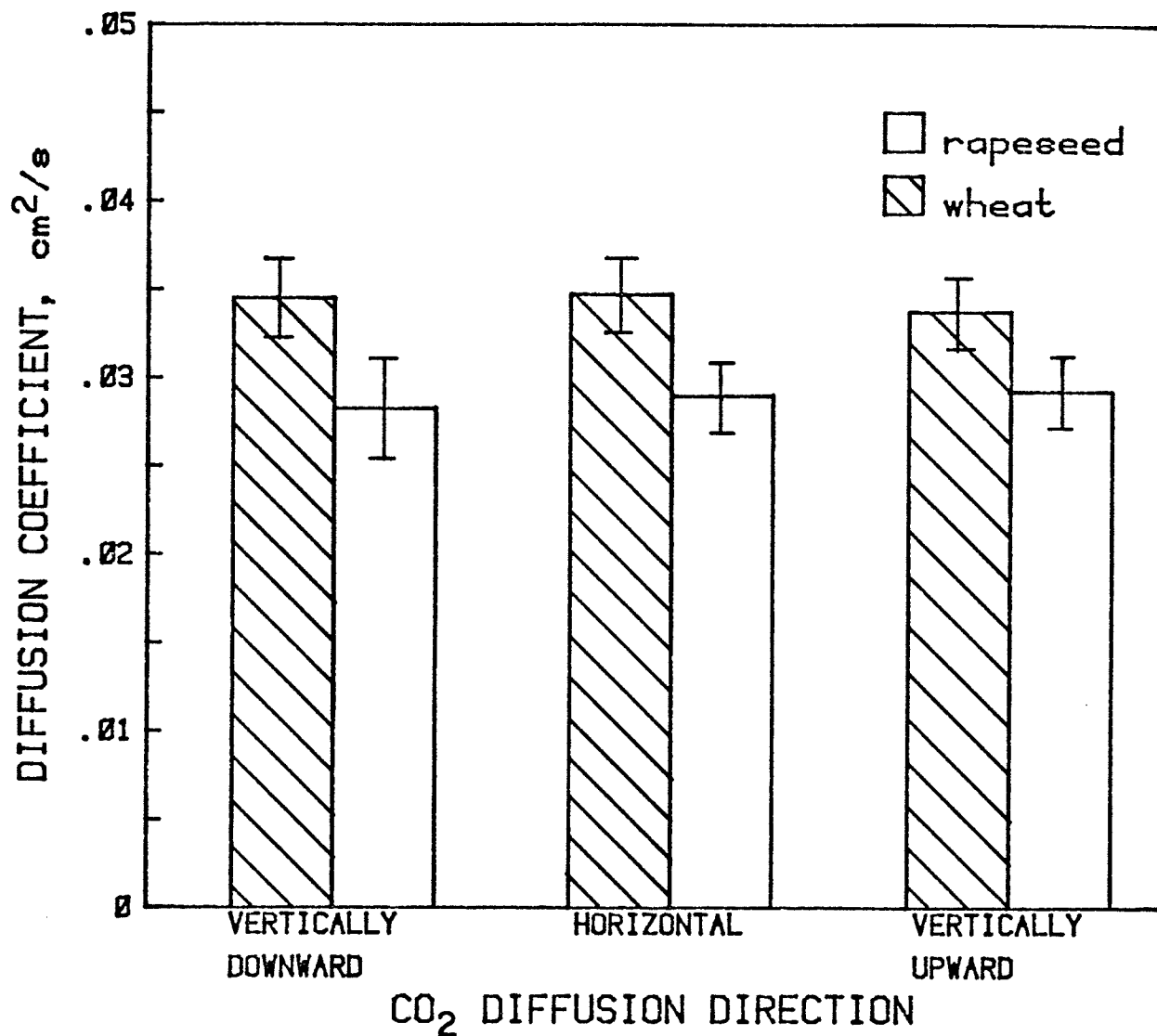


Fig. 5.2: Effect of CO₂ diffusion direction on diffusion coefficient for wheat (13% moisture content wet basis) and rapeseed (8% moisture content wet basis) at 10 ± 1°C. Number of replicates is 3.

and type of seed were studied only for the case when CO_2 was introduced at the top of the seed column and was allowed to diffuse vertically downward. This direction was arbitrarily selected over the other two.

5.3 Effect of Porosity of Diffusion Coefficient through Wheat Bulks:

Three porosity levels 37.9%, 40.0% and 41.9% were obtained by filling the cylindrical grain chamber with 8.808, 8.500 and 8.228 kg of wheat at 13% moisture content. The effect of this variation in porosity on diffusion coefficient was statistically insignificant (Table 5.2). It appears that the change in the porosity is not sufficient to vary the mechanical resistance offered to the diffusion of CO_2 through wheat kernels.

5.4 Effect of Moisture Content on Diffusion Coefficient of CO_2 through Wheat Bulks:

Coefficient of diffusion of CO_2 through wheat decreased with increasing moisture content. The porosity of the wheat was kept constant (40.0%) at 13% and 15% moisture content but decreased slightly to 39.9% at 18% moisture content. At 10°C the diffusion coefficients of CO_2 through wheat for 13%, 15% and 18% moisture content are 0.0346, 0.0278 and $0.0273 \text{ cm}^2/\text{s}$ respectively. Values of diffusion coefficient at 15% and 18% moisture content are significantly different ($P > 0.05$) from the value at 13% moisture content but are not significantly different from each other (Appendix A).

It appears that when moisture content of wheat is raised above 13% the affinity of CO_2 for the water decreases

Table 5.2: Effect of Porosity on Diffusion Coefficient through Wheat (13% moisture content) at 10°C and CO₂ Diffusing Downward.

Porosity (%)	Diffusion coefficient* (cm ² /s)
37.9	0.0334 ± 0.0012
40.0	0.0346 ± 0.0020
41.9	0.0337 ± 0.0020

* N = 3, mean and standard deviation.

the diffusion coefficient. The constant coefficient of diffusion above 15% moisture content suggests that the pore sites along the seed coat covering the endosperm available for water are saturated at about 15% moisture content and thus the amount of water which interacts with CO_2 stays constant.

5.5 Effect of Temperature on Diffusion Coefficient through Wheat and Rapeseed:

With an increase in temperature the diffusion coefficient of CO_2 through wheat and rapeseed is increased (Fig. 5.3). Bailey (1959) has indicated the temperature dependence of the diffusion rate of O_2 through wheat and he suggested that in the temperature range 1.7°C to 42°C the relationship is satisfactorily described by a quadratic curve. In the present study the diffusion coefficient of CO_2 through wheat is best described by a quadratic curve ($R^2 = 0.9431$) in the temperature range of -10°C to 30°C . Jost (1960), Cunningham and Williams (1980) and Fuller and Giddings (1965) have reported that the diffusion coefficient is proportional to the $3/2$ power of the absolute temperature. The diffusion coefficients for both wheat and rapeseed follow this relationship in the temperature range of -10°C to 20°C , but from 20°C to 30°C the coefficients increase more rapidly.

It appears that the relationship between diffusion coefficient of gases through grains and temperature is better described by a quadratic relationship than by the $3/2$ power of temperature. Present theories do not explain this effect.

