ROOM USE CALY

ABSTRACT

ENGINEERING ANALYSIS OF THE CONTROLLED ATMOSPHERE STORAGE

by David Gurevitz

An engineering analysis of some of the unit operations in several phases of controlled atmosphere (CA) storage design, and also some new approaches and suggestions are presented. This thesis deals with the CA storage of apples, but most of the observations are applicable to other types of produce.

The methods for control of the gas atmosphere have been critically reviewed and design information to make possible the selection and operation of equipment in a CA storage are presented. A new way to remove carbon dioxide using a selective membrane is suggested. A cost analysis of the various methods to remove excess carbon dioxide and oxygen in order to control the atmosphere is presented.

A method showing which system to use to control the atmosphere under particular conditions is outlined. As there are many alternatives to reduce carbon dioxide and oxygen, many different combinations can be used to control the atmosphere. As a guide to the choice of the most suitable method of controlling the atmosphere some preliminary elimination of these alternatives can be made easily according to the

deg (si: eli: ma (T

C.

13

0°

.

degree of tightness of the room and the management practices (single or multiple opening of room during season) used. After this elimination step, the most economical combination among the remaining can be chosen from tables of the cost data for CA operation (Tables 2J-3, 4, 5 and 6).

A critical literature review of the basic problems involved in using vapor barrier, gas seal materials and their location within the CA enclosure was made. The problems of moisture migration through the insulation, the effect of weather, reversible vapor flow and room operational conditions were discussed. A discussion of other possible solutions to water vapor transfer, CA gas tightness and pressures and temperature cycles in the CA storage is presented.

A new approach to precooling and air distribution in a CA apple storage room is suggested. In this approach all the spaces between the pallet boxes will be closed and the stacking will be arranged in such a way that the air will be forced to flow through the void spaces between the apples in the pallet boxes. Suction fans distributed uniformly on a false ceiling will be used to move the air through the system and give even distribution in the stack. The most important advantage of this method to CA operation is that there are no spaces between the boxes in the room and more apples can be stored in the same size room. There is a possible saving on storage construction

costs per bu. The time to reduce the oxygen level in the room is shorter than in a regular CA room and the gas consumption using burner units to reduce the oxygen is lower. This study was based on a theoretical analysis and since no experimental work was done at this stage it presents only a speculation of a new air distribution method.

ENGINEERING ANALYSIS OF THE CONTROLLED ATMOSPHERE STORAGE

Ву

David Gurevitz

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Food Science

1966

() Copyright by

DAVID GUREVITZ

1967



his maj

T

and con

T. I. H

G

as mem

constru

T

interes ship th

Depart

availa)

(

Mr. K

ACKNOWLEDGEMENTS

The author wishes to express particularly his appreciation to his major professor, Dr. I. J. Pflug for his inspiring advice, help and constant encouragement throughout this study.

Grateful appreciation is extended to Prof. L. J. Brazler, Dr. T. I. Hedrick, Dr. J. S. Boyd and Dr. R. F. Gonzalez who served as members of the committee, reviewed the manuscript and made constructive comments.

Thanks are expressed to the Whirlpool Corporation, for their interest and support of this project including the graduate assistant-ship that made this study possible.

To Dr. B. S. Schweigert, Chairman of the Food Science

Department, I should like to express my appreciation for making

available the graduate assistantship.

Grateful acknowledgement is extended to Mr. C. Borrero and Mr. K. Fox for their patience and help in editing the manuscript.

LIST OF

LIST OF

LIST OF

X0WEX

SECTIO

SECTIO

2A. 2B. 2C.

2D

2E 2F 2G 2H 2I 2J

SECTI

3,

TABLE OF CONTENTS

		Page
LIST OF	TABLES	vii
LIST OF	FIGURES	viii
LIST OF	APPENDICES	x
NOMENCI	LATURE	xi
SECTION	1. INTRODUCTION	1
SECTION	2. THE CONTROL OF THE ATMOSPHERE	3
2A.	Introduction	3
2B.	Restricted Ventilation	3
2C.	Removal of Excess Carbon Dioxide	5
	2C1. Introduction	5
	2C2. Physical absorption processes	7
	2C3. Chemical absorption processes	18
	2C4. Removal by use of molecular sieves	44
	2C5. Removal by using a selective membrane	53
2D.	Oxygen Reduction	57
	2D1. Fruit or product generated atmosphere	57
	2D2. The addition of nitrogen or carbon dioxide.	60
	2D3. Hydrocarbon fuel burner	67
	2D4. External gas generator	75
2E.	External Gas Generator	76
2F.	Complete Systems for the Control of the Atmosphere	81
2G.	CO ₂ and O ₂ Measurement and Control Systems	84
2H.	Humidity Control	93
2I.	Air Purification	107
2J.	Engineering Cost Analysis Study of CA Storage	
	Systems	112
SECTION	3. GENERAL CONSIDERATIONS IN THE DESIGN AND SELECTION OF VAPOR BARRIER AND GAS SEAL MATERIALS	127
3 A .	Introduction	127
	3A1. General	

3] 3(

> 3! 3!

SECT

4

SECI

5

.

SEC

T!II Ybb

		Page
	3A2. Water vapor barriers	128
	3A3. Thermal insulation	129
3B.	Moisture Migration Through Materials	1 30
3C.	The Effect of Weather and Reversible Vapor	
	Flow	132
3D.	Gas Sealing the CA Room	134
3E.	Analysis of Design Principles and Possibilities	138
	3E1. One direction vapor flow	138
	3E2. Reverse flow	140
SECTION	4. OPERATIONAL FACTORS AFFECTING GAS	
BECTION	LEAKAGE IN CA ROOM PERFORMANCE	147
	LEARAGE IN CA ROOM PERFORMANCE .	147
4A.	Pressure and Temperature Cycles in the CA	
	Storage Room · · · · · · · · · · · · · · · · · ·	147
4B.	Eliminating Pressure Changes and Devices to	
4C.	Prevent Room Damage Due to Pressure Changes Measuring the Gas Tightness of CA Storage	155
40.	Rooms	158
	Rooms	156
SECTION	5. PRECOOLING AND AIR DISTRIBUTION IN	
	A CA APPLE STORAGE ROOM	161
5 A .	Introduction	161
5B.	General Design of New Method of Storage	163
5C.	General Outline for Analytically Determining the	
	Value of the Variables in the "Packed-Bed" Type	
	Storage Room Operating System	165
5D.	The Method to Calculate Design Data for the	
	"Packed-Bed" RoomPrecooling and Air	
	Distribution	167
	5D1. The approximate calculation of T_1 and h .	168
	5D2. Calculation of the "exact" cooling curve.	169
	5D3. The determination of the air velocity v	10)
	needed and Qcfm	172
		112
	ъ	172
	needed for air distribution	173
	5D5. Evaluation of the total refrigeration load	175
5E.	Advantages, Disadvantages and Discussion of the	1
	New Approach	176
SECTION	6. DISCUSSION AND CONCLUSIONS	178
APPENDI	CES	186
LITERAT	IRE CITED	201

Tab 202 2C3 2D) 2F 23. 2J-2,5 2,3 2.5 2.5

LIST OF TABLES

Table		Page
2C2-1	Mass transfer rate in packed absorbers list of references	9
2C3-1	Mass transfer rate in chemical reaction packed absorberslist of references	19
2D1-1	Time required for CA storage room to reduce oxygen level to 0.030, carbon dioxide level to 0.025, as a function of type of carbon dioxide absorption system, leakage rate and room fullness	61
2F-1	Possible combination for complete system for the control of the atmosphere in a CA room	82
2J-1	Annual cost for carbon dioxide removal (cents per bushel)	114
2J-2	Annual cost for oxygen reduction (cents per busher for 4 pull down periods)	115
2J-3	Annual cost in cents per bushel for combination of carbon dioxide removal and oxygen reduction-small scale operation	116
2J-4	Annual cost in cents per bushel for combination of carbon dioxide removal and oxygen reductionlarge scale operation	118
2J-5	Annual cost in cents per bushel for a several existing complete CA systems	120
2J-6	Estimated annual cost in cents per bushel for a "polastream" modification and dry lime scrubbing as CA system for the whole season	121

Fig: 2C2

2C2

2C3

201

2C:

2C.

20

2C

5D 5D

2 E

5E 5E

5C 5E

LIST OF FIGURES

Figure		Page
2C2-1	Simple basic design of tower with full jet spray nozzle for water scrubbing	12
2C2 - 2	Cross section diagram of water absorber for CA fruit storage	13
2C3-1	Barrel type absorption unit	26
2C3-2	Brine spray absorption unit	26
2C3-3	Schematic diagram of the M.S.U. absorption system	27
2C3-4	Dry lime scrubber for CA apple storages	32
2C3-5	Diagram of the Sulzer scrubber	39
2C4-1	Schematic diagram of the CA system	49
2C4-2	Flow diagram of Atlantic Research Corp. controlled atmosphere generator	51
2C5-1	General design of CO_2 diffuser using selective membrane	56
2D2-1	"Polastream" refrigeration system	64
2D3-1	Oxygen vs. carbon dioxide from combustion in air	69
2D3-2	Effect of room leak on oxygen pulldown time using Arcat burner	71
2D3-3	Oxygen controller for CA storages	74
2E-1	Atmospheric control factors affecting the storage	77
2E-2	Tectrol atmospheric generator schematic	78
2G-1	Schematic drawing of CO ₂ and O ₂ instrumentation system for multiple CA rooms	92

Figure

2H-2

2H-1

3C-1

3C-2

3E-1

4A-

4B-

åB∙

5B

53

5E

5

5

Figure		Page
2H-1	Blow through vs. draw through	98
2H-2	Schematic sketch of jacketed cold room	100
3C-1	Wetting and drying potentials for CA storage structural components	133
3C-2	Histogram of diurnal average vapor pressures	135
3E-1	Features of design for moisture control within CA storage structural components	144
4A-1	Trap that allows water to flow from absorption section to desorption section without gain or loss of storage room gas	154
4B-1	Safety device to prevent excessive pressure in the CA room	157
4B-2	Relief valve to prevent excessive pressure in CA room	157
5B-1	Schematic drawing of "packed-bed" room side view	164
5B-2	Schematic drawing of "packed-bed" room top view	164
5B-3	The use of an extra pallet every second row to prevent horizontal air channeling	166
5B - 4	Short circuit air flow in regular room precooling during loading period	166
5B-5	Precooling during loading"packed-bed"	166

2-1

2-2

2-3

2-4

LIST OF APPENDICES

		Page
2-1	Comparison of Annual Cost of Operation of Orsat and Instrumentation System	186
2-2	CO ₂ Removal Costs	190
2-3	Oxygen Reduction Costs	194
2-4	Complete Systems Annual Costs	197

NOMENCLATURE

Section 2

a _o	total amine concentration, mols/volume
ACCR	annual cost, \$
В	quantity of fruit in storage, bushels (bu.)
C	controlled CO_2 level in storage, cu. ft. $CO_2/\text{cu.}$ ft. atmosphere
$(CO_3^{=})$	arithmetic average (top and bottom of column) normality of carbonate
CRF	capital recovery factor
ΔC	log mean concentration difference, lb. mol of solute cu. ft./soln.
D	diffusivity of solute gas in liquid, sq. cm./sec.
f	fraction of total base present as carbonate
G	gas rate, lb./(hr.)(sq. ft.)
h	height of packing
Н	Henry's law constant, (lb. mol/cu. ft.)/atm.
i	interest rate as a decimal
k La	liquid film coefficient, lb. mols/(hr.)(cu. ft.) (lb. mol/cu. ft.)
K_{Ga}	overall gas coefficient, lb. mols/(hr.)(cu. ft.)(atm.)
K _{La}	overall liquid coefficient, lb. mols/(hr.)(cu. ft.) (lb. mol/cu. ft.)
L	liquid rate, lbs./(hr.)(sq. ft. tower cross section)