5.6 Effect of the Type of the Grain on Diffusion Coefficient:

The measured coefficients of diffusion of CO_2 through

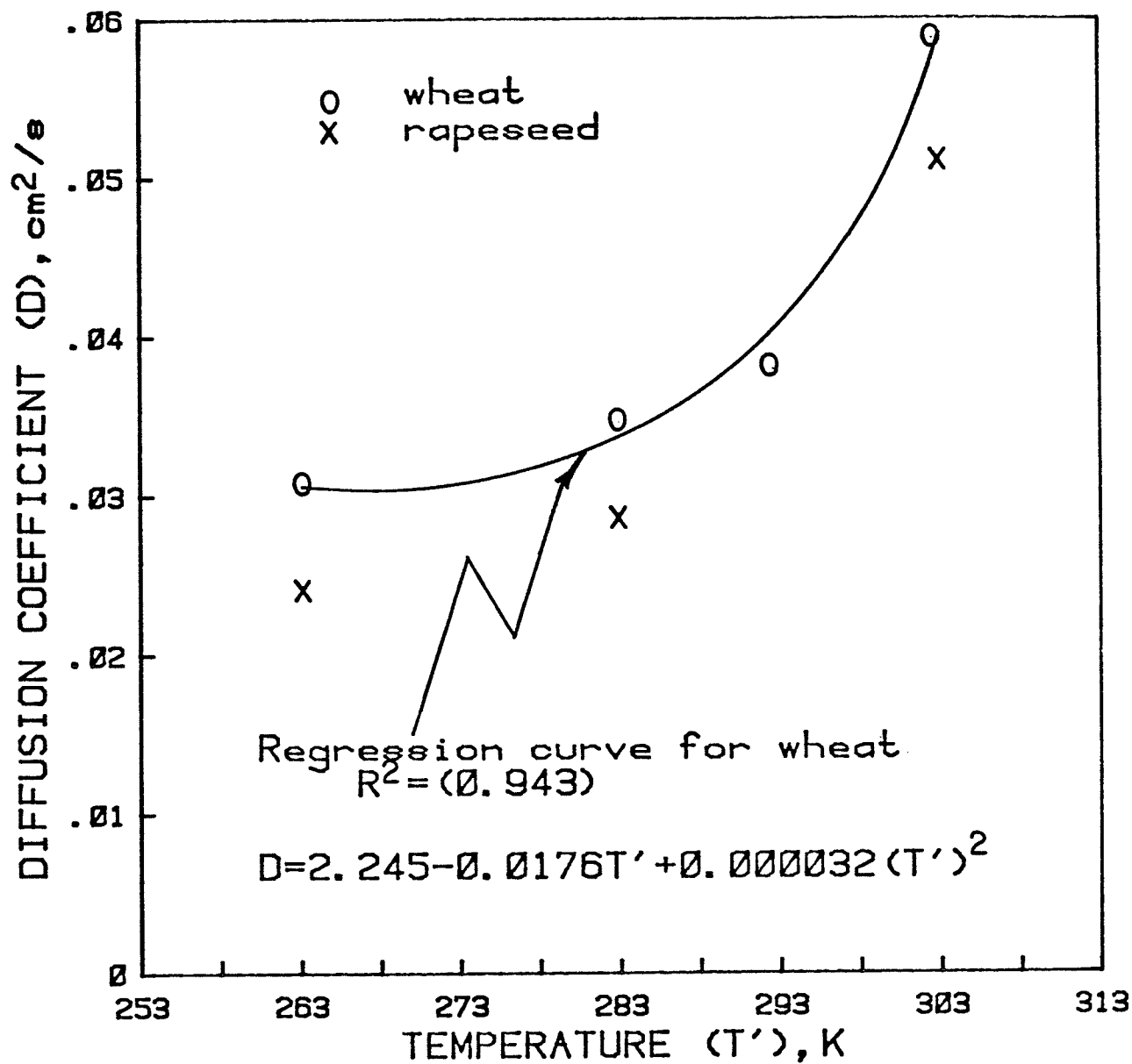


Fig. 5.3: Variation of diffusion coefficient with temperature for wheat (13% moisture content) and rapeseed (8% moisture content), CO_2 diffusing vertically downward.

rapeseed (8% moisture content and 34.5% porosity), wheat (13% moisture content and 40.0% porosity), corn 14% moisture content and 40.1% porosity) and oats (14.5% moisture content and 54.6% porosity) at 10°C are 0.0284, 0.0346, 0.0302 and 0.0391 cm²/s respectively.

The measured and predicted (by the quadratic relationship fitted to test data) coefficients of diffusion of CO₂ through wheat (13% moisture content and 38.9% porosity) at 20°C are 0.0373 and 0.0414 cm²/s respectively. Henderson and Oxley (1944) have reported the diffusion coefficient of CO₂ through has red spring (Manitoba No. 1) wheat (12% moisture content and 38% porosity) to be 0.0415 cm²/s at room temperature. The measured value of the diffusion coefficient of CO₂ through wheat (0.0374) is significantly different at the 5% level from the value of Henderson and Oxley but the predicted value based on the quadratic relationship of the diffusion coefficient and temperature (0.0414) is not significantly different from the value of Henderson and Oxley. The difference between my measured value and that of Henderson and Oxley can be further explained by the effect of moisture content of the grain because in the present experiments the moisture content was slightly higher (12.96%) than that observed by Henderson and Oxley (12%). Also Manitoba No. 1 in 1944 may have had different physical attributes than Neepawa.

Coefficients of diffusion of CO₂ through rapeseed, wheat, corn and oats have been compared in Fig. 5.4. Based on ascending porosity these grains are arranged as rapeseed, wheat, corn and oats but based on diffusion coefficient the order

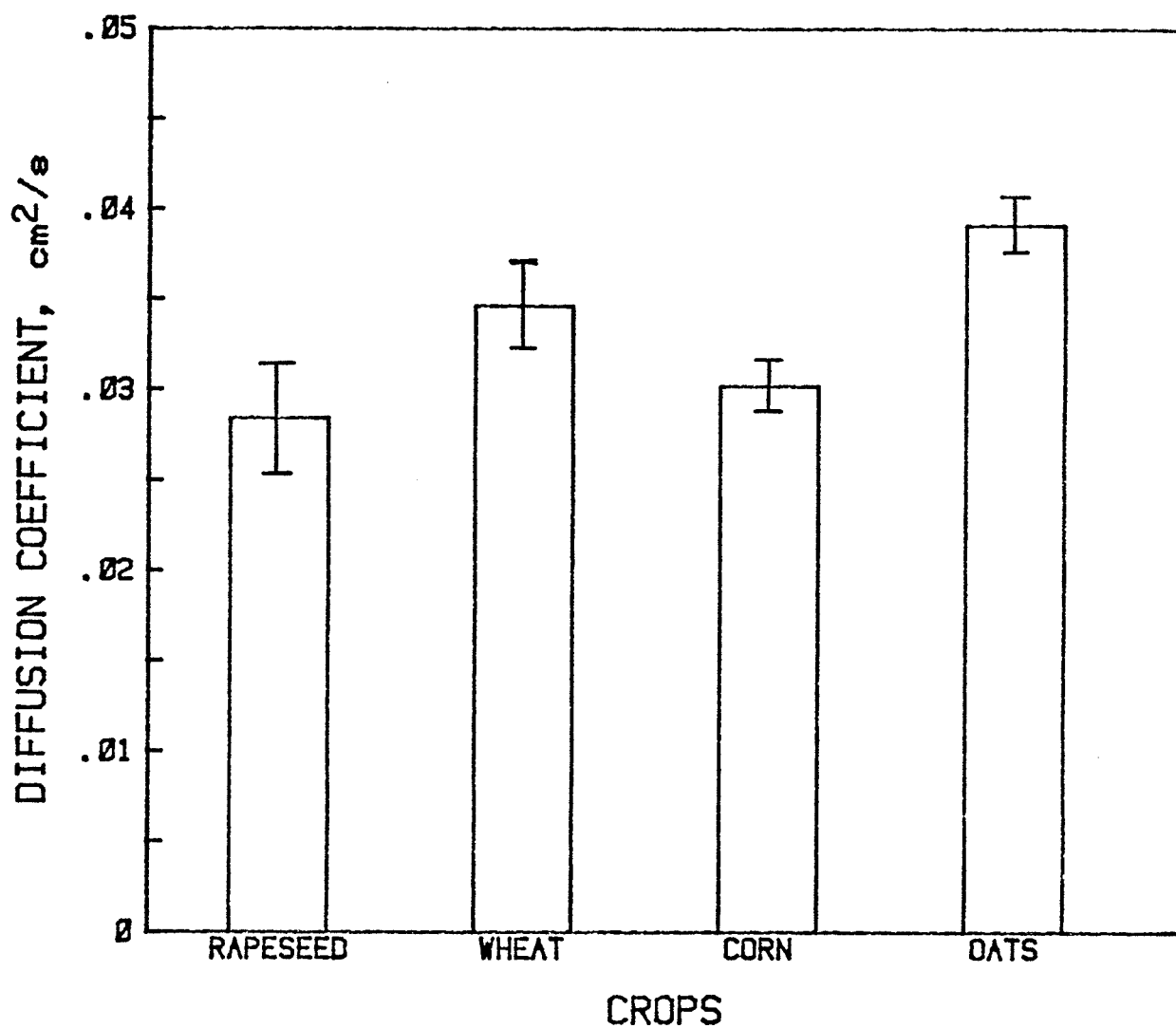


Fig. 5.4: Variation in diffusion coefficient with different crops at $10 \pm 1^\circ\text{C}$ temperature and straight grade grain moisture content (wheat 13%, rapeseed 8%, oats 14.5% and corn 14%) for CO_2 diffusing vertically downward. Number of replicates is 3.

is rapeseed, corn, wheat and oats. Furthermore the change in the diffusion coefficient is not proportional to the change in porosity. The reversal in order of wheat and corn suggests that some other factors in addition to grain porosity like shape, size and natural wrinkle on the seed coat, are affecting the diffusion coefficient. A similar phenomenon was observed by Bailey (1959). He found that rate of diffusion of oxygen through four seed bulks (corn, wheat, barley and oats) increased in order of increasing porosity of the seeds except for wheat and barley. In Bailey's study the porosity of corn was less than wheat whereas in the present study it was not. This may be because of differences in variety, year of harvest, shape and size of kernels and method of filling.

5.7 Detection of CO₂ in Granaries:

In Western Canada grain is harvested by combine and stored in the bins at mean temperatures as high as 36°C (Prasad et al. 1978). Most of the years grain is harvested dry (ca. 12-14% moisture content). High temperature (ca. 32-35°C) and relatively dry grain conditions are most suitable for important pest insects, such as the Cryptolestes ferrugineus (Steph.) to multiply optimally. Under these conditions some species of insects may increase 50 to 70 times a month (Howe 1965). Infestation in freshly stored grain can start with a few adult insects laying eggs in some parts of the grain bulk having some relatively moist pockets of sound kernels, mechanically damaged kernels and dockage. These insects are usually present

in uncleaned grain bins and may migrate from nearby infested grain. If unfavourable weather conditions prevail during the harvesting period the grain may be harvested damp. Such conditions will favour the growth of seed-borne fungi on this damp grain. Usually heavy insect and mite infestations that lead to creation of "hot spots" are restricted to the 30 cm layer of grain along the surface, while mold can grow along the entire vertical grain column (Sinha and Wallace 1966, Sinha 1971). Because of insect infestation or mold growth or both, carbon dioxide is produced in the stored grain. The diffusion of CO_2 produced at three different spoilage locations, in the absence of convection currents, has been studied in a 6-m diameter circular steel bin using finite element models (Singh and Muir 1981). The exact location of pockets of spoilage in farm granaries has rarely been documented in detail. It was therefore concluded that the best location to detect spoilage in grain bins by CO_2 measurement is the vicinity of the center of the bin.

Warm autumn grain cools slowly and unevenly in storage as winter approaches. The rate of cooling at the center depends on its distance from a cooling surface. Grain stored at 35°C during August in a 6-m diameter bin, stays above 30°C until mid-January (Yaciuk et al. 1975). Naturally occurring temperature gradients in the grain bin allows cool air to settle down near the wall and forces warm air up in the central portion of the bin. These convection currents may possibly carry

the CO_2 towards central portion of the bin. Due to lower temperatures near the wall the diffusion of CO_2 in the radial direction would be less than in the vertical direction (see section 5.5) and CO_2 would accumulate near the top center of the bin. Thus the most probable location for high levels of CO_2 accumulation in granaries is in the vicinity of the top center of the grain bin.

As spring approaches the grain warms up slowly. The confined insect population in an insect induced hot spot migrates toward the top of the bin and horizontally in the top layer of the bin (Sinha and Wallace 1966). Because of relatively low moisture content (ca. 13-14%) of the grain in the granary the chances of mold growth are less, and thus CO_2 produced in the other parts of the granary are also less. The CO_2 levels remain high near the top center of the grain bin.

During summer the grain near the bin ball is warmer than the central grain and thus convection currents reverse in direction. The downward movement of convection currents in the central portion of the bin may carry the CO_2 with it from the source of its production. Thus in summer the center of the bin also remains the most probable location for the occurrence of high levels of CO_2 . Therefore it is hypothesized that the best location in the grain bin to detect spoilage by measuring CO_2 levels in Western Canada would be in the vicinity of the center of the grain bin.

6. CONCLUSIONS

Based on the results of this study the following conclusions were drawn:

1. The diffusion coefficient of CO_2 through both rapeseed and wheat was independent of CO_2 flow direction in relation to the force of gravity.
2. The effect of variation in porosity of wheat (37.9% to 41.9%) on diffusion coefficient was statistically insignificant.
3. The coefficient of diffusion of CO_2 through wheat decreased with increasing moisture content from 13% to 15% while a further increase in moisture content to 18% was ineffective in changing the diffusion coefficient.
4. For wheat the relationship between diffusion coefficient and temperature is satisfactorily described by a quadratic function in the temperature range of -10°C to 30°C .
5. The measured coefficients of diffusion of CO_2 through rapeseed (8% moisture content), wheat (13% moisture content), corn (14% moisture content) and oats (14.5% moisture content), listed in order of increasing porosity were 0.0284, 0.0346, 0.0302 and $0.0391 \text{ cm}^2/\text{s}$ respectively.
6. The diffusion coefficient of CO_2 through grains is not proportional to the porosity of the grains.

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APPENDIX A

OBSERVED CO₂ CONCENTRATIONS AT THE INLET OF THE WHEAT COLUMN AT DIFFERENT TIME INTERVALS AFTER INITIAL GAS INJECTION, MEASURED CO₂ CONCENTRATIONS AT THE OUTLET OF THE WHEAT COLUMN AND THE CALCULATED DIFFUSION COEFFICIENTS. CORRELATION COEFFICIENTS (R²) ARE GREATER THAN 0.99 EXCEPT WHERE SPECIFIED.

Experiment No.	Carbon dioxide diffusion direction	Moisture* content (%)	Temperature (°C)	CO ₂ concentrations* at the inlet (µg/cm ³)				CO ₂ concentration at outer end (µg/cm ³)	Diffusion coefficient (cm ² /s)	Mean diffusion coefficient (cm ² /s)
				21h	27h	33h	45h			
Wheat (40.0% porosity)										
1	↓	12.94 ± 0.13	10.0 ± 1.0	91.8 ± 0.4	84.5 ± 0.3	77.6 ± 0.2	65.9 ± 0.5	1.0 ± 0.10	0.0371	0.0346
2	↓	12.94 ± 0.13	10.0 ± 1.0	70.7 ± 0.4	65.9 ± 0.3	61.1 ± 0.6	52.6 ± 0.3	0.9 ± 0.05	0.0333	
3	↓	12.94 ± 0.13	10.0 ± 1.0	95.5 ± 0.2	87.8 ± 0.4	81.2 ± 0.4	70.9 ± 0.6	1.0 ± 0.06	0.0335	
4	→	12.94 ± 0.13	10.0 ± 1.0	61.0 ± 0.2	57.5 ± 0.2	53.1 ± 0.3	44.7 ± 0.1	0.9 ± 0.05	0.0353	0.0347
5	→	12.94 ± 0.13	10.0 ± 1.0	59.0 ± 0.3	55.1 ± 0.1	50.6 ± 0.3	42.8 ± 0.2	0.8 ± 0.00	0.0362	
6	→	12.94 ± 0.13	10.0 ± 1.0	102.3 ± 0.7	96.6 ± 0.5	88.6 ± 0.5	76.8 ± 0.5	0.8 ± 0.09	0.0326	
7	↑	12.94 ± 0.13	10.0 ± 1.0	76.9 ± 0.4	72.8 ± 0.8	67.2 ± 0.6	57.9 ± 0.4	0.9 ± 0.10	0.0324	0.0338
8	↑	12.94 ± 0.13	10.0 ± 1.0	89.1 ± 0.3	80.7 ± 0.2	75.6 ± 0.2	64.2 ± 0.4	0.9 ± 0.00	0.0360	
9	↑	12.94 ± 0.13	10.0 ± 1.0	100.1 ± 0.7	93.7 ± 0.5	86.7 ± 0.2	74.8 ± 0.5	1.0 ± 0.06	0.0329	
Wheat (37.9% porosity)										
10	↓	13.06 ± 0.11	10.0 ± 1.0	58.1 ± 0.4	54.0 ± 0.2	49.5 ± 0.3	42.9 ± 0.2	1.1 ± 0.10	0.0345	0.0334
11	↓	13.06 ± 0.11	10.0 ± 1.0	35.1 ± 0.4	32.6 ± 0.1	30.6 ± 0.1	26.0 ± 0.1	0.9 ± 0.05	0.0337	
12	↓	13.06 ± 0.11	10.0 ± 1.0	115.5 ± 0.5	107.2 ± 0.3	99.5 ± 0.5	86.8 ± 0.3	1.0 ± 0.06	0.0320	
Wheat (41.9% porosity)										
13	↓	13.06 ± 0.11	10.0 ± 1.0	99.5 ± 0.6	91.3 ± 0.6	86.1 ± 0.8	73.8 ± 0.3	1.0 ± 0.10	0.0323	0.0337
14	↓	13.06 ± 0.11	10.0 ± 1.0	54.5 ± 0.2	51.2 ± 0.3	47.1 ± 0.3	39.7 ± 0.2	0.9 ± 0.05	0.0360	
15	↓	13.06 ± 0.11	10.0 ± 1.0	107.0 ± 0.5	100.0 ± 0.4	93.3 ± 0.5	80.0 ± 0.5	1.0 ± 0.08	0.0329	
Wheat (40.0% porosity)										
16	↓	15.21 ± 0.03	10.0 ± 1.0	117.6 ± 0.3	110.1 ± 0.4	103.5 ± 0.4	92.1 ± 0.5	1.2 ± 0.10	0.0276	0.0278
17	↓	15.21 ± 0.03	10.0 ± 1.0	130.7 ± 0.7	122.2 ± 0.2	116.4 ± 0.4	102.9 ± 0.2	1.1 ± 0.06	0.0267	
18	↓	15.21 ± 0.03	10.0 ± 1.0	96.2 ± 0.4	89.3 ± 0.2	83.9 ± 0.8	72.1 ± 0.1	0.8 ± 0.00	0.0292	