L_m
L_s

Z u

Na

p P

r S

t T

v

Ţ

r p

Ţ

7,

Хg

```
^{L}_{m}
          liquid rate, lb. mols/(hr.)(sq. ft.)
          prospective salvage value, $
L_{\mathsf{g}}
          amine concentration of the solution, g. mols/liter
M
          unit life, number of years
n
          lb. mol of solute transferred per hr.
N
          moles transferred, lb. mols/(hr.)(sq. ft. of tower cross
Na
          sodium normality
N_{Na}
(OH)
          arithmetic average (top and bottom of columns) normality
            of hydroxide
          partial pressure of soluble gas
p
P
          initial cost, $
          respiration rate, cu. ft. O<sub>2</sub> consumed/1000 bu. day
r
S
          solubility of CO<sub>2</sub> in water under a pressure of one atm. of CO<sub>2</sub>
          time
t
\mathbf{T}
                          °C - degrees Centigrade
          temperature,
                          °F - degrees Fahrenheit
          air velocity
v
V
          storage room volume (gross), cu. ft.
          vapor pressure
V_{t}
          tower volume, cu. ft.
          oxygen diffusion ratio, cu. ft. O2 added/cu. ft. CO2 removed
w
W
          weight of water
```

mole fraction of gas in liquid phase

Χg

X

X

Y: Z

a

rr G

p

.

]

X leakage or ventilation rate,

air changes (based on empty room volume) 24 hr.

- Y oxygen level in storage, cu. ft. O₂/cu. ft. atmosphere
- Yt oxygen level in storage at time t
- Z space factor $Z = \frac{V}{R}$, cu. ft./bu.
- α empirical constant given for different packing materials
- carbonation ratio, mol CO₂/mol amine
- μ liquid viscosity
- μ' ionic strength
- ρ liquid density, lb./cu. ft.

Section 3

- A area of cross section of flow path, sq. ft.
- H dry weight of hygroscopic material, lbs.
- length of flow path, in.
- m' initial equilibrium moisture content of material, lb./lb.
- m" allowable equilibrium moisture content of materials, lb./lb.
- Δp vapor pressure difference, in. of Hg
- t time of transition, hrs.
- W total weight of vapor transmitted, grains
- W_s moisture storage capacity, grains
- permeability, grain in./(sq. ft.)(hr.)(in. Hg vapor pressure difference)

A 3

a_s

D f

F Go

Ħ h

į

k И

X Bi **4**P

Section 5

A	cross section of bed (stack)
a ;	the radius of the apple (sphere)
a _s	apple (sphere) surface area per unit bed area
C	specific heat:
	C _{PS} specific heat (at constant pressure) of apple
	C _{PA} specific heat (at constant pressure) of air
D	defined in Eq. 5D2-6
f	time required for the asymptote of a cooling curve to cross one log-cycle, the time required for a 90 percent reduction of temperature on the linear portion of the cooling curve
F	defined in Eq. 5D2-7
G _o	superficial mass velocity ($\rho v \epsilon$).
Н	height of bed (stack)
h	surface heat transfer coefficient
j	log factor - dimensionless
	j _c log factor at the geometric center
	j log factor for the mean temperature in the apple
	js log factor for the surface temperature
k	thermal conductivity
M	weight of apples in the room
$^{ m N}_{ m Bi}$	Biot number ha/k - dimensionless
$^{\Delta P}_{B}$	pressure difference across the packed bed

$^{\Delta P}_{D}$	pressure difference across ceiling wall and floor
$\Delta P_{ ext{T}}$	total pressure difference the fan has to overcome
$Q_{ m cfm}$	quantity of air, cu. ft./min.
Q_{R}	heat of respiration
r	variable distance from the center of the apple
Re	Reynold number - dimensionless
T	temperature of the apple
T_0	initial temperature of the apple
T_1	temperature of cooling media (air)
T_2	temperature of refrigerant
T _a	the apparent initial temperature as described by the linear portion of the cooling curve
$^{\mathrm{T}}$ d	temperature of apple after 24 hours cooling
T_{os}	initial temperature of surface
T_s	surface temperature
t	time
v	average flow velocity in the cross section available for flow
α	thermal diffusivity $k/C_{{ extbf{P}}^{, ho}}$
€	void fraction volume of void volume of bed
μ	viscosity
$^{\mu}\mathrm{_{f}}$	fluid film viscosity
ρ	density

extens

merc py con

and p

comr

por**ć**

ther

tro]

th.e

W.S

âr

Þ

1

SECTION 1

INTRODUCTION

The objective of CA (controlled atmosphere) storage is the extension of the storage life of food products beyond that attainable by conventional cold storage practice. At the present time, commercial application of CA storage is limited principally to apples and pears, but it is envisioned that this technique will also be used commercially for the storage of other fruits, vegetables and food products.

CA has become more complicated and whereas a few years ago there was only one method of producing the atmosphere and controlling carbon dioxide, today there are many to choose from. This thesis deals with the CA storage of apples, but most of the observations are applicable to other types of produce. The objective of this study was to assemble information in an orderly manner that will make possible better decisions in the area of CA construction and operation.

This is an engineering analysis of some of the unit operations available for CA storage and some new approaches and suggestions for improving CA operations. This study was limited to the control of the atmosphere, sealing against gas and vapor transfer and cooling and air distribution in the CA room.

A o

desi

A critical literature review was made of the unit operations involved in the control of the atmosphere: The necessary design information for the selection and operation of equipment in a CA storage was assembled. The performance and costs of operating the available systems to control the atmosphere in the room were compared and analyzed, and specific recommendations were made regarding which method to use for a given set of conditions.

A critical literature analysis was made of the basic problems involved in using a vapor barrier and a gas seal. The problems of gas leakage in the CA storage structure were investigated. The purpose was also to discuss and show possible solutions to water vapor transfer, CA storage gas tightness and pressure and temperature cycles in the CA storage structure as influenced by weather conditions, material used and various design procedures.

Since the refrigeration requirements for cooling the apple in the storage are large for the first few days of the storage, the possibility of using liquid nitrogen for partial precooling and atmosphere control was analyzed. As an improvement of air distribution in the room during precooling and storage is needed, the objective was also to present a possible new approach to precooling and air distribution design in a room filled with apples.

down 1

increa

Contr

fruit

carbo

quire

ехре

cox

ir

Ÿζ

Þ

SECTION 2

THE CONTROL OF THE ATMOSPHERE

2A. Introduction

After harvest, living fruits carry on respiration, which is slowed down by lowered temperatures, and by reducing the oxygen content and increased concentration of carbon dioxide in the air around the fruit. Controlled atmosphere (CA) storage is a method of keeping living fruit longer by refrigeration, reduced oxygen and higher than normal carbon dioxide concentration in gas tight rooms. The optimum requirements for the different varieties vary and can only be determined experimentally.

The purpose of this section is to analyze the various methods of controlling the atmosphere.

2B. Restricted Ventilation

The composition of the air in a gas-tight storage room containing fruit will be changed due to fruit respiration. The fruit absorbs oxygen from the atmosphere and gives off carbon dioxide in approximately equal volumes. As the concentration of carbon dioxide rises to 5, 10 or 15 percent the concentration of the oxygen will fall to 16, 11, or 6 percent,

the survalue of carbon lift a condition drops s

the des

into the

1

18 pero

CO_{2 an}

deterio

below t

(

Ventila

simple

and it v

is anal

the sum of the CO₂ and O₂ remaining approximately 21 percent, i.e., the value of the original oxygen content. All the oxygen will be replaced by carbon dioxide unless ventilation is introduced at some intermediate level. If a complete lack of oxygen persists over a period of few days, the fruit becomes alcoholic and develops off flavors. Therefore, when the oxygen drops slightly below the desired level, fresh outside air is introduced into the room.

Ventilation can be used to regulate the atmosphere but only when the desired oxygen and carbon dioxide level totals 21 percent. A combination of low oxygen and high carbon dioxide (for example 3 percent O_2 and 18 percent CO_2) will cause damage to the fruit because of the high CO_2 content. The combination of low CO_2 and high O_2 (for example 5 percent CO_2 and 16 percent O_2) will cause the respiration rate to be high and the deterioration of the fruit to be precipitated.

Our present needs are low oxygen and carbon dioxide levels well below the total sum of 21 percent, which cannot be achieved by restricted ventilation only. Even though restricted ventilation operation is very simple and the cheapest one to build, it is not recommended for use today and it will not be described nor analyzed any further.

The control of the atmosphere to achieve desired CO_2 and O_2 level is analyzed in the following sections.

2C1. <u>I</u>

(

cent, (

oxide

"scrub

tion u

(2) do

(3) o

be d

Stor

to h

 M_{\odot}

to

o:

i

2C. Removal of Excess Carbon Dioxide

2C1. Introduction

Other combinations than CO₂ and O₂ concentrations, totaling 21 percent, (restricted ventilation) can be obtained by removing the carbon dioxide produced by respiration. Removal of CO₂ can be effected by "scrubbing" the atmosphere from the storage room through an absorption unit.

The main requirements for scrubbers are: (1) economical in use,
(2) does not give off volatile products likely to damage the stored produce,

(3) operate also as an air purifier, (4) can be operated by unskilled labor.

The carbon dioxide absorption system of a CA storage room should be designed on the basis of the quantity of fruit in the CA room, the carbon dioxide production rate of this fruit, and the carbon dioxide level in the storage.

Each room must be equipped with an absorber of adequate capacity to handle the most difficult carbon dioxide removal job. This condition in Michigan and in the Northeastern United States is produced by the McIntosh variety of apples which requires a storage temperature of 36° to 38°F and a carbon dioxide level of 2.5 percent during the first month of the storage (Pflug 1960).

The CO_2 solvent should have high CO_2 solubility which will result in minimum solvent rate needed. The solvent should be relatively

U

]

non-volatile, cheap, non-corrosive, stable, non-viscous, non-foaming and preferably non-flammable.

Usually the apparatus used for contacting a liquid and a gas stream continuously is either a packed tower filled with solid packing material, an empty tower into which the liquid is sprayed, or a plate-type unit containing a number of bubble-cap or sieve plates. Ordinarily, the gas and liquid streams are made to flow countercurrently to each other as they pass through the equipment.

The physical and chemical principles involved in the scrubbing process and the application of scrubbers in the chemical industry will be discussed. The scrubbers used in the chemical industry are quite different in scale, available source of heat (steam) and operational pressure from those used in CA storages. This comparison is designed to show design possibilities, effect of variables, problems involved and their solution and potential improvement in scrubbers for CA storage use.

The application of the scrubber in CA storages, its general design, specific problems, advantages and disadvantages in use will be discussed. The economic analysis is given in Section 2J.

The following is a broad division of CO₂ removal processes convenient for this discussion:

Physical absorption processes

Chemical absorption processes

2C2.

liquid

where

tity of Over t

the hi

solver

ture,

quanti

press.