Experiment No.	Carbon dioxide diffusion direction	Moisture* content (%)	Temperature (°C)	CO ₂ concentrations* at the inlet (µg/cm ³)				CO ₂ concentration at outer end§ (µg/cm ³)	Diffusion coefficient (cm ² /s)	Mean diffusion coefficient (cm ² /s)
				21h	27h	33h	45h			
Wheat (39.9% porosity)										
19	↓	17.95 ± 0.12	10.0 ± 1.0	76.0 ± 0.2	73.2 ± 1.0	67.6 ± 0.2	60.0 ± 0.3	1.1 ± 0.05	0.0275	0.0273
20	↓	17.95 ± 0.12	10.0 ± 1.0	88.1 ± 0.2	82.8 ± 0.2	77.6 ± 0.2	69.3 ± 0.2	1.0 ± 0.08	0.0272	
21	↓	17.95 ± 0.12	10.0 ± 1.0	144.5 ± 0.3	135.3 ± 0.4	127.4 ± 0.3	113.5 ± 0.2	1.1 ± 0.13	0.0271	
Wheat (40.0% porosity)										
22	↓	13.06 ± 0.11	-10.0 ± 1.0	115.2 ± 0.6	106.8 ± 0.5	99.9 ± 0.4	87.3 ± 0.9	1.0 ± 0.05	0.0310	0.0306
23	↓	13.06 ± 0.11	-10.0 ± 1.0	98.6 ± 0.4	93.1 ± 0.6	87.0 ± 0.2	75.9 ± 0.3	1.0 ± 0.05	0.0296	
24	↓	13.06 ± 0.11	-10.0 ± 1.0	99.4 ± 1.0	92.2 ± 0.6	86.2 ± 0.4	75.3 ± 0.6	1.0 ± 0.05	0.0311	
25	↓	12.96 ± 0.10	20.0 ± 1.5	119.7 ± 0.7	108.8 ± 0.3	101.6 ± 0.1	85.8 ± 0.2	0.9 ± 0.10	0.0368	0.0374
26	↓	12.96 ± 0.10	20.0 ± 1.5	33.9 ± 0.3	31.3 ± 0.1	28.9 ± 0.3	24.4 ± 0.6†	1.0 ± 0.15	0.0374	
27	↓	12.96 ± 0.10	20.0 ± 1.5	43.3 ± 0.2	39.7 ± 0.2	36.4 ± 0.3	30.9 ± 0.2	0.9 ± 0.20	0.0379	
28ζ	↓	12.96 ± 0.10	30.0 ± 1.5	106.6 ± 0.5	93.6 ± 0.6	81.7 ± 0.2	65.4 ± 0.5	0.8 ± 0.05	0.0584	0.0593
29	↓	12.96 ± 0.10	30.0 ± 1.5	126.7 ± 0.6	110.6 ± 0.6	97.9 ± 0.3	73.1 ± 0.4	0.8 ± 0.13	0.0582	
30	↓	12.96 ± 0.10	30.0 ± 1.5	35.2 ± 0.2	31.0 ± 0.2	26.7 ± 0.2	20.1 ± 0.2	0.8 ± 0.05	0.0614	

* N=6, mean and standard deviation

§ N=4, mean and standard deviation

↓ Vertically downward

→ Horizontal

↑ Vertically upward

† Maximum deviation from the mean (2.5%)

ζ R²=0.985

APPENDIX B

OBSERVED CO₂ CONCENTRATIONS AT THE INLET OF THE RAPESEED COLUMN AT DIFFERENT TIME INTERVALS AFTER INITIAL GAS INJECTION, MEASURED CO₂ CONCENTRATIONS AT THE OUTLET OF THE RAPESEED COLUMN AND THE CALCULATED DIFFUSION COEFFICIENTS. CORRELATION COEFFICIENTS (R²) ARE GREATER THAN 0.99 EXCEPT WHERE SPECIFIED.

Experiment No.	Carbon dioxide diffusion direction	Moisture* content (%)	Temperature (°C)	CO ₂ concentrations* at the inlet (µg/cm ³)				CO ₂ concentration at outer ends (µg/cm ³)	Diffusion coefficient (cm ² /s)	Mean diffusion coefficient (cm ² /s)
				21h	27h	33h	45h			
Rapeseed (34.5% porosity)										
1	↓	8.14 ± 0.08	10.0 ± 1.0	123.9 ± 0.8	119.0 ± 0.6	111.3 ± 0.5	98.7 ± 0.7	0.9 ± 0.14	0.0262	0.0284
2	↓	8.14 ± 0.08	10.0 ± 1.0	54.5 ± 0.2	51.0 ± 0.3	47.1 ± 0.1	41.3 ± 0.1	1.0 ± 0.10	0.0317	
3†	↓	8.14 ± 0.08	10.0 ± 1.0	158.1 ± 0.6	146.8 ± 0.5	138.3 ± 0.7	123.7 ± 0.6	1.0 ± 0.10	0.0274	
4	→	8.14 ± 0.08	10.0 ± 1.0	88.7 ± 0.3	84.6 ± 0.5	78.6 ± 0.3	69.1 ± 0.5	0.9 ± 0.00	0.0287	0.0290
5	→	8.14 ± 0.08	10.0 ± 1.0	77.4 ± 0.4	71.8 ± 0.6	66.8 ± 0.3	58.5 ± 0.4	1.0 ± 0.06	0.0315	
6	→	8.14 ± 0.08	10.0 ± 1.0	176.3 ± 0.7	164.8 ± 0.4	155.5 ± 0.5	138.7 ± 0.4	1.0 ± 0.10	0.0268	
7	↑	8.14 ± 0.08	10.0 ± 1.0	157.8 ± 0.7	147.9 ± 0.8	140.7 ± 0.7	124.5 ± 0.6	1.0 ± 0.11	0.0259	0.0269
8	↑	8.14 ± 0.08	10.0 ± 1.0	31.3 ± 0.1	29.0 ± 0.1	27.2 ± 0.1	23.6 ± 0.1	1.0 ± 0.05	0.0287	
9	↑	8.14 ± 0.08	10.0 ± 1.0	192.9 ± 1.1	183.0 ± 0.7	172.2 ± 0.5	153.2 ± 0.4	1.1 ± 0.10	0.0261	
10	↓	7.99 ± 0.44	-10.0 ± 1.0	170.5 ± 0.9	160.6 ± 0.7	152.7 ± 0.4	137.8 ± 0.6	0.9 ± 0.08	0.0239	0.0236
11	↓	7.99 ± 0.44	-10.0 ± 1.0	175.6 ± 0.6	166.6 ± 0.7	160.8 ± 0.7	143.3 ± 0.4	1.2 ± 0.20	0.0227	
12	↓	7.99 ± 0.44	-10.0 ± 1.0	128.4 ± 0.4	121.3 ± 0.4	115.2 ± 0.0	103.7 ± 0.3	1.0 ± 0.10	0.0241	
13	↓	7.99 ± 0.44	30.0 ± 1.5	91.3 ± 0.4	85.3 ± 0.6	75.8 ± 0.1	61.2 ± 0.2	0.8 ± 0.10	0.0446	0.0521
14	↓	7.99 ± 0.44	30.0 ± 1.5	101.9 ± 0.3	90.7 ± 0.3	78.9 ± 0.4	60.0 ± 0.0	0.8 ± 0.05	0.0573	
15	↓	7.99 ± 0.44	30.0 ± 1.5	62.0 ± 0.4	55.7 ± 0.2	48.6 ± 0.4	37.8 ± 0.3	0.8 ± 0.10	0.0545	

* N=6, mean and standard deviation

§ N=4, mean and standard deviation

↓ Vertically downward

† R²=0.989

→ Horizontal

↑ Vertically upward

APPENDIX C

OBSERVED CO₂ CONCENTRATIONS AT THE INLET OF THE COLUMN OF OATS AND CORN AT DIFFERENT TIME INTERVALS AFTER INITIAL GAS INJECTION, MEASURED CO₂ CONCENTRATIONS AT THE OUTLET OF THE COLUMN OF OATS AND CORN AND THE CALCULATED DIFFUSION COEFFICIENTS. CORRELATION COEFFICIENTS (R²) ARE GREATER THAN 0.99.

Experiment No.	Carbon dioxide diffusion direction	Moisture* content (%)	Temperature (°C)	CO ₂ concentrations* at the inlet (µg/cm ³)				CO ₂ concentration at outer end§ (µg/cm ³)	Diffusion coefficient (cm ² /s)	Mean diffusion coefficient (cm ² /s)
				21h	27h	33h	45h			
Oats (54.6% porosity)										
1	↓	14.55 ± 0.08	10.0 ± 1.0	77.0 ± 0.4	70.1 ± 0.1	64.7 ± 0.2	54.6 ± 0.1	1.0 ± 0.05	0.0382	0.0391
2	↓	14.55 ± 0.08	10.0 ± 1.0	48.3 ± 0.3	44.2 ± 0.0	40.6 ± 0.3	33.6 ± 0.2	1.1 ± 0.14	0.0407	
3	↓	14.55 ± 0.08	10.0 ± 1.0	99.2 ± 0.5	90.6 ± 0.3	83.0 ± 0.2	70.3 ± 0.5	1.3 ± 0.14	0.0385	
Corn (40.1% porosity)										
4	↓	14.15 ± 0.05	10.0 ± 1.0	130.0 ± 0.5	121.0 ± 0.3	113.0 ± 0.2	100.0 ± 0.4	0.9 ± 0.14	0.0294	0.0302
5	↓	14.15 ± 0.05	10.0 ± 1.0	68.8 ± 0.1	63.9 ± 0.3	59.9 ± 0.1	52.5 ± 0.2	1.2 ± 0.20	0.0305	
6	↓	14.15 ± 0.05	10.0 ± 1.0	82.3 ± 0.3	76.3 ± 0.2	71.5 ± 0.4	62.5 ± 0.3	1.0 ± 0.10	0.0308	

* N=6, mean and standard deviation

§ N=4, mean and standard deviation

↓ Vertically downward

Appendix D

FINITE ELEMENT MODELLING OF CARBON DIOXIDE DIFFUSION IN
STORED WHEAT

ASAE Paper No. NCR 81-019

PAPER NO. NCR 81-019FINITE ELEMENT MODELLING OF CARBON DIOXIDE
DIFFUSION IN STORED WHEAT

by

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North Central Region ASAE and
Manitoba Region CSAE

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Winnipeg, Manitoba
October 16 and 17, 1981

SUMMARY:

Using a finite element model the diffusion of CO₂ from pockets of spoiled wheat located at three depths in a grain bin has been compared for homogeneous Neumann and Dirichlet boundary conditions at the bin wall. In the absence of prior knowledge of the location of the hot spot a sensor capable of detecting CO₂ levels of 2 g·m⁻³ (0.1%) should be located at the center of the bin.