The da

the qu

tersiv

Removal using molecular sieves

Removal using selective membranes

2C2. Physical absorption processes

General

The solubility of gasses in liquids is normally expressed in liquids is normally expressed in terms of Henry's law; $p = Hx_g$ (2C2-1) where: p = the partial pressure of the soluble gas

 x_g = the mole fraction of gas in liquid phase

H = Henry constant

Henry's law states that the quantity of gas dissolved in a given quantity of solvent or solution is directly proportional to its partial pressure over the solution, therefore, the higher the pressure of the gas stream, the higher the partial pressure of the CO₂ and its solubility in the solvent. H is constant (or practically constant) for a given temperature, but increases with an increase in temperature.

Absorption in Water

The solubility of carbon dioxide in water is relatively low. The quantity of CO₂ absorbed is practically directly proportional to its partial pressure and decreases with increasing water temperature (Perry 1963). The data of the gas-liquid equilibrium relationship are used to determine the quantity of water needed to absorb the required carbon dioxide, Extensive work has been done on physical absorption processes of CO₂ in

wate: ence

2C2-

tion stud

pac'r

. bead

obta

des

ine

whe

water in the chemical industry. A summary of mass transfer rate references for different types of packing and tower sizes is given in Table 2C2-1.

Yoshida (1958) summarized the work done in the area of absorption of CO_2 in water and methanol in packed absorption columns. He studied the absorbance of pure CO_2 into water and methanol in a column packed with spheres, Rashing rings, and Berl saddles as well as in a bead column containing spheres. Reasonable correlations were obtained.

Sherwood and Holloway (1940) have correlated their data on the desorption of oxygen, CO_2 and H_2 from water in a packed column using the equation

$$\frac{k_{La}}{D} = \alpha \left(\frac{L}{\mu}\right)^{0.25} \left(\frac{\mu}{\rho D}\right)^{0.50}$$
 (2C2-2)

where:

kLa liquid film coefficient, lb. mols/(hr.)
(cu. ft.) (lb. mol/cu. ft.)

- D diffusivity of solute gas in liquid, sq. cm/sec.
- α empirical constant given for different packing materials
- L liquid rate, lbs./(hr.) (sq. ft. tower cross section.)
- μ liquid viscosity, poises
- ρ liquid density, lb./cu. ft.

TABLE 2C2-1. Mass transfer rate in packed absorbers-List of References

water Rashing rings water Steel rashing water Berls saddles water Berls saddles water Berls saddles water Spheres water Spheres						
SolventPacking typein.ReferencewaterRashing rings5FujitawaterRashing rings4.5YoshidawaterRashing rings9.7SchulmanwaterRashing rings6Deed et al.waterSteel rashing30 squareCooperwaterRashing rings20SherwoodwaterBerls saddles4.5YoshidawaterBerls saddles5FujitawaterBerls saddles5FujitawaterSheres4.5Yoshida	1940	Sherwood	20	Spiral tile	water	CO_2
Solvent Packing type in. Reference in. Rashing rings 5 Fujita water Rashing rings 6.8 Koch water Rashing rings 9.7 Schulman water Steel rashing sings 20 Sherwood water Berls saddles 20 Sherwood water Berls saddles 5 Fujita water Berls saddles 20 Sherwood Sherwood water Berls saddles 20 Sherwood Sherwood Sherwood Sherwood Sherwood Sherwood Sherwood	1958	Yoshida	4.5	Spheres	water	CO_2
Solvent Packing type in. Reference water Rashing rings 4.5 Fujita water Rashing rings 6.8 Koch water Rashing rings 6 water Rashing rings 6 water Rashing rings 20 water Rashing rings 20 sherwood water Rashing rings 5 Fujita	1940	Sherwood	20	Berls saddles	water	CO_2
Solvent Packing type in. Reference water Rashing rings 6.8 Koch water Rashing rings 9.7 Schulman water Rashing rings 6 water Rashing rings 6 water Rashing rings 20 sherwood water Steel rashing 20 water Rashing rings 30 square Cooper water Rashing rings 4.5 Yoshida	1956	Fujita	5	Berls saddles	water	CO_2
Solvent Packing type in. Reference water Rashing rings 6.8 Koch water Rashing rings 9.7 Schulman water Rashing rings 6 water Rashing rings 6 water Rashing rings 20 Schulman sharer Steel rashing 20 Schulman Steel rashing 20 Schulman Steel rashing 20 Schulman	1958	Yoshida	4.5	Berls saddles	water	CO_2
Solvent Packing type in. Reference water Rashing rings 6.8 Koch water Rashing rings 6.8 Koch water Rashing rings 9.7 Schulman water Rashing rings 6 water Steel rashing	1940	Sherwood	20	Rashing rings	water	CO_2
Solvent Packing type in. Reference water Rashing rings 6.8 Koch water Rashing rings 6.8 Koch water Rashing rings 6.8 Chulman water Rashing rings 6.7 Schulman water Rashing rings 6	1941	re Cooper	30 squa	Steel rashing	water	CO_2
Solvent Packing type in. Reference water Rashing rings 4.5 Yoshida water Rashing rings 6.8 Koch water Rashing rings 9.7 Schulman	1947	Deed et al.	9	Rashing rings	water	CO_2
Solvent Packing type in. Reference water Rashing rings 4.5 Yoshida water Rashing rings 6.8 Koch	1952	Schulman	6.7	Rashing rings	water	CO_2
Solvent Packing type in. Reference water Rashing rings 4.5 Yoshida	1949	Koch	8.9	Rashing rings	water	CO_2
Solvent Packing type in. Reference water Rashing rings 5 Fujita	1958	Yoshida	4.5	Rashing rings	water	CO_2
glameter Solvent Packing type in.	1956	Fujita	5	Rashing rings	water	CO_2
Tower		Reference	Tower diameter in.	Packing type	Solvent	Solute

1

pres

oxid

and I

iem;

norn

Pack

and :

ner :

bre

37776

Caus

(194

Made It wa

Ther

€080

The important results from their studies are:

- 1. Liquid film coefficient k_{La} increases rapidly with temperature, presumably due to a decrease in liquid viscosity. Data for carbon dioxide and oxygen are practically identical since the diffusivity of CO_2 and O_2 in water differ only by 15 percent. $k_{La} \propto e^{0.023T}$ where T-water temperature °C.
- 2. Effect of gas velocity- $k_{\mbox{La}}$ is independent of gas velocity in the normal velocity ranges.
 - 3. There is a marked effect of liquid rate on k_{I.a}.
- 4. An addition of wetting agents to the liquid or coating of the packing with paraffin caused a considerable reduction of $k_{\rm La}$.
- 5. The data showed relatively small variation of k_{La} with size and type of packing, liquid distribution at the top of the tower and manner of placing the packing in the tower.

Cooper et al. (1941) suggested that in a CO_2 -water absorption tower, the ratio of the liquid flow to gas flow must be very large because of low solubility of the gas. A scrubbing apparatus particularly suited for this application using cascade packing is described by Cooper (1945).

The CO₂ absorption by water and water-glycerol mixtures was also made using bubble-tray absorption columns (Walter and Sherwood 1941). It was shown that the higher the viscosity the lower the plate efficiency. There is no advantage in using water-glycerol mixtures nor bubble-tray absorption column in CA room.

The application of the water scrubbing in the CA

Palmer (1959) was the first to suggest the use of water absorptiondesorption system to remove carbon dioxide from CA storages. Several types of water scrubbers are in use in New York State (Smock 1960, Kendenburg 1959) in which the carbon dioxide is absorbed in the water circulated over a wet type refrigeration evaporator and removed from this water in an aeration tower located outside the CA storage (Fig. 2C2-1) The disadvantage of the combination of this water scrubber and refrigeration coils is that when operating at low temperatures (31-32°F) a wet coil would require an antifreeze material in the water, which significantly reduces the carbon dioxide absorption efficiency of the system. This disadvantage and the possible use of dry type refrigeration evaporators led Pflug (1961) to design a single tower water absorption-desorption system to remove carbon dioxide from CA storage. This system operates independently of the refrigeration system and its design is based on chemical engineering principles of absorption-desorption packed-bed tower. (Sherwood and Pigford 1952, Leva 1953). Starting at the top of the tower, (Fig. 2C2-2) water flows downward through the absorption section where it comes into contact with air from the storage, which may contain, for example, 5.0 percent carbon dioxide. Some of the carbon dioxide diffuses into and is absorbed by the water. The water next flows through the desorbing section where it comes into contact with normal atmosphere

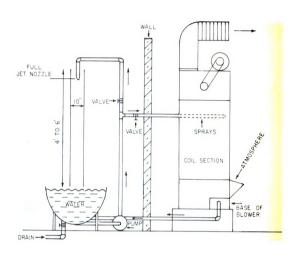


Fig. 2C2-1. Simple basic design of tower with full jet spray nozzle for water scrubbing (Smock et al 1950)

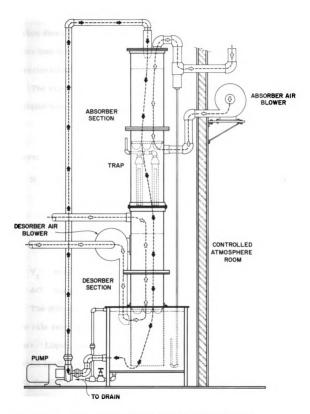


Fig. 2C2-2. Cross section diagram of water absorber for CA fruit storage (Pflug 1961)

that may have but 0.03 percent carbon dioxide and where some of the carbon dioxide is desorbed from the water and diffuses out of the water into this low carbon dioxide atmosphere. The water normally is recirculated for continuation of the absorption-desorption process.

The mass transfer of carbon dioxide to or from a water solution is liquid-film controlled and can be described by the equation:

$$N = K_{La} V_t \Delta C \qquad (2C2-3)$$

where:

N lb. mol of solute transferred per hr.

 V_{t} tower volume, cu. ft.

 ΔC log mean concentration difference $\frac{lb. \text{ mol of solute}}{cu. \text{ ft. / soln}}$

The diffusion coefficient, liquid viscosity, temperature and liquid flow rate determine the overall coefficient K_{La} for carbon dioxide in water. Liquid flow rate is the most important of these variables; the overall coefficient varies approximately directly with liquid flow rate. Both the diffusion coefficient and viscosity are temperature dependent, increasing the temperature increases the diffusion coefficient and reduces viscosity. Therefore, K_{La} is increased by an increase in the

diffus
gas f
liquid
oxide
conce

ine lo water differ

decre

in wa There

ture i

creas

differ the la

tion d

speci

creas.

1

by Pfl

diffusion and decrease in the liquid viscosity. Under usual conditions, gas flow rate does not significantly affect the absorption coefficient.

The carbon dioxide concentration difference at any point in a liquid-film controlled system is the difference between the carbon dioxide concentration in the bulk of the liquid and the equilibrium liquid concentration of the carbon dioxide in the gas phase expressed as molar concentration. The concentration difference of the system is the log mean of the inlet and outlet conditions. Since carbon dioxidewater equilibriums are the function of temperature the concentration difference is a function of temperature; increasing the temperature decreases the equilibrium concentration. The equilibrium concentration (expressed as mole fraction) of 5.0 percent carbon dioxide gas in water is 3.08×10^{-5} at 77° F (25°C) and 4.88×10^{-5} at 50° F (10°C). Therefore, the change in absorption rate due to a change in temperature is quite small since the increase in $K_{\mathrm{L},\mathrm{a}}$ brought about by an increase in temperature is offset by the decrease in concentration difference. In general the carbon dioxide level of the CA storage is the largest single factor in determining the carbon dioxide concentration difference, and therefore, the carbon dioxide removal rate for a specific system.