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FINITE ELEMENT MODELLING OF CARBON DIOXIDE DIFFUSION IN STORED WHEAT

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ABSTRACT

Incipient deterioration of stored grain may be detected by measuring the increased carbon dioxide (CO_2) produced by spoilage organisms and the grain. Using a finite element model the diffusion of CO_2 from a pocket of spoiled wheat located at three depths (viz 0.3 m, 2.0 m and 4.3 m from the top surface of the wheat bulk) has been compared for the two cases of homogeneous Neumann and Dirichlet boundary conditions at the bin wall. The most suitable location for the sensing device is the center of the spoiling pocket and the required resolution of the detector should be at least $8 \text{ g}\cdot\text{m}^{-3}$ (0.41%). In absence of prior knowledge of the location of the hot spot a sensor capable of detecting CO_2 levels of $2 \text{ g}\cdot\text{m}^{-3}$ (0.1%) should be located at the center of the bin.

INTRODUCTION

Over 80 Mt of grain and oilseeds, worth more than 3 billion dollars are stored in elevators and on farms in Canada with little or no equipment to detect any loss in quality or quantity due to deterioration. The presently employed monitoring system to detect spoilage in bulks is to take point measurements of temperature in the bulk. Because of the low thermal diffusivity of grain a point temperature measurement must be within about 0.5 m of an active spoilage spot to detect the spoilage (Sinha and Wallace 1965). Measured temperatures cannot be readily interpreted without prior knowledge of the temperature history of the grain bin. As an example a temperature of 35°C in a large bin in mid-winter may mean that there is an active hot spot or that the grain has not yet begun to cool at the center of the bin (Yaciuk et al. 1975).

The presence of a mouldy odour is a method frequently used by elevator managers to detect spoiled rapeseed (Mills 1976). But the managers report that considerable spoilage has occurred before they are able to detect it by odour.

Consequently there appears to be a need for a new monitoring system, that can warn the storage manager or farmer when his stored product begins to undergo unacceptable deterioration. Previous work (Muir et al. 1980) has shown that intergranular carbon dioxide (CO_2) concentrations can be indicators of

grain spoilage, because CO_2 is one of the by-products of decomposed carbohydrates. The measured CO_2 concentrations can be readily compared with ambient air and knowledge of the storage history is not required to interpret the readings.

A project to develop a scientifically valid and commercially feasible monitoring system to detect deterioration of cereal grains and oilseeds during storage in large bulks was undertaken. Rates of production of CO_2 in wheat and rapeseed at different temperatures and moisture contents (White et al. 1981) and diffusion properties of CO_2 through wheat and rapeseed (Singh 1981) have been studied. Field tests to study the rate of diffusion of CO_2 through and out of large bulks of cereal grains and oilseeds stored in various types and sizes of bins are being conducted.

In the study reported here a finite element model of the diffusion of CO_2 through wheat was used to predict the required resolution and the most suitable bin location for a spoilage sensing device.

FORMULATION OF THE PROBLEM

The diffusion of gases from a pocket of spoiled grain is governed by Fick's Second law of diffusion (Jost 1960):

$$\nabla \cdot (D \nabla C) = \frac{\partial C}{\partial t} \quad (1)$$

where: C is the concentration of diffusing gas, $[\text{ML}^{-3}]$

D is the diffusivity or diffusion coefficient, $[\text{L}^2\text{T}^{-1}]$

t is time, $[\text{T}]$

For a homogeneous material the material property, diffusivity, is independent of position, thus Eq. (1) is simplified to:

$$\nabla^2 C = \frac{1}{D} \frac{\partial C}{\partial t} \quad (2)$$

When expanded, Eq. (2) results in the general three dimensional diffusion equation in Cartesian Coordinates:

$$\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} = \frac{1}{D} \frac{\partial C}{\partial t} \quad (3)$$

and in cylindrical coordinates, for the case of axial symmetry:

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{\partial^2 C}{\partial z^2} = \frac{1}{D} \frac{\partial C}{\partial t} \quad (4)$$

For steady state conditions concentration does not change with time so the rate of change of concentration with time becomes zero and Eq. (4) becomes:

$$D\left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right) = 0 \quad (5)$$

Eq. (5) has been solved for six distinct finite element (FE) models with homogeneous Dirichlet and Neumann boundary conditions as defined in Fig. 1 (Neuman and Narasimham 1977, Narasimham et al. 1977).

ASSIGNMENT OF BOUNDARY CONDITIONS

A circular steel bin with a concrete floor, 6 m in diameter and filled to a height of 4.6 m with wheat (14% moisture content wet basis and diffusion coefficient $0.01368 \text{ m}^2\text{h}^{-1}$) (Singh 1981) was considered for the study.

The concrete floor of the bin was assumed to be impermeable to the diffusing carbon dioxide gas thus resulting in the homogeneous Neumann boundary condition ($\partial c / \partial n = 0$). This condition is analogous to an open circuit in Electrical Engineering field problems and an insulated boundary in heat conduction problems.

Due to symmetry about the central axis and assuming no variation in the concentration with the angle θ (i.e. around the bin), the boundary at the center of the bin is also homogeneous Neumann.