The quantity of carbon dioxide removed from a CA storage increases linearly with packing depth, however, 4.5 ft. was mentioned by Pflug as the approximate maximum economical packing depth for

ing I

4.5:

tion

the I

the I

with

the sect

stru

pape

both

<u>Adv</u>

eco

Sor

tiee

both the absorption and desorption sections. This was based on gas pumping requirements; up to 4.5 ft. a centrifugal blower can be used, above 4.5 ft. some type of positive air pump is required. A detailed description of the MSU water scrubber is given by Pflug (1961) (Fig. 2C2-2) but the most important and unique is the liquid trap section which enables the construction of absorption and desorption section in one compact unit. In the liquid trap located between the absorber and desorber sections, water flows from the absorber section to the desorber section without removal of CA storage room gas from the absorber section, or the addition of outside air from the desorber section into the absorber section (Fig. 4A-1). The MSU water absorber was designed and constructed so that caustic soda could be used in an emergency. In the same paper Pflug (1961) also showed a way to size the MSU water absorber needed for specific application.

Advantages of water scrubbing

- 1. Compared to caustic soda scrubbing, water scrubbing is more economical because it saves on the use of caustic soda.
- 2. It is cleaner and less caustic in operation than the caustic soda scrubber.
- 3. The manipulation is faster with water scrubbing as caustic soda need not be drained out.

and r

the C.

Disac

:he C

air th

abson (Pflu

but t

than

 ${\tt also}$

filled

üsed

apov

sire

the (

cres

It is

4. Prevent the continuous increase of the ethylene concentration and reduce the ethylene and the nonethylenic volatile concentration in the CA room.

Disadvantages of water scrubbing

Oxygen is slightly soluble in water and some oxygen is added to the CA room with water aeration in addition to the oxygen added in the air that replaces the carbon dioxide. An analysis of the effect of water absorption of carbon dioxide on the operation of the CA storage room (Pflug 1960) showed that tight CA rooms filled with fruit should require but two or three days longer to develop a 3 percent oxygen atmosphere than similar rooms operated with caustic soda absorber. This analysis also showed that rooms which are borderline in tightness or partially filled will not operate satisfactory when a water absorption system is used for carbon dioxide removal. Because of the reasons mentioned above the water scrubber is not recommended for use when the desired CO₂ level in the room is less than 5 percent.

Other Physical Absorption Systems

In order to have a complete picture of physical absorption of CO_2 in the chemical industry two other processes will be mentioned:

1. <u>Absorption is methanol</u>. The solubility of CO₂ in methanol increases sharply with a decrease in temperature (Hoogendoorn 1963). It is practical in the chemical industry because of the advantage of the

absorp not pra

and wo

2.

an org

as in a gas pr

is no l

ior us

2C 3.

A ried o

rever

the so

strip

sorpt

1

the in

simul

tioned

impor

absorption of other gases like hydrocarbons, hydrogen sulphide but is not practical for CA because the methanol is more expensive, volatile and would introduce extra refrigeration expense.

2. The Fluor Solvent process (Hoogendoorn 1963). In this process an organic solvent such as propylene carbonate is used. This process, as in all physical absorption systems, is most suitable with high total gas pressures and high concentration of carbon dioxide. Since there is no high gas pressure and high CO₂ concentration it is not suitable for use in CA storage.

2C3. Chemical absorption processes

General

Absorption of gases with low solubility in water is frequently carried out by using liquid absorbents that react either irreversibly, or reversibly-forming a compound that is easily decomposed by heating the solution. In the last case usually the solvent is recovered in a stripping operation using heat or air.

There is no sharp line dividing pure physical absorption from absorption accompanied by rapid chemical reaction. Most cases fall in the intermediate range. Table 2C3-1 lists experimental studies on simultaneous absorption (or desorption) and reaction systems mentioned in the literature. The use of experimental values is particularly important when absorption or desorption occurs simultaneously with

TABLE 2C3-1. Mass transfer rate in chemical reaction packed absorbers-List of references

				Tower		
				diameter		
Solute	Solvent	Reagent	Packing type	in.		
CO2	water	KOH	Rashing	2.8, 4	Blum	1952
CO ₂	water	NaOH	Rashing	∞	Greenwood	1953
i					Leva	1955
CO2	water	NaOH	Rashing	2.8, 4	Blum	1952
CO	water	NaOH	Rashing	9	Tepe	1943
CO_2	water	NaOH			Spector	1946
CO	water	NaOH	Berl saddles	&	Leva	1955
COS	water	NaOH	Intalox saddles	80	Leva	1955
CO_2	water	NaOH	Pall rings	30	Eckert	1958
CO_2	water	NaOH	Lessing rings	∞	Greenwood	1953
COS	water	Hot K ₂ CO ₃	Rashing	6, 8	Benson	1956
CO_2	water	Hot K ₂ CO ₃		Commercial plant	Buck	1958
COS	water	$K_2 CO_3$	Rashing	3	Comstock	1937
CO_2	water	$Na_2 CO_3$	Rashing	2.8, 4	Blum	1952
CO_2	water	Na ₂ CO ₃	Rashing and	12	Furnas	1938
I			Berl saddles			
CO_2	water	$Na_2 CO_3$	Rashing	3	Comstock	1937
CO_2	water	Mono			Kohl	1956
		ethanol amine	ne			
CO_2	water	Mono		2,4	Kondo	1958
		ethanol amine	ле			
CO_2	water	Mono	Rashing	12	Gregory	1937
		ethanol amine	ле			
CO_2	water	Mono	Steel rashing	∞	Teller	1958
		ethanol amine	ле			

·
r
Ţ.
•
,
-
:
,
•
•
;
:
:
•
,
·
•
:
;
•

TABLE 2C3-1. (Continued)

CO_2	water	Mono	Berl saddles	∞	Teller	1958
		ethanol amine	e e			
CO_2	water	Mono	Tellerettes	8	Teller	1958
		ethanol amine	v			
CO_2	water	Diethanol	Rashing	8	Cryder	1941
		amine				
CO_2	water	Diamino i- Rashing		12	Gergory	1937
		propanol				

chemical reaction, since prediction methods are not well developed for these cases.

Mainly two groups of chemical absorption of carbon dioxide will be discussed:

- 1. Irreversible chemical absorption
 - a. Milk of lime
 - b. NaOH and KOH solutions
 - c. Dry lime (Ca(OH)₂) (May be regenerated)
- 2. Reversible chemical absorption
 - a. Carbonate solutions
 - b. Ethanolamine solutions

Irreversible Chemical Absorption

Milk of Lime

Milk of lime is safe to handle but is not readily dissolved in water and therefore it is used in the form of a suspension rather than a solution. If the liquid is allowed to stand for any length of time, solid matter (Ca CO₃) is deposited which is difficult to remove from the scrubber unit. It is also necessary to drain out spent solution and recharge fairly frequently and considerable amount of labor is necessary.

The use of milk of lime is limited at present, it is not recommended and therefore it will not be discussed further.

Sodium or Potassium Hydroxide Solutions

Caustic soda is the commercial name for sodium hydroxide (NaOH). Dry, solid, commercial grade caustic soda, contains at least 98.90 percent of NaOH, NaO or Na₂O and is available as regular flake, fine flake, crystal flake and powder, all forms are readily soluble in water.

Caustic soda solution absorbs carbon dioxide by chemical reaction in two steps: I. NaOH + $CO_2 \rightarrow Na_2CO_3 + H_2O$ (2C3-1). II. $CO_2 + Na_2CO_3 + H_2O \neq 2NaHCO_3$ (2C3-2). As can be shown from these equations, 1 lb. of pure sodium hydroxide will absorb 1.1 lb. or carbon dioxide. One-half is absorbed in each step, but step I takes place much faster than II. Reaction II is reversible, sodium hydroxide will react with sodium bicarbonate to form sodium carbonate.

The rate of absorption of CO₂ is affected by the state of completion of the chemical reaction. At the beginning, with fresh NaOH, there is great affinity of NaOH for CO₂ (Pflug et al. 1957a). The rate of absorption decreases due to the increased concentration of sodium carbonate as reaction I nears completion and decreases even more as the sodium carbonate is neutralized to sodium bicarbonate.

Blum et al. (1952) developed an equation for representing the CO_2 absorption by hydroxide in packed tower.

Na = 0.0176.
$$L_{m}^{0.84} h \frac{(OH^{-})(CO_{3}^{-})}{(\mu')^{1.09}}$$
 (2C3-3)

where

Na

 Γ^{m}

(OH

(CO

μ

h

Sev

non of

Pf

cussed

sorptio

absorb

reactio

sorbin

gas a:

:0]]o;;

inrou

1

Ž

of the

where

Na moles transferred, lb. mols/(hr.)(sq. ft.) of tower cross area

L liquid rate, lb. mols/(hr.)(sq. ft)

(OH⁻) arithmetic average (top and bottom of column) normality of hydroxide.

(CO₃) arithmetic average (top and bottom of column) normality of carbonate.

μ' ionic strength

h height of packing, ft.

Several researchers (Table 2C3-1) have extensively studied the absorption of sodium hydroxide in absorption tower in the chemical industry.

Pflug et al. (1957c) used the chemical engineering principles discussed by these researchers and presented the fundamental of CO₂ absorption with NaOH as applied to CA and designed the MSU packed tower absorber. In addition to the effect of state of completion of the chemical reaction mentioned earlier, Pflug studied the effects of liquid flow, absorbing surface area, liquid temperature, concentration of CO₂ in the gas atmosphere and the air flow rate. His results are summarized as follows:

- 1. The rate of absorption increases as the rate of solution flow through the absorber increases.
- 2. The rate of absorption is proportional to the surface contact area of the solution with the atmosphere containing CO_2 .

sorbi

3

4

tion.

affec

since

in the

and t

J2!!

the t

voir

;op c

fora:

equi

iowe The

air :

••

- 3. The rate of absorption increases as the temperature of the absorbing solution is raised.
- 4. The rate of absorption increases with increase in CO_2 concentration.
- 5. The rate of air flow through the absorber does not materially affect the absorption coefficient. High air flow rates are undesirable since they waste power and cool the absorbing solution.

There are three types of absorbing systems that were commonly used in the U.S.: The barrel type designed by Smock and Van Doren (1941) (Fig. 2C3-1), the brine spray type that was first suggested by Smock and the system is described by Kedenberg (1953) (Fig. 2C3-2) and the MSU packed tower designed by Pflug et al. (1957c) (Fig. 2C3-3).

The barrel type absorber (Fig. 2C3-1) uses perforated plates in the upper portion of the tank while the lower portion is used as a reservoir. The NaOH solution is pumped from the bottom reservoir to the top of the absorption section and allowed to flow down through the perforation of the plates. The air from the storage room is forced up through the holes in the plates and back into the storage room.

The brine spray diffuser (Fig. 2C3-2) is a standard refrigeration equipment. It serves the dual purpose of evaporator and absorption tower by replacing brine with NaOH solution. Absorption takes place when the NaOH solution is sprayed on the evaporator pipes over which air is rapidly circulated.

The MSU packed tower (Fig. 2C3-3) operates independently of the refrigeration system of the storage room. It consists of an absorption tower, reservoir tank, circulating pump, air blower and connecting piping. The atmosphere of the CA room is forced by an air-circulating blower through the packed absorption tower (Interlox saddle packing is recommended). It enters the tower beneath the packing at a point just above the liquid level of the filled reservoir and returns to the room from the top of the tower. The liquid is pumped from the bottom of the reservoir into the top of the tower, where it flows over the packing in contact with the room atmosphere and drains into the reservoir.

Angelini (1956) observed that the time required to utilize 90 percent of the NaOH was more than 60 min./lb. for barrel unit, 12 to 22.5 min./lb. for brine-spray units, and 18 min./lb. for the packed tower.

Eckert et al. (1958) showed in their studies using 4 percent NaOH solution for the absorption of CO_2 in the chemical industry, an improvement of 30 up to 67 percent in the $K_{\mbox{Ga}}$ using the new Pall rings compared to the rashing type.

Advantages of hydroxide solution scrubbing

This is a very efficient CO_2 scrubbing operation which permits reduction of the oxygen level in the room in a short time. The use of hydroxide solutions is advantageous at the first period and in emergency in some water scrubbing units.

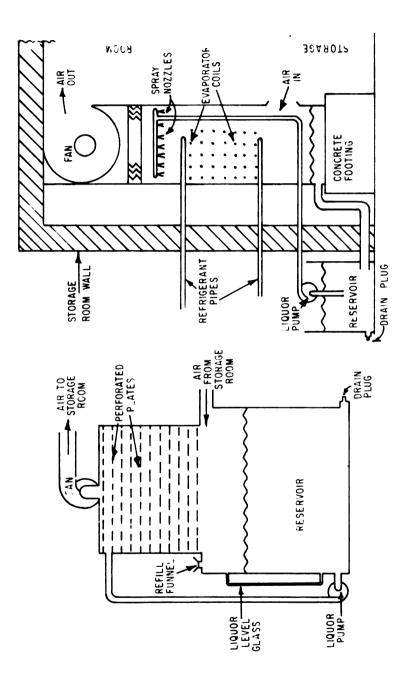


Fig. 203-1. Barrel type absorption unit (Angelin: 1956)

Fig. 203-2. Brine spray absorption unit (Angelini 1955)

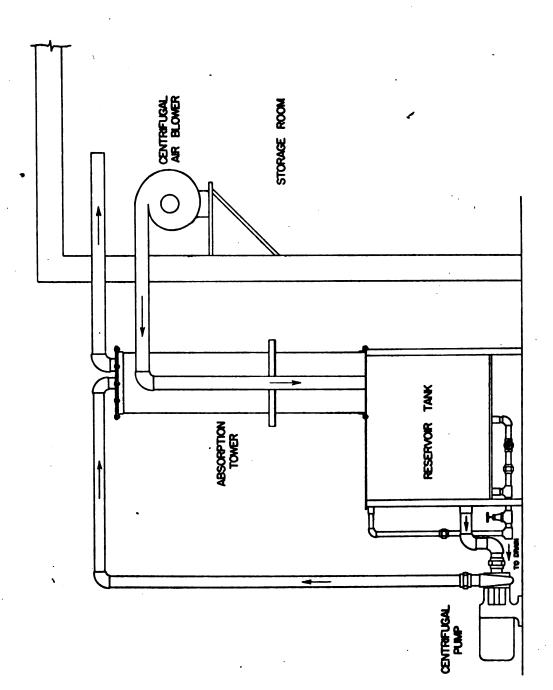


Fig 2C3-3. Schematic diagram of the MSU absorption system (Pflug et al 1957c)

Disadvantages of hydroxide solution scrubbing

The CO₂ reacts irreversibly with the NaOH causing a decrease in rate of absorption during the absorption period and frequent recharging with fresh NaOH solution. This last step is expensive, troublesome, laborious, and is a danger to health.

As the solution is highly corrosive there are problems with the construction of the absorber, charging the absorber and discarding of the spent liquor.

Dry Lime Scrubbing

Eaves (1964) observed that fresh hydrated lime Ca(OH)₂ will absorb carbon dioxide from a CA storage room atmosphere when the hydrated lime is itself still inside closed paper bags. The chemical reaction is:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Theoretically, one lb. of lime will absorb 4.4 cu. ft. of carbon dioxide. Since one bu. of McIntosh apples at 38°F will produce approximately 4.7 cu. ft. of carbon dioxide during a 6-month storage period, the dry lime requirement would be approximately one lb. per bushel. Eaves (1964) estimated that 1-1.5 lb lime was being used per bu. for apple storage in Nova Scotia; and indicated, based on Smock's findings, that as much as 4 lb. of lime per bu. was used in New York State.

Usually no tests are made to determine whether the lime has absorbed

100 **p**e

somet

capac

that it

ine at

С

duced absor

hydro

heat h

load.

90 **p**e:

325 m

E

tics o

Was r

loss c

midit

storaj

what s . ^{CO}NSta

dry li

is no ,

100 percent of the carbon dioxide it is capable of absorbing, therefore sometimes the lime is replaced though considerable carbon dioxide removal capacity remains. There is also the fact that lime may not be fresh and that it will have absorbed a considerable amount of carbon dioxide from the atmosphere before it is used in the storage.

Observing the chemical reaction above, we note that water is produced by the reaction; however, it is also possible that the dry lime absorbs some moisture from the storage room atmosphere. The calcium hydroxide reaction with carbon dioxide produces 103 Btu's per mole; this heat has to be taken into account when calculating the total refrigeration load. Normally the dry lime used for carbon dioxide removal contains 90 percent calcium oxide and 10 percent magnesium oxide and is of 325 mesh.

Eaves (1964) reported on a survey to evaluate quality characteristics of fruit that had been stored in CA storages where carbon dioxide was removed using dry lime. He reported that there was no weight loss or odor due to the dry lime and that 90-92 percent relative humidity was easily maintained in the storage. The operation of CA storage rooms when dry lime is used to remove carbon dioxide is somewhat simplified in that the carbon dioxide level normally remains quite constant due to the rather uniform removal of carbon dioxide by the dry lime. Oxygen level problems are somewhat reduced since there is no oxygen brought into the room during the scrubbing operation as

ior ve the sta dioxid with a well is room of diff room When consid of the portic to uti are u abilit

happer

It is s

]

iime

and the

the ba

happens when a water type scrubber is used. The dry lime can be used for very low carbon dioxide levels, for example, in the Pacific Northwest the standard practice is to store Delicious apples with a maximum carbon dioxide level of 2 percent. It is relatively difficult to maintain this level with a water type absorption system; however, the dry lime functions very well in this situation. The movement of carbon dioxide from the storage room atmosphere into the dry lime will take place according to the laws of diffusion. The higher the concentration of carbon dioxide in the storage room atmosphere, the faster will the carbon dioxide move into the lime. When the lime remains in the bag diffusion into this mass of lime must be considered. It is probable that when lime is discarded, the outer portions of the bag are more fully saturated with carbon dioxide than the inner portions. Also, when high carbon dioxide levels are used, it is possible to utilize the dry lime more fully than when low carbon dioxide levels are used. The larger the dry lime room, the greater will be the ability to utilize the total capacity of the bags of the lime.

There is considerable difference among different sources of lime.

It is suggested that some type of absorption test be run on the lime to determine its carbon dioxide absorbing ability or more preferably, the lime should be certified from the manufacturer indicating that it is fresh and that it meets carbon dioxide absorption standards. The permeability of the bag will effect the dry lime absorber performance, especially where the bags are not open or holes are not punched in the bag. Plastic bags

must not be used. A diagram of the dry lime scrubber is shown in Fig. 2C3-4. The dry lime box has to be air tight since it is an integral part of the CA storage room. The dry lime box should be designed in such a way that the dry lime can be moved into and the spent lime removed out of the lime box rapidly and with a minimum amount of labor.

Advantages of dry lime scrubbing.

- 1. The operation of the room is simplified in that constant levels of carbon dioxide are easily maintained and rapid oxygen reduction rates are obtained.
- 2. Power requirements are low and the only part to deteriorate or cause problems is the blower and damper system.
- 3. High carbon dioxide removal capacities are available during the pull down period on a no penalty basis.
 - 4. Operation is very simple.
 - 5. There are no corrosion problems.
 - 6. The system is relatively easy to construct with local labor.

Disadvantages of dry lime scrubbing.

- 1. Relative humidity in dry lime storages may be slightly lower than in storages using a water absorption system. Also, the water absorption system may have greater odor removal capacity than the dry lime system.
 - 2. The dry lime itself creates a number of problems; the sources

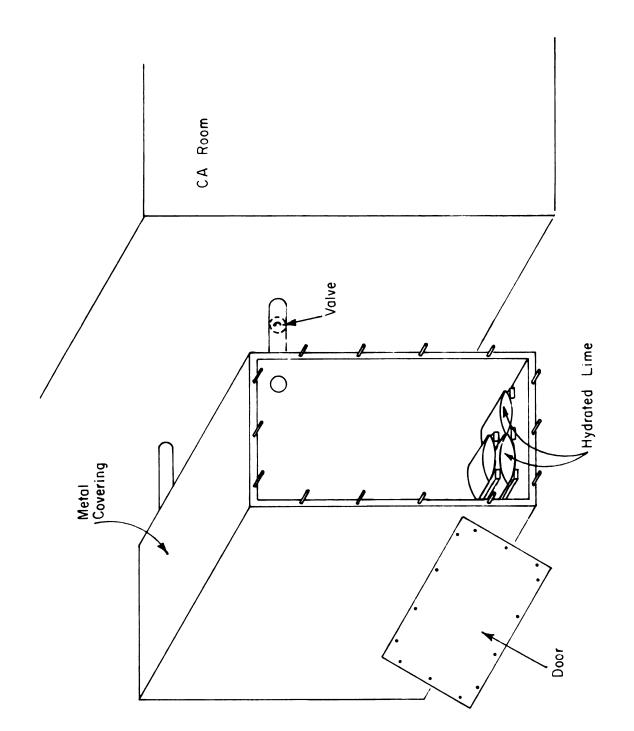


Fig. (C. -4.) Dry lune scrubber for CA apple storages (Eaves 1764)

of supply are limited; the variability in supply is large; the material is bulky to handle and to store; the dry lime presents a real disposal problem.

3. The dry lime room requires a considerable amount of space; often times space that could for the same cost be utilized as fruit storage space.

A practice is gaining use which is to put approximately 1/10 lb. of dry lime per bu. of apples inside the CA storage room and therefore the dry lime box can be made smaller. This lime is put either on top or in some obscure place where it does not normally take up space that would be occupied by apples, for example, underneath the floor mounted diffuser, etc. This dry lime, of course, has an initial high affinity for carbon dioxide which means that it aids in controlling the carbon dioxide level during the pull down period and since no oxygen is added as carbon dioxide is removed, this aids in oxygen come down. The dry lime tapers off toward the end of the season as it becomes saturated and at the point where the dry lime ceases to be very important the water absorber can easily carry the carbon dioxide removal load.

Reversible Chemical Absorption

Carbonate Solution

When carbon dioxide is dissolved in an aqueous solution of sodium or

potassium carbonate the following reversible reaction occurs:

$$Na_2 CO_3 + CO_2 + H_2O \neq 2NaHCO_3$$
 (2C3-5)

The solubility of CO_2 in such a solution depends on the ratio of carbonate to bicarbonate, the total amount of carbonate in the solution, the temperature, and the partial pressure of carbon dioxide in the gas.