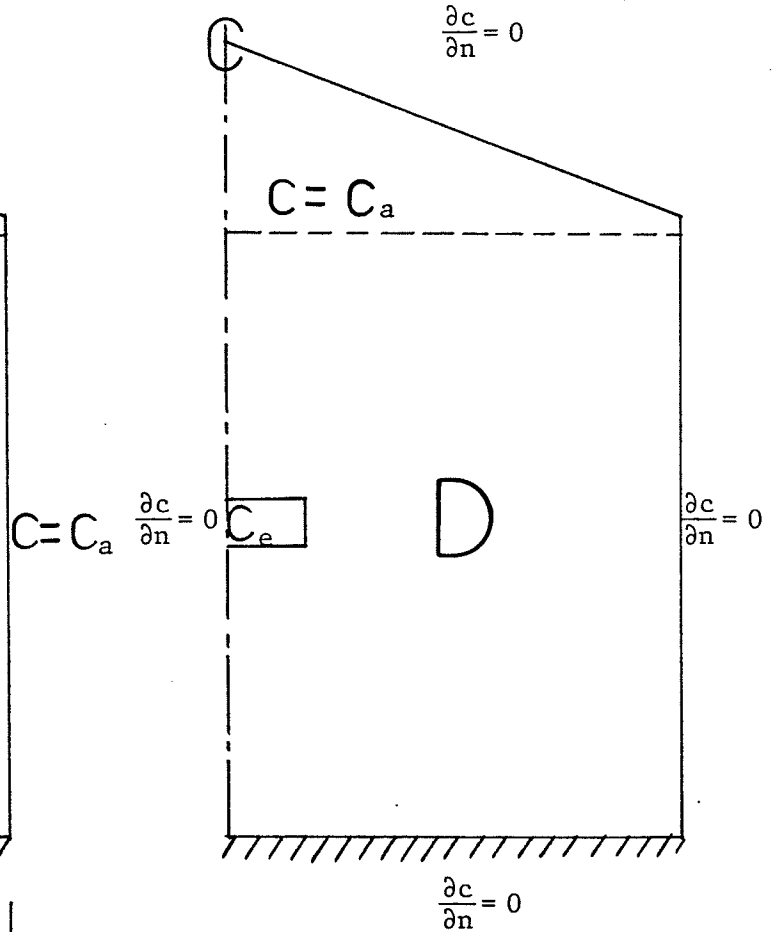
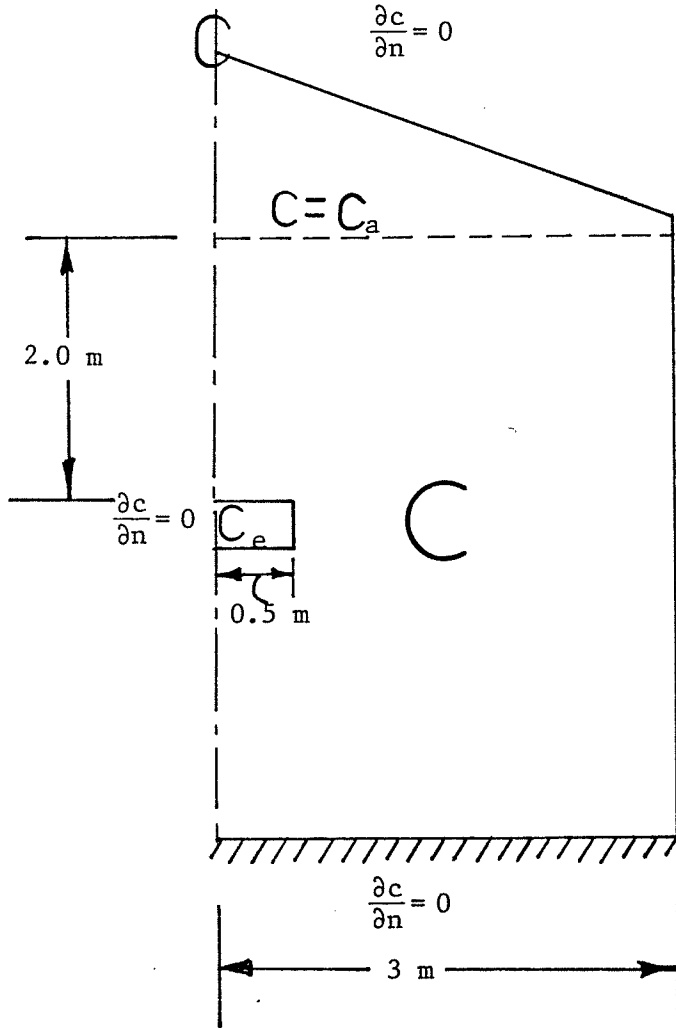
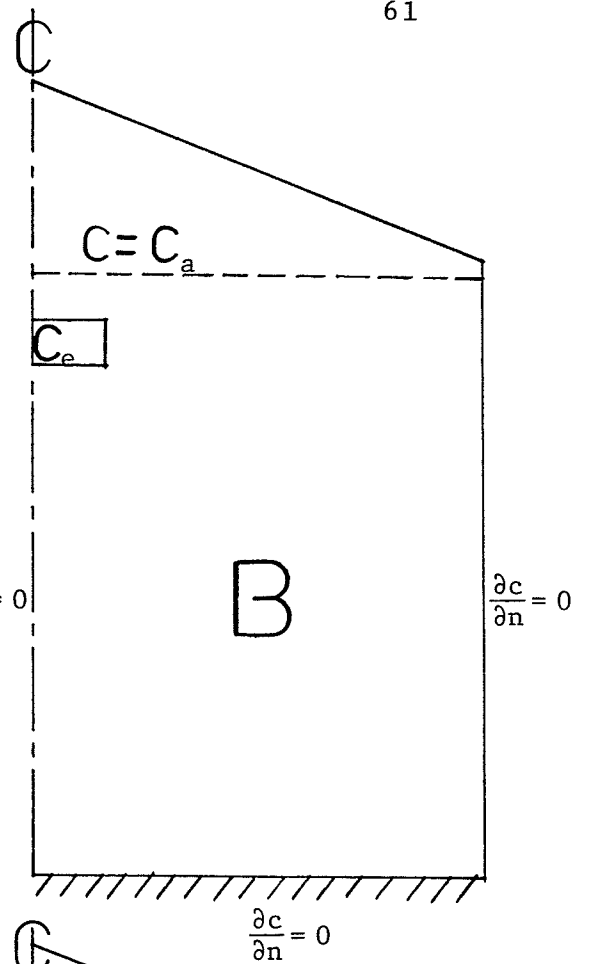
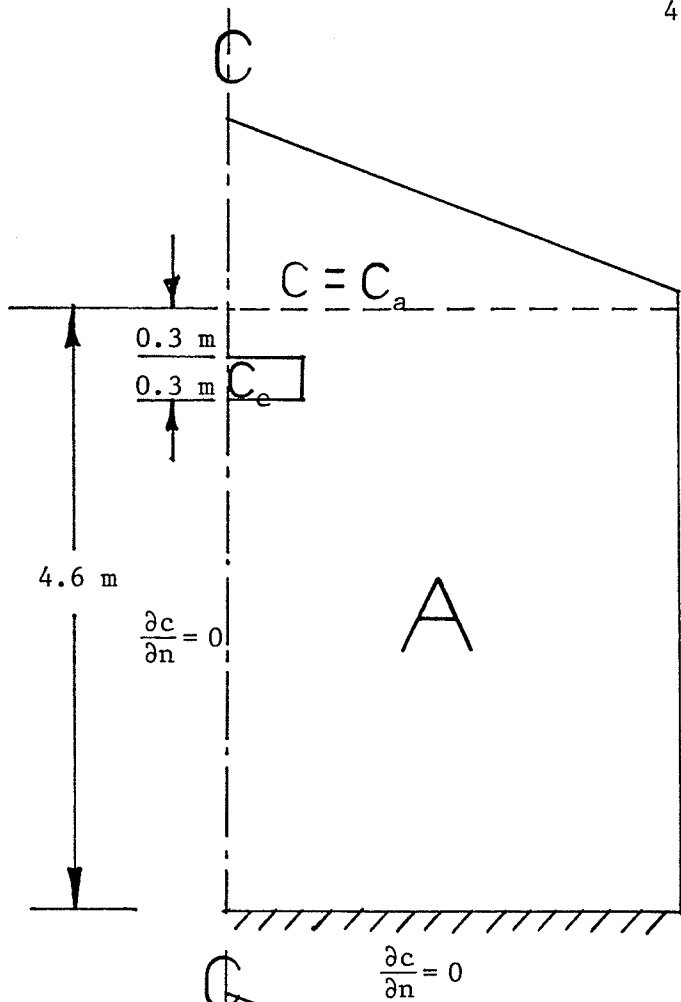
The top surface of grain is open to atmospheric air. On the assumption that CO_2 leaving the grain mass is instantaneously diffused to the atmosphere, the CO_2 concentration at the top of the grain mass was defined to be constant and equal to the CO_2 concentration in the atmosphere ($0.9 \text{ g}\cdot\text{m}^{-3}$), leading to the Dirichlet boundary condition.

The bin wall was assumed to be (1) infinitely permeable to CO_2 thus leading to Dirichlet boundary condition, and (2), impermeable to CO_2 thus leading to the homogeneous Neumann boundary condition. These are two extreme cases which could occur in the field depending on the amount of leakage through the bin wall. Probably most steel bins would be somewhere between the two extremes. The rates of diffusion of CO_2 through bin walls are not yet known, thus the two extreme possibilities have been considered.

DETERMINATION OF LOCATION AND DIMENSIONS OF SPOILING POCKET

The spoiling disc was assumed to be 0.30 m deep, 1 m in diameter and located at a depth of 0.3 m from the top grain surface in the bin. Moisture migration and snow blowing into bins can cause hot spots to occur at this location (Muir et al. 1978, Muir et al. 1980), (Fig. 1A, B).

Moisture migration in the summer or the movement of melted snow water from the top to the bottom of the bin may result in hot spots developing at the bottom of the bin (Muir et al. 1978) (Fig. 1E, F).