Harte et al. (1933) expressed the relation in an empirical formula, which reduces to

$$P_{CO_2} = \frac{(137 f^2 N_{Na})^{1 \cdot 29}}{S(1-f) (365-T)}$$
 (2C3-6)

where

 P_{CO_2} partial pressure of CO_2 , mm H_g

f fraction of total base present as bicarbonate

 N_{Na} sodium normality

S solubility of CO_2 in water under a pressure of 1 atm. of CO_2 , g. mol/liter

T temperature °F

Eq. 2C3-6 has been tested over the temperature range of 65° to 150°F and sodium normalities from 0.5 to 2.0. Sherwood and Pigford (1952) reported that the data on the potassium system may be approximated by the equation:

$$P_{CO_2} = \frac{(45f^2N_K)^{1\cdot 29}}{S(1-f)(302-T)}$$
 (2C3-7)

whe

Eq.

can

ar.d

lent

Use

high

r001

proc

of C

(dow

the :

and

forn

his

þack

the c

Gian

where

 $N_{_{\mathbf{K}}}$ is the potassium normality.

Eq. 2C3-7 has been tested over the temperature range of 30° to 100°F and potassium noramlities from 1.0 to 2.0. Crystals of bicarbonate can be formed above a concentration of 30 percent carbonate equivalent.

Use of hot potassium carbonate

There is no advantage in using carbonate compared to water at room temperature. The solubility of CO₂ in the carbonate is appreciably high at higher temperatures, therefore the hot potassium carbonate process was developed. It was developed especially for bulk removal of CO₂ from a gas when a high degree of removal is <u>not</u> necessary (down to 0.5 percent) and where the inlet concentration of CO₂ is in the range of 5 to 50 percent.

Sieve trays have been found advantageous for use in CO_2 absorption and regeneration in hot K_2 CO_3 solution, a substantial quantity of performance data have been reported by Buck and Leitch (1958). For this system, sieve trays are reported to be more economical than packed absorption towers.

Recently small quantities of various chemicals have been added to the carbonate solution to accelerate the absorption process. The Giammorco-Vetrocoke process (Hoogendoorn 1963), is a modification

of the sorp

tellu

solu

by R

max

equi

equi

V0<u>1</u>U

gen

res

ine

abs per

220

pot:

act

in (

lar

chi

€at Je:

by

of the hot potassium carbonate process. In this process the CO2 absorption rate is considerably increased by the addition of selenious, telluric, arsenous oxides and amino acids to the potassium carbonate solution. The kinetics of this pseudo first order reaction was studied by Richards (1964). The use of these additives will not increase the maximum volume of carbon dioxide which can be absorbed under equilibrium condition. However, it does make a closer approach to equilibrium possible, resulting in more CO2 actually absorbed per volume of solvent and also smaller towers can be used. In the regeneration step, the same effect produces a leaner solvent with less residual CO₂, which means that a lower outlet concentration of CO₂ in the scrubbed gas can be obtained and also the volume of CO2 that can be absorbed per volume lean solvent is larger. The usual absorption temperature (Hoogendoorn 1963) is 140°F and regeneration takes place at 220°F. Air stripping is also possible (at 160°F). An advantage of potash (KOH) solution containing arsenous oxide is that the arsenous oxide acts as a corrosion inhibitor so that normal carbon steel can be used in constructing the equipment. Mayland (1964) described also a similar process in which ethanolamine and corrosion inhibitors such as dichromate are added to the hot carbonate solution. Fundamental investigation on the effect of additives by Ryan and Carter as described by Jeffreys and Bull (1964) reported that the absorption rate was increased by small addition of methanol, many sugars and particularly

formaldehyde. The explanation was that the additives depressed the surface tension of the absorbent which in turn brought about an increase in the absorption rate. Jeffreys and Bull (1964) also showed that the addition of glycine to sodium carbonate solution increased the rate of absorption. This is believed to be due to glycinate ion accumulating in the surface of the liquid catalyzing the absorption reaction.

The application of carbonate scrubbing in the CA

The Sulzer Company in Switzerland (Meyer 1961) is using potassium carbonate solution in its CO₂ absorber. They claim the ability to wash out carbon dioxide economically in a circulation system practically without pressure and without thermal requirement. The choice of this process was decided mainly because of the following factors: $K_2 \ CO_3$ is odorless, inexpensive, non-toxic and as an absorption medium it can be regenerated with air. It is possible also to install the absorption unit even at ambient temperature of 32-50°F, without adversely affecting either the economical operation of the absorber or the refrigeration condition in the CA storage. The Sulzer Company mentioned the use of a new type of mixing nozzle for distribution of liquid in spray towers, drop washers, washing towers with filter elements, sprinkler towers or packed washer, that doubles or triples the absorption rate compared with other systems. The principle of the gas bubble washer is described in a schematic diagram (Fig. 2C3-5). The mixture of air

plates, in the amou mixture mixture at the to which se in the li pipe, af air mix top of th absorpt mixture process the sys using th Europe for was

in its u

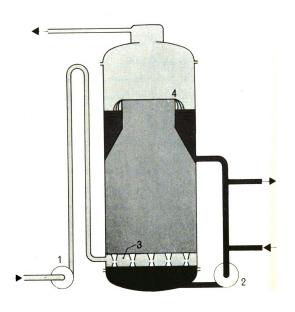
sorptio

eugine€

and CO_2 i

.

and CO₂ is led via a blower into several mixing nozzles located between two plates, in the bottom of the washing tower. A circulation pump supplies the amount of liquid required for distributing the gas. After an intimate mixture of gas and liquid has been achieved in the mixing nozzles, the mixture rises inside the washing tower. The gas and liquid are separated at the top end of the tower. The liquid spills over into a collecting chamber, which serves at the same time as a separator for the gas bubbles entrained in the liquid. The liquid is led back to the circulation pump through a fall pipe, after which the cycle begins again. After separating the gas and air mixture from the washing fluid, the former leaves the washer at the top of the tower. The process described can be carried out both as an absorption process, i.e., washing the carbon dioxide out of the gaseous mixture with simultaneous charging of washing fluid, and as an exsorption process, i.e., regeneration of the washing fluid by blowing air through the system accompanied by enrichment of the latter with carbon dioxide, using the same equipment in either case. This scrubber is used in Europe and was claimed to operate satisfactorily, it can be used also for washing the air in storage with water. There is not any disadvantage in its use from operational reasons. Although water has a better absorption coefficient for CO₂ than the cold K₂CO₃ there may be some engineering design advantages in this unit.



- 1 Blower for air laden with CO2
- 2 Circulating pump for absorbent
- 3 Nozzle assembly
- 4 Mixture overflow

Fig. 2C3-5. Diagram of the Sulzer scrubber (Meyer 1961)

Ethanolamine Solutions

Aqueous solutions of weak organic bases such as mono-, di-, or triethanolamines can be used to absorb acid gas like CO₂ and the alkaline absorbent can be regenerated by heating. The vapor pressures of CO₂ from mono-, di-, and triethanolamine solutions of various concentrations and at temperatures of 0° to 75°C are given in Perry (1963). Amine carbonate is formed according to the overall reaction

$$2RNH_2 + CO_2 + H_2O \neq (RNH_2)_2H_2CO_3$$
 (2C3-8)

The amines are relatively non-volatile and have a high absorption capacity. The use of monoethanolamine (MEA) as the alkaline absorbent showed greater absorption coefficient compared to the diand tri- while the solubilities in the different solutions are not greatly different.

Rates of absorption of CO_2 in absorption towers were extensively studied (Table 2C3-1) and the factors affecting the rate of absorption are mainly:

1. Total amine concentration a_0 (moles/vol) and the <u>carbonation</u> ratio, α_c (mole CO_2 /mole amine) (a) as long as $\alpha_c < 0.5$, second order fast chemical absorption takes place (Astarita <u>et al</u>. 1964) and the overall reaction is

$$CO_2 + 2RNH_2 \rightarrow RNHCOO^- + RNH_3^+$$
 (2C3-9)

An a

whe

rate

visc

ord

Ab:

lyz

tio

ab,

tin

St

10

(K

(E

th

C)

An approximate equation for calculation of RNH2 concentration is

$$(RNH_2) = a_0 (1-2\alpha_c)$$
 (2C3-10)

where (RNH₂) is the RNH₂ concentration, mols/volume. Absorption rates increase with increasing a and decreasing α , as long as viscosity effect does not influence. (b) When α > 0.5, pseudo first-order slow chemical absorption takes place, the overall reaction is

$$RNHCOO^{-} + CO_2 + 2H_2O \rightarrow RNH_3^{+} + 2HCO_3$$
 (2C3-11)

Absorption rates decrease with increasing a_0 and with increasing a_c . The step $CO_2 + H_2O \rightarrow HCO_3^- + H^+$ is a slow reaction which is catalyzed by arsenite ions and therefore arsenite may help in the absorption of CO_2 by MEA. Clarke (1964) explained the kinetics of CO_2 absorption accompanied by chemical reaction but at short contact time.

- 2. <u>Gas rate</u>. In a packed tower the rate of absorption is substantially independent of the gas rate (G) but when using bubble plate tower at low gas velocities in an atmospheric-pressure CO₂ absorber (Kohl 1956), appreciably higher efficiencies were obtained.

 (Bubbling mechanism on the plate is greatly influenced by gas rate.)
- 3. <u>Liquid rate</u>. Rate of absorption increased with increase of the liquid rate.
- 4. $\underline{\text{CO}_2}$ concentration. The rate decrease linearly with increase of CO_2 concentration in a solution at atmospheric pressure

and rel

5.

range 6.

increa

Tange

7 aimos

ethyle

iectiv I

CO⁵

Ther

.

and relatively low CO₂ partial pressure (0 to 0.5 atm).

- 5. CO₂ partial pressure. K_{Ga} appears to vary with $e^{-3.4p}$ in the range $0\rightarrow0.5$ atm (CO₂ partial pressure).
- 6. <u>Temperature</u>. In the range 77° to 167°F, K_{Ga} increased with increased temperature up to 122°F and leveled off or decreased in the range from 122° to 167°F.
- 7. Type of packing. The performance of 1-in. Berl saddles is almost identical with that of 1-in. steel Rashing rings but the polyethylene Tellerettes (Teller 1958) achieved 23 to 72 percent more effectiveness in mass transfer rate as a function of the flow condition.

Kohl (1956) summarized the factors affecting the absorption of CO₂ in aqueous solutions of MEA in packed tower in the equation:

$$K_{Ga} = \frac{0.56}{\mu 0.68} [1 + 5.7(0.5 - \alpha_C) \text{ M} \cdot \text{e}^{0.0067 \text{T} - 3.4 \text{p}}]$$
 (2C3-12)

where:

 K_{Ga} overall coefficient lb. mols/(hr.)(cu. ft.) (atm)

μ viscosity, centipoises

 α_{C} concentration of CO_2 in the solution, mols/mols MEA

M amine concentration of the solution (g. mols/liter)

T temperature °F

p partial pressure, atm.

The applica

In cons age it was injury by e of the ethan ethanolami ranging the acsorbing

> place at th J. and

> arranging

Their abso with the al

irom the c means of

solution,

tion of CC

irom the 1

fank wher

tot TEA f

tirough th

the liquid

The ?