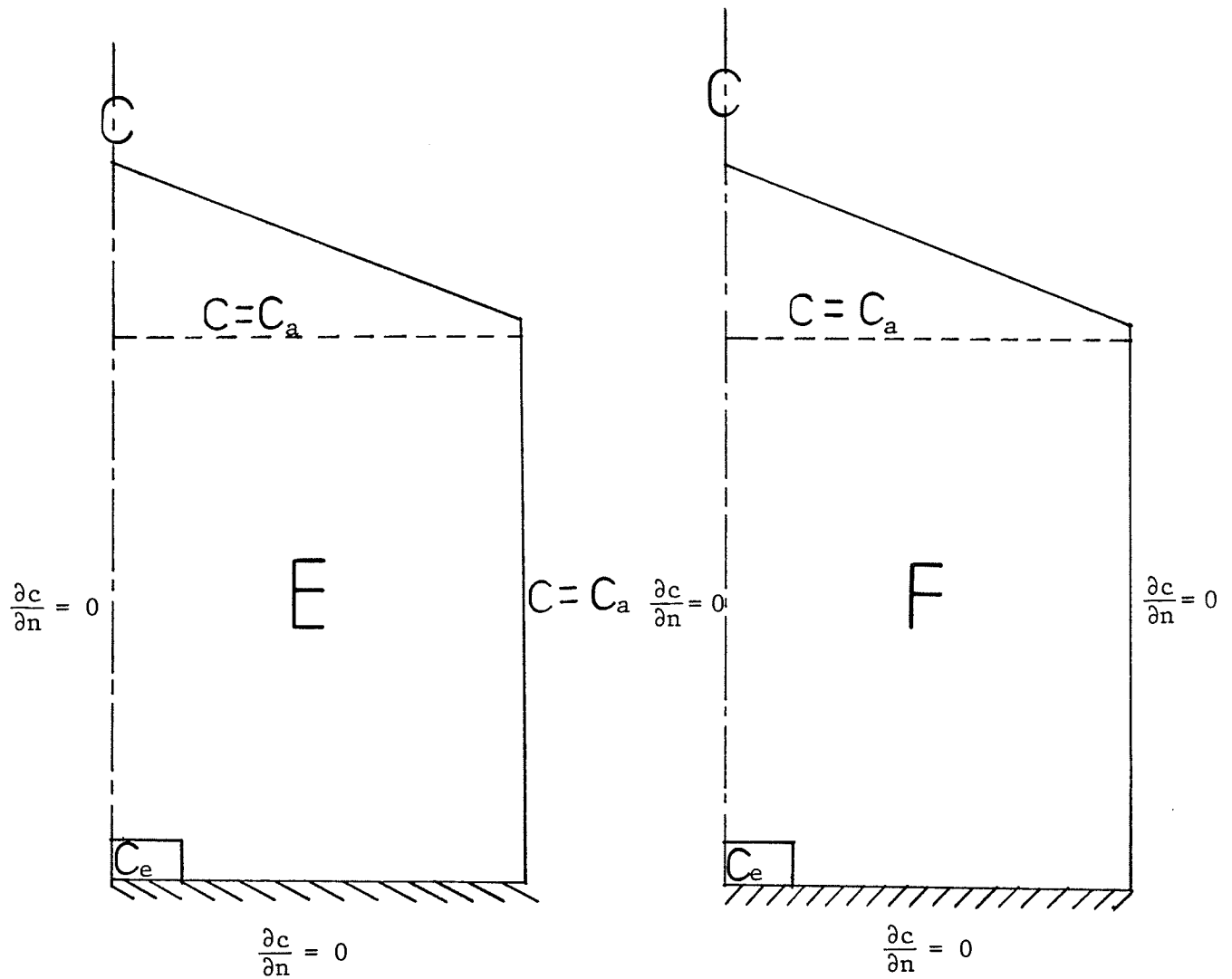


Fig. 1: Finite Element Models

C = Carbon dioxide concentration ($\text{g} \cdot \text{m}^{-3}$),

C_a = Carbon dioxide concentration in air ($0.9 \text{ g} \cdot \text{m}^{-3}$),

C_e = Spoiling pocket CO_2 concentration ($\text{g} \cdot \text{m}^{-3}$),

$\frac{\partial c}{\partial n}$ = Concentration gradient in normal direction ($\text{g} \cdot \text{m}^{-4}$)

A third location for the spoiling disc was taken at the center of the bin, 2.0 m from the top grain surface (Fig. 1C, D).

The spoiling pocket was assumed to be at 30°C, 20% moisture content wet basis and producing CO₂ at a rate 0.006 gh⁻¹kg⁻¹ of wheat, based on equations of White et al. (1981). The Dirichlet boundary conditions in the spoilage pockets were determined on the basis of assuming constant concentrations within the pocket.

FINITE ELEMENT MODELLING

For the six boundary conditions (Fig. 1), Eq. (5) was solved by using MANFEP (Manitoba Finite Element Program) package (Stevens and Wexler 1978a, 1978b). The package of Fortran Subroutines is capable of accommodating the problems governed by the general symmetrical Laplacian or Helmholtz operators. The region under consideration is discretized into isoparametric triangular elements and the linear equations that result from the discretization are solved by the Zollenkopf bifactorization method. The basic principle behind the Variational Method is to seek a function ϕ (concentration C, g·m⁻³ in the present case), that under fairly broad conditions causes the minimization of the function, F, (Wexler 1974, 1976):

$$F = \iint [a(\frac{\partial^2 \phi}{\partial x^2})^2 + 2b \frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} + c(\frac{\partial \phi}{\partial y})^2 + d\phi^2 - 2\phi p] dx dy + \int_{c_1} (\sigma\phi^2 - 2h\phi) ds_1 \quad (6)$$

This minimizing function is the solution of the general two dimensional second order partial differential equation:

$$A \frac{\partial^2 \phi}{\partial x^2} + 2B \frac{\partial^2 \phi}{\partial x \partial y} + C \frac{\partial^2 \phi}{\partial y^2} + D \frac{\partial \phi}{\partial x} + E \frac{\partial \phi}{\partial y} + F\phi + G = P \quad (7)$$

which with proper values for the coefficients A, B, C, D, E, F, G and P could be reduced to Laplace or Helmholtz equation.

RESULTS AND DISCUSSIONS

An initial constant CO₂ concentration (18.5 g·m⁻³) was assumed to exist in the spoiling pocket. This was based on 2 g CO₂ in the spoiling pocket and assuming that the amount of CO₂ produced in each hour is equal to the amount diffused from the bin in 1 h for the six Finite Element (FE) models (Fig. 1). As the spoiling pocket is moved from the top to the bottom of the bin the amount diffused from the top of the bin, for CO₂ concentration of 18.5 g·m⁻³ at the pocket and for a bin wall open to the air, is reduced from 0.8 gh⁻¹ to 0.07 gh⁻¹. The amount diffused through the side is maximum (1.7 gh⁻¹) when the pocket

is near the center compared with 0.66 gh^{-1} with the pocket at the top and 1.28 gh^{-1} with the pocket at the bottom. This could be explained on the basis of geometrical considerations. For the same bin the distance from the pocket to the wall varies from 3 m to 5 m when the spoiling pocket is either near the top or the bottom whereas for the center location of the pocket the distance is 3.0 to 3.9 m. This results in nearly constant concentration gradients for the latter case in comparison with varied gradients for the former, and thus higher amounts of CO_2 diffused for the center location of the pocket than the top or bottom locations. The amount diffused from the top of the bin for the bin wall being impermeable to air and the same concentration ($18.5 \text{ g}\cdot\text{m}^{-3}$) at the pocket, reduces from 1.2 gh^{-1} to 0.6 gh^{-1} as the pocket is moved downward from the top open surface to the bottom.

For each of the six finite element models, the dynamic-equilibrium concentration level in the pocket (Table 1) was reached when the amount of CO_2 diffused from the bin was equal to the amount produced by the spoiling grain (White et al. 1981). For these concentration levels at the spoiling disc the lines of equi-concentration of CO_2 and CO_2 concentrations at 15 points in the bin were determined (Fig. 2 and Table 1).

With the assumed spoilage pocket the concentrations of CO_2 built up in the bin are low (Fig. 2, Table 1). This requires a sensing instrument with high resolution to detect spoilage in the bin. When the bin wall is permeable to the atmosphere, to detect spoilage within 2 m of an active hot spot an instrument capable of detecting $2 \text{ g}\cdot\text{m}^{-3}$ (0.1%) CO_2 is required (the CO_2 concentration in the ambient air is $0.9 \text{ g}\cdot\text{m}^{-3}$ (0.03%) by volume). To detect the spoilage within 1 m from the pocket the equipment should detect a CO_2 concentration of about $4 \text{ g}\cdot\text{m}^{-3}$ (0.2%). The best location to detect spoilage is in the vicinity of the active hot spot where the concentrations are highest, about 14 to 17 times that of atmospheric concentration.

The concentrations of CO_2 in the spoilage pocket are about the same (12.0 to $14.8 \text{ g}\cdot\text{m}^{-3}$) for four of the models considered (Table 1). A slightly lower concentration ($8.7 \text{ g}\cdot\text{m}^{-3}$) occurs with the spoilage pocket at the center with an open wall and almost double the concentration ($26.2 \text{ g}\cdot\text{m}^{-3}$) occurs with the spoilage pocket at the bottom and a closed wall. Therefore if the sensor can be located within the spoilage pocket it should be capable of accurately sensing CO_2 levels of at least $8 \text{ g}\cdot\text{m}^{-3}$ (0.4%).

CONCLUSIONS

1. To detect grain spoilage within 2 m of the spoilage location in grain storage models with open walls an instrument capable of detecting $2 \text{ g}\cdot\text{m}^{-3}$ CO_2 is required.
2. For the grain storage model with the hot spot developed at the bottom and with an impermeable wall the spoilage could be detected with a less sensitive instrument (capable of detecting $4 \text{ g}\cdot\text{m}^{-3}$) within 2 m of the active hot spot.

Table 1: Predicted CO₂ Concentrations (g·m⁻³) at 15 selected points for the six FE Models (Fig. 1).

Point Location		Spoilage Location					
Radius (m)	Height (m)	Top		Center		Bottom	
		Open Wall	Closed Wall	Open Wall	Closed Wall	Open Wall	Closed Wall
0.5	4.3	12.0*	14.3*	1.4	2.0	1.0	1.7
0.5	3.3	4.5	5.9	3.6	6.7	1.4	4.5
0.5	2.3	2.1	3.6	8.7*	14.8*	2.2	7.5
0.5	1.3	1.4	3.1	3.3	8.1	4.4	12.2
0.5	0.3	1.2	3.0	2.2	7.1	13.3*	26.2*
1.5	4.3	1.7	2.0	1.1	1.8	1.0	1.7
1.5	3.3	2.1	3.1	2.0	4.6	1.2	4.4
1.5	2.3	1.6	3.1	2.5	6.6	1.6	7.1
1.5	1.3	1.1	3.0	2.0	6.7	2.7	10.0
1.5	0.3	1.0	3.0	1.7	6.7	3.7	12.3
2.5	4.3	1.1	1.3	1.0	1.6	1.0	1.7
2.5	3.3	1.0	1.3	1.2	3.7	1.0	4.3
2.5	2.3	1.0	2.8	1.3	5.3	1.2	6.7
2.5	1.3	1.0	2.9	1.2	6.1	1.4	8.8
2.5	0.3	1.0	2.9	1.2	6.3	1.6	10.0

*Concentration of CO₂ in the spoilage pocket.

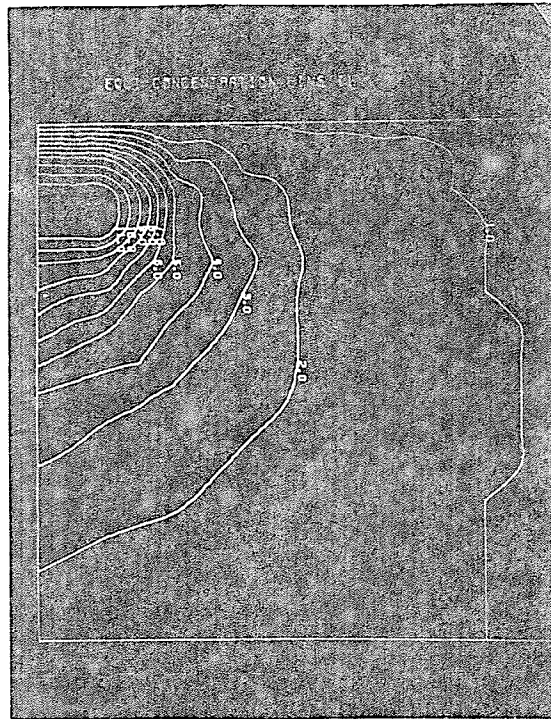


Fig. 2(A): Lines of equi-concentration of CO_2 in the top 3 m of a 6 m diameter wheat bin with the spoilage disc at the top and with an open wall (Fig. 1A).

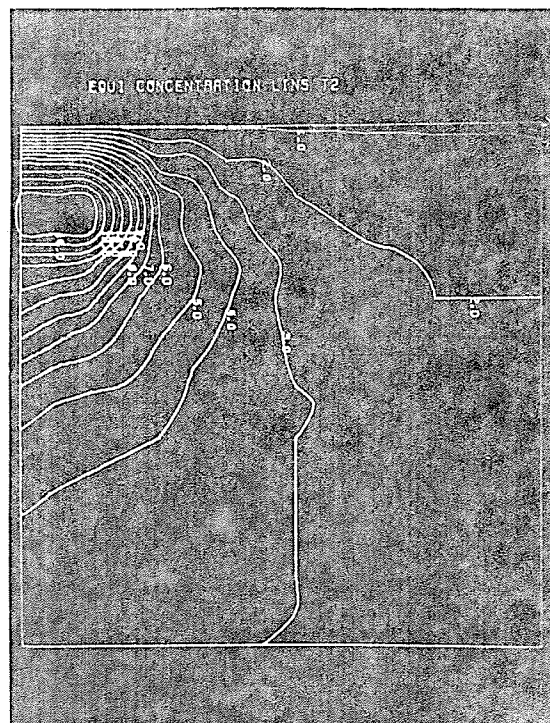


Fig. 2(B): Lines of equi-concentration of CO_2 in the top 3 m of a 6 m diameter wheat bin with the spoilage disc at the top and with a closed wall (Fig. 1B).

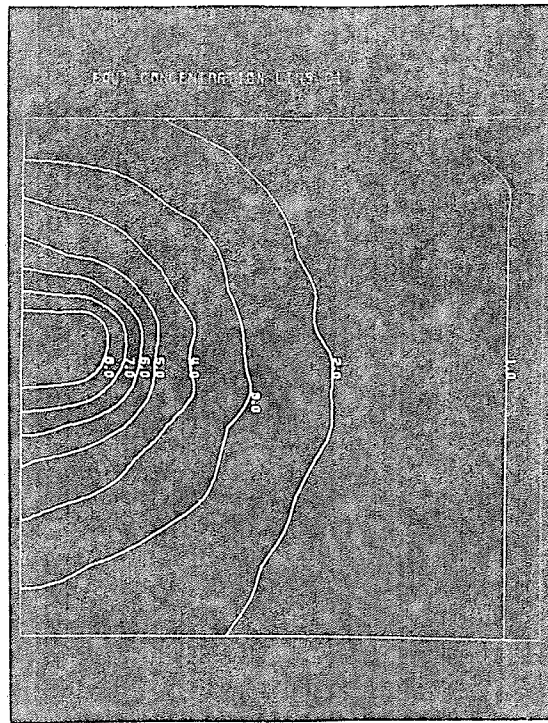


Fig. 2(C): Lines of equi-concentration of CO_2 in the wheat 0.8 to 3.8 m from the top grain surface of a 6 m diameter wheat bin with the spoilage disc at the centre and with an open wall (Fig. 1C).

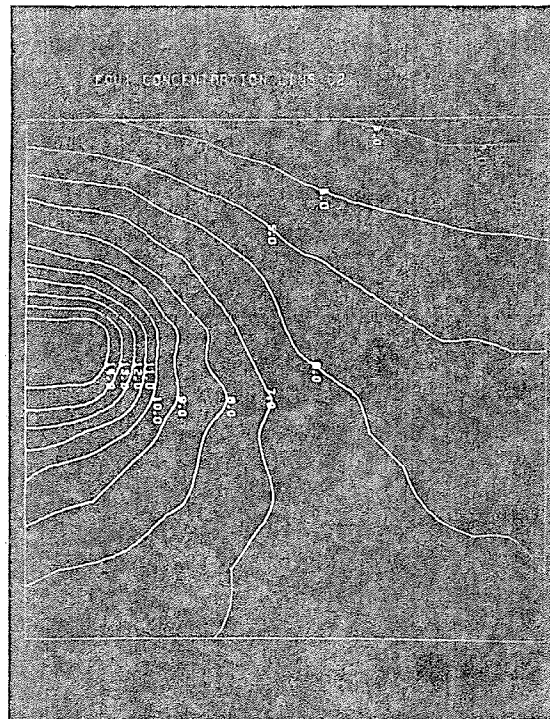


Fig. 2(D): Lines of equi-concentration of CO_2 in the wheat 0.8 to 3.8 m from the top grain surface of a 6 m diameter wheat bin with the spoilage disc at the centre and with a closed wall (Fig. 1D).

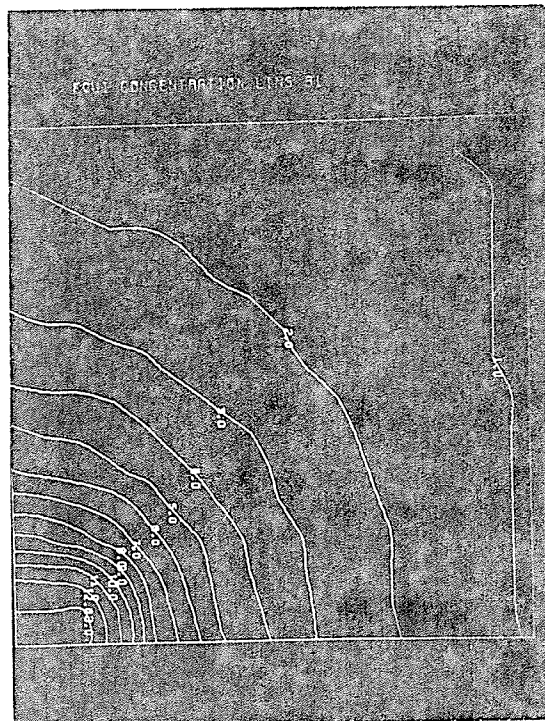


Fig. 2(E): Lines of equi-concentration of CO_2 in the bottom 3 m of a 6 m diameter wheat bin with the spoilage disc at the bottom and with an open wall (Fig. 1E).

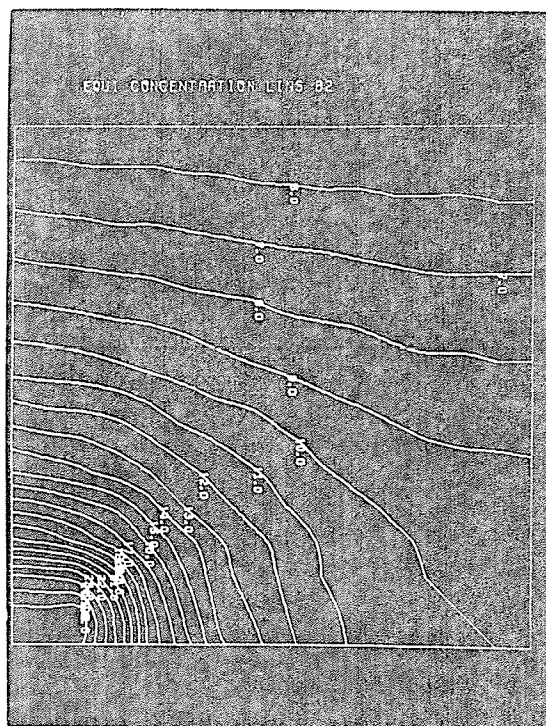


Fig. 2(F): Lines of equi-concentration of CO_2 in the bottom 3 m of a 6 m diameter wheat bin with the spoilage disc at the bottom and with a closed wall (Fig. 1F).

3. The best location for a sensor to detect spoilage is in the vicinity of the hot spot. If the sensor can be located within the spoilage pocket it should be capable of accurately sensing CO_2 levels of at least $8 \text{ g}\cdot\text{m}^{-3}$.
4. If the spoilage location is unknown but is located at any of the three considered locations, the most suitable location for the sensor is the center of the bin and the resolution of the instrument should be at least $2 \text{ g}\cdot\text{m}^{-3}$.

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