The application of ethanolamine scrubber in the CA

In considering the use of ethanolamine in scrubbers for CA storage it was shown by Mann (1958) that the apples suffered no apparent injury by exposures to vapors of ethanolamines. The most economical of the ethanolamines was the monoethanolamine (MEA) although triethanolamine (TEA) is used too. Mann suggested two methods of arranging the scrubber unit; (1) having two identical units, one in use absorbing carbon dioxide while the other is being regenerated or (2) arranging some system whereby absorption and regeneration take place at the same time and continuously.

J. and E. Hall Ltd. (1957) have developed continuous absorber. Their absorber consists of two tahks located one above the other, with the absorption taking place in the upper tank. The atmosphere from the chamber being scrubbed is drawn into the upper tank by means of a small compressor and the gases bubble up through the solution, after which the atmosphere containing a reduced concentration of CO₂ is returned to the storage chamber. The solution of TEA from the upper tank flows down through a heat exchanger into the lower tank where it is reactivated by warming with electric heaters. The hot TEA from the lower tank is returned to the upper tank by a pump through the heat exchanger, and passes through an aftercooler, where the liquid is cooled to approximately atmospheric temperature.

The MEA scrubber is very effective in keeping any desired CO₂

lev

ŋ**:** (

tag

01:

ine

sho

eth.

2C-

sili

mi

hat

is

for Sta

the

00;

Th

âĠ

level. It is very useful where the treated gas must be virtually free of CO₂ but this is not needed in CA storage operations. A disadvantage using this system is that the gas atmosphere is heated unless there is cooling of the solution after reactivation. In the construction of scrubbing units using ethanolamine solutions nonferrous metals should not be used. As there are no operational problems using ethanolamine unit, it will be judged economically only (Sec. 2J).

2C4. Removal by use of molecular sieves

Synthetic Molecular Sieves (MS) are crystalline metal aluminosilicates that have been activated for adsorption by removing their water of hydration. Because little or no change in structure occurs during this dehydration, unusual highly porous adsorbents are formed that have strong affinity for water and certain gases and liquids.

MS act as physical adsorbents in which the adsorbed molecule is held within the crystal structure by relatively weak Van der Waals force. When the sieve is desorbed, the crystal retains its original state. Adsorption by MS is characterized by a Langmuir-type isotherm--the amount of a compound that is adsorbed increases rapidly up to a saturation value; this saturation or equilibrium value usually corresponds to completely filling the internal void volume of the MS. The desorption of MS shows no measureable hysteresis, that is, the adsorption and desorption are reversible. Not only will MS separate

mole eren of m

pola

with

adso

MS 1

and

(Cla

atmo

sup;

of N

beer

pon

Weig adso

they

ţe σ

Eas

molecules based on size and configuration, but will also adsorb preferentially based on polarity or degree of unsaturation. In a mixture of molecules small enough to enter the pores, the less volatile, more polar, or more unsaturated the molecule, the more tightly it is held within the crystal lattice.

MS are available in a wide variety of types and forms. For the adsorption of CO2 and water from a stream of gas, Union Carbide MS type 5-A (Hersh 1961) and type 4-A (Johansson 1963) are used, and recently a MS especially designed for this purpose was patented (Clarke, R. G. 1964). Clarke, R. G. (1964) developed a gel for the purpose of adsorbing carbon dioxide and water from environmental atmosphere that can be readily regenerated by drawing a vacuum, supplying heat or by using a combination of these two methods. This gel was made of K_2CO_3 , Mg $(NO_3)_3 \cdot 2H_2O$ and Al $(NO_3)_3 \cdot 9H_2O$. A gel of MgO · Al₂O₃ co-precipitate with the evaluation of CO₂ gas. It has been noted that the gel bodies do not lose their ability to adsorb carbon dioxide although they pick up a considerable portion of their weight in water. It has been found, to the contrary, that the gel adsorbed CO2 more efficiently when they contain water than when they are dry.

In designing an MS adsorption unit the following factors should be considered: 1. Adsorption equilibria of the MS. -- The amount of gas or liquid adsorbed when equilibrium is established at the critical

tempe

rate a

der o

life. -

to the

is red

?

shape

syste

56 to

bed.

!÷g₅!

Place

Wher

of ±6

Deso:

I

jė cl^g

counpi

temperature and pressure. 2. Adsorption rate and kinetics. -- The rate at which a given material will be adsorbed by MS pellets, powder or beads at the critical temperature and pressure. 3. Cyclic life. -- During cyclic operation, (will be discussed later) damage to the adsorbent may occur and the equilibrium adsorption capacity is reduced.

MS may be used in the following types of adsorption systems:

- 1. Static adsorption. --When formed into wafers or other shapes, MS can be used as static adsorbers in closed gas or liquid system.
- 2. Single-bed adsorption. --When interrupted produce flow can be tolerated, it is sometimes convenient to use a single adsorption bed. When the adsorption capacity of the bed is reached, it can be regenerated for further use.
- 3. Multiple-bed adsorption. --A typical dual-bed installation places one bed on adsorption, while the other is being regenerated. When the process design requires shorter time for the adsorption step, additional beds can be added to permit continuous processing of the feed.

Desorption or regeneration cycles for MS

Desorption, which is the most inefficient step in the cycle can be classified into four types, which may be used separately or in combination.

1.

400 and

is retur

duction

2.

tional ti

sure cy

3.

tial pre

Sorbate

picked i

4.

all or p

Increas

increas

Gr

cal indi

ŝtream

ine sati

S:à∏t o

ad;;anta

molecu

- 1. Thermal cycle. -- The MS is heated to a temperature between 400 and 600°F, the bed is flushed with a dry purge gas and the MS is returned to an adsorption condition. A cooling step is then needed.
- 2. <u>Pressure cycle</u>. --Desorption can be accomplished by a reduction in total pressure at isothermal conditions. Because additional time is not required for heating and cooling the beds, the pressure cycle can be designed to operate rapidly.
- 3. Purge gas stripping cycle. -- The purge gas reduces the partial pressure of the adsorbed component and affects desorption. Adsorbates pass from the adsorbent into the vapor over the bed, are picked up by the purge gas, and swept from the bed.
- 4. <u>Displacement cycles.</u> -- Use an adsorbable fluid to displace all or part of the material loaded in the bed.

Increased pressure adsorption on MS

Gregory et al. (1963) mentioned a number of advantages in using increased pressure adsorption (about 50 lb./in., gage) in the chemical industry. Firstly, as the partial pressure of CO₂ in a given gas stream rises, the quantity of MS required falls. Secondly, since the saturation content of water in the MS remains approximately constant on a volume basis, the mass ratio falls. This gives a further advantage of the use of MS by reducing the sites taken up by the water molecules and also by a reduction of the temperature of adsorption,

sin

CO

ing

pre ter

ac!

ext

<u>Tr.</u>

tio Ca

eth Si:

fin

ph

þŝ

1.5

20

be cu

į.

•: •:[since relatively less water is adsorbed. (The heat of adsorption of CO_2 is low compared with that of water). He also found that cooling is of considerable importance. Reactivation at atmospheric pressure gave advantages over reactivation at higher pressures, in terms of purge losses, heater rating required, and adsorption capacity achieved. In-bed heating reduced the heat consumption compared to external heaters.

The use of MS in CA storage

The use of MS as a CO₂ adsorbent in CA room was first mentioned in the literature by Johansson (1963). Johansson used Union Carbide MS type 4-A which adsorbs water, CO₂, methanol, ethanol, ethylene, acetylene, propylene, n-propanal and ethylene oxide. Since water is a very strong polar compound it has a stronger affinity for the adsorbent than do the other components of the atmosphere. The atmosphere from the storage chamber was drawn (Fig. 2C4-1) through the adsorption column containing the MS. After passing through the adsorption unit, the air was forced through water in a gas washing bottle in order to saturate the atmosphere before it reentered the storage chamber. The atmosphere was circulated by an air pump. By adjusting the amount of atmosphere passing through the adsorption column, according to the rate of respiration, the CO₂ level of the atmosphere could be held at a fairly constant



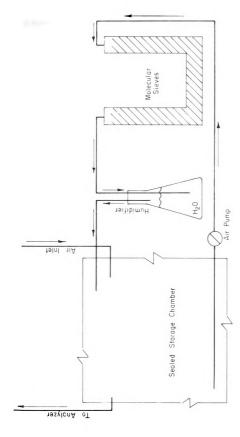


Fig. 2C4-1. Schematic diagram of the CA system ..iohansson 1963)

level. The MS was reactivated by heating to 500°F; during the reactivation cycle air was purged through the adsorption column in a direction opposite to that during the adsorption phase. The control of the CO₂ level was satisfactory.

It is believed that two companies (Tectrol Division of Whirlpool Corporation and Atlantic Research Corporation) are using synthetic or natural MS in their carbon dioxide scrubbers in their CA gas generating equipment. Tectrol is using it as part of their complete external generator. Atlantic Research corporation on the other hand is using their CO₂ scrubber-Arcosorb with and without their catalytic burner-Arcat. The Arcosorb is designed to handle the CO₂ load generated by the Arcat too.

Fig. 2C4-2 is a flow diagram of the Arcosorb-Arcat (Arcagen). It consists of dual tower design which operates alternatively as adsorption and reactivating and allows continuous fully automatic operation. Tower 1 of the Arcosorb is in adsorbing position with downward air flow. The room atmosphere passes through the adsorbent and CO₂ is extracted. Tower 2 in reactivating position has heaters energized and reactivation air flow sweeping the desorbed CO₂ to the outside air. The adsorbent is thus readied for a new adsorption cycle, and after a programmed time period the 4-way valves reverse, tower 1 is put on reactivation, and tower 2 on adsorption. As water is adsorbed in this process rehumidification is provided to maintain the desired high

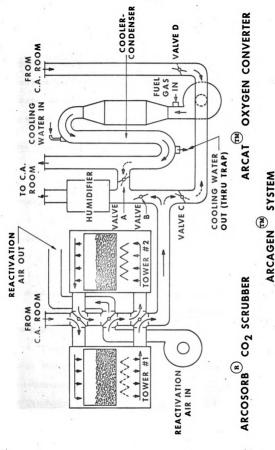


Fig. 2C4-2. Flow diagram of AtaIntic Research Corporation controlled atmosphere generator (Jensen 1965)

humidity level in the room. The particular unit Arcosorb-8 has the capacity to remove 8 lb. CO₂ per hr. at 1.5 percent entering CO₂ concentration (for handling of about 60,000 bu. apples). The air flow is 150 cfm, the pressure drop is 8 in. water and one gpm water is needed for the rehumidifier.

Advantages and disadvantages of MS CO₂ scrubber for CA storage

Advantages:

- 1. Carbon dioxide level as low as needed can be achieved with simple adjustment of the unit.
- 2. The only make-up air required is that to replace the extracted CO₂ and the operation does not add more oxygen to the storage atmosphere (compared to water scrubber).
- 3. Uses no chemical apart from the MS thus eliminating the adding and disposal of chemicals, and corrosion problems.
- 4. Can be designed into a continuous fully automatic operation thus requires negligible servicing.
 - 5. Compact in size.
- 6. Will remove ethylene and other trace gases and eliminate the requirement for activated charcoal filters.

Disadvantages:

- 1. High initial cost.
- 2. The need for rehumidification of the storage room gas before reentering the room.

3.

tion stag

4.

quality ! at a rea

2C5. R

thetic s

Re

gases (

thick, c

selecte

bility ir

normal

pends o

mechan

adsorb

necessa

brane d

Sin

^{nee}ded,

remova

ary anal

- 3. There is heat input into the room because of the regeneration stage. This heat has to be removed.
- 4. It is a rather sophisticated system that requires a maintenance quality level that often is not available to storages in remote areas at a reasonable cost.

2C5. Removal by using a selective membrane

Recently the General Electric Company introduced a thin synthetic silicone rubber membrane that can be used for separation of gases (General Electric Laboratory 1964). This membrane, 1-mil thick, can be applied to gas-gas separation. The mechanism whereby selected molecules pass through the film is a combination of solubility in the membrane and diffusion through it. This contrasts with normal diffusion across the membrane, in which the mechanism depends on the presence of intermolecular holes, which function as mechanical sieves. This also differs from molecular sieves that adsorb and occlude the molecule and where a desorption step is necessary. Since the selected gas passes to the other side of the membrane directly it can be used for specific separation.

Since there are no chemicals involved and no regeneration step needed, the possibility of using the silicone rubber membrane for removal of CO₂ from the CA storage looked attractive and a preliminary analysis was made.

The per

Gas Pe

N₂ -

0, -

CO2 -

H₂O .

It certainly through the

the outside

this would

a unit desi

order to fi

to calculat

calculation

air change

³6°F. At

^{ls abo}ut 75

tie ratio o

ਹlerated.

removed ea

The permeation rates for the membrane are given below:

Gas Permeability = $\frac{\text{liters (at normal temperature and pressure)}}{\text{hr. sq. yd. } \frac{\Delta P \text{ (across the membrane)}}{1 \text{ mil thickness}}$

(2C5-1)

 N_2 - 25

 O_2 - 54

CO₂ - 288

 H_2O - 3420

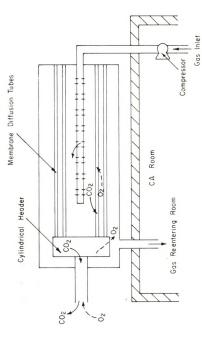
It certainly appears that at the same time that carbon dioxide is going through the membrane toward the outside, oxygen will be passing from the outside air into the contained atmosphere. It was calculated that this would amount to approximately 200 cu. ft. of oxygen per day for a unit designed to remove 300 cu. ft. CO₂ per day (Robb 1964). In order to find out if this added O₂ can be tolerated Eq. 2D1-5 was used to calculate the O₂ and CO₂ percent during the pulldown period. The calculation was made for 15,000 bu. room, space factor 2.47, 0.02 air changes per 24 hr. and respiration rate of McIntosh apples at 36°F. At the time of pulldown the maximum CO₂ volume to be removed is about 750 cu. ft. per day and during this time it was calculated that the ratio of 200 cu. ft. O₂ added per 300 cu. ft. CO₂ removed cannot be tolerated. After the pulldown period about 300 cu. ft. CO₂ have to be removed each day and it was calculated that a ratio fo 0.6 cu. ft. O₂

added per cu. ft. CO₂ scrubbed can be tolerated (or the room has to be tighter and 200 cu. ft. O₂ per 300 cu. ft. CO₂ removed can be tolerated when there is 0.017 air changes per 24 hr., which is very close to the existing conditions of 0.02 air changes per 24 hrs.)

This oxygen in-leakage during pulldown period or afterwards could be prevented by compressing the recirculated air so that the oxygen partial pressure next to the membrane would be increased above 0.03 at one atmosphere. This would also reduce the membrane area required to remove the carbon dioxide but would require compressive work.

A very general design of a diffuser is shown in Fig. 2C5-1. The unit consists of a series of membrane tubes that are arranged concentrically around the gas inlet tube. The membrane tubes are closed on one end, and brazed to the CO₂ discharge header which is open to the atmosphere. The feed stream circulates (under pressure, as needed) over the outside of the tubes. CO₂ diffuses through these tubes and is discharged to the atmosphere, while O₂ diffuses into the system.

This design of the diffuser type of scrubbing system as applied to a CA storage is only speculative and further study on its feasibility is recommended.



_C5-1 General design of CO2 diffuser using selective membrane

2D. Oxygen Reduction

The general methods of oxygen reduction are:

- a. Fruit or product generated atmosphere.
- b. Externally generated atmosphere
 - The addition of liquid or compressed nitrogen or carbon dioxide.
 - (2) Hydrocarbon fuel burner.
 - (3) External gas generator.

2D1. Fruit or product generated atmosphere

After the CA room is closed, the apples continue respiring which requires O_2 and simultaneously produces CO_2 . There is a decrease in O_2 level and an increase in the CO_2 level. As the respiration continues the CO_2 level will reach the controlled condition (5 percent for example) and until this point is reached, in a relatively gas tight storage, the total material balance has not been disturbed volumetrically and the materials have only been changed in composition. However, as respiration continues, the CO_2 level will rise above 5 percent the excess CO_2 will be removed by scrubbing, and the material balance on a volumetric basis is changed.

Pflug and Dewey (1956) and Pflug (1960) discussed this problem extensively and developed a procedure for a numerical calculation of the rate of oxygen reduction. Pflug used the following variables and units:

	Symbol	Units
Storage room volume (gross)	V	cu. ft.
Quantity of fruit in storage	В	bushels (bu.)
Space factor	$Z = \frac{V}{B}$	cu. ft.
Respiration rate	r	cu. ft. O ₂ consumed 1000 bu. day
Oxygen level in storage	Y	cu. ft. O ₂
Controlled CO ₂ level in storage	c	cu. ft. CO ₂
Leakage or ventilation rate	x	air changes (based on empty room volume) 24 hr.
Temperature	Т	°F
Oxygen in standard atmosphere		0.21 cu. ft. cu. ft. atmosphere
Carbon dioxide in standard atmosphere		0.0003 cu. ft. cu. ft. atmosphere
Bushel of apples		45 lb.
Time	t	days
Oxygen diffusion ratio	w	cu. ft. O ₂ added cu. ft. CO ₂ removal

It was also estimated that 1 bu. of apples occupies a volume of 0.74 cu. ft. (the box was included in the calculation of the volume). The oxygen level Y of a CA storage at any time t is given by the equation

7

Ti

K.

C

10

U

4

(0

In ge

S]

6

$$Y = 0.21 \sum_{0 \to t \text{ days}} \frac{O_2}{\text{day}}$$
 (2D1-1)

where the change in oxygen level was evaluated on a day basis:

$$\frac{\Delta O_2}{\text{day}} = \frac{\text{r-O}_2 \text{ added through leakage - O}_2 \text{ added through CO}_2 \text{ absorption}}{\text{volume of atmosphere}}$$
(2D1-2)

The summary of the relationships of Pflug (1960) for the caustic soda absorption system also will be true for any other absorption process in which there is no oxygen added by absorber through diffusion.

Oxygen consumed and
$$CO_2$$
 produced = $r = \frac{cu. ft.}{1000 bu. day}$

Oxygen added through air leakage

$$\frac{1000}{B}$$
 Vx (0.21-Y) = 1000 Zx (0.21-Y) = $\frac{cu. ft.}{1000 bu. day}$

Oxygen added through CO_2 removal = 0.21 (r - 1000 Z x C) = $\frac{\text{cu. ft.}}{1000 \text{ bu. day}}$

Volume of atmosphere per 1000 bu. = 1000 (Z - 0.74) = cu. ft.

$$\frac{\Delta O_2}{\text{day}} = \frac{\mathbf{r} - 1000 \ Z \times (0.21 - Y) - 0.21 \ (\mathbf{r} - 1000 \ Z \times C)}{(1000 \ Z - 0.74)} \tag{2D1-3}$$

$$Y_{t} = 0.21 - \frac{\Delta O_{2}}{day} = 0.21 - \sum_{O \to t \text{ days}} \left[\frac{0.79 \text{r}}{1000 (Z - 0.74)} - \frac{2 \text{x}}{(Z - 0.74)} \right]$$

$$(0.21 - Y - 0.21C)$$

$$(2D1-4)$$

In the same way, Pflug (1960) shows a way to calculate the effect of oxygen added through diffusion, as with water scrubber. This enables him to show the effect of the water scrubber on the O₂ reduction. The general equation derived:

 $Y_t = 0$.

Using :

reduce

1.

time n

2.

filling
the ap

bushel

3.

the ra

sorpti

atmos

In the

T ber, (

lated :

5D5⁻

away :

A

This i

$$Y_{t} = 0.21 - \sum_{O \to t \text{ days}} \left[\frac{0.79 \text{r (l-w)}}{1000 (Z-0.74)} - \frac{Z_{x}}{(Z-0.74)} (0.21-Y-0.21C-0.79wC) \right]$$
(2D1-5)

Using Eq. 2D1-5 Pflug shows the following effects of:

- 1. Room leakage rate. The higher the leakage the longer the time to reduce the oxygen content. This shows the importance of a tight room.
- 2. Room fullness. The lower the space factor Z the shorter the time needed to reduce the oxygen. This shows the importance of completely filling the room with apples, the disadvantages of leaving a space between the apple boxes, and the advantage of using a pallet box compared to a bushel box.
- 3. Type of scrubber. Oxygen is added through diffusion, therefore, the rate of oxygen reduction is slower with the water absorber. The absorption will take about 20 percent longer to develop a 3 percent oxygen atmosphere than when chemical absorption (caustic for example) is used. In the adequately tight, fully-loaded room that means 2 to 3 days longer.

Table 2D1-1 shows the effect of leakage, fullness and type of scrubber, on the time required to develop the desired atmosphere as calculated by Pflug (1960): (See Table 2D1-1, p. 61).

2D2. The addition of nitrogen or carbon dioxide

As was mentioned in the last section, the CO_2 which is scrubbed away is replaced with air which in turn contains 21 percent oxygen. This is not desired since a fast reduction of oxygen is needed. One way

TABLE 2D1-1. Time required for CA storage room to reduce oxygen level to 0.030, carbon dioxide level to 0.025, as a function of type of carbon dioxide absorption system, leakage rate and room fullness

	Space factor Z, <u>cu. ft.</u> bu.	Days to reduce oxygen level to 0.030				
Type of CO ₂ absorption		Leakage rate, x, air changes per day				
system		0	0.01	0.02	0.03	
	2.5	13	15	20	over 25	
Water	3.0	19	·23	over 25		
	3.5	24	over 25			
Caustic	2.5	11	13	15	20	
soda	3.0	16	19	25	over 25	
absorption	3.5	21	over 25			

to pre

relati

the m

final

1

of sto balan

tinue

throu

is ke

react

(Sout

 $\frac{N_2 fl_1}{N_2 fl_1}$

can b

obtai1

2

tion i

oxyge

Ţ

€∉8e0

to prevent this is the addition of N_2 . In this way the CO_2 level is held relatively constant, the apples continue to bring the O_2 level down and the material balance is further maintained by the addition of N_2 until final process conditions are reached.

When the final process conditions are achieved, after 10-20 days of storage, air must be added instead of N_2 to maintain the material balance (usually the normal leakage is sufficient) since the apples continue to respire and require the presence of O_2 in the air.

The addition of the N_2 is done by releasing N_2 gas from a cylinder through a pipe leading to the CA room, or the breather bag (Sec. 4B) is kept inflated by adding nitrogen until the proper oxygen level is reached at which time the breather bag may be kept inflated with air (Southwick and Zahradnik 1958).

N₂ flushing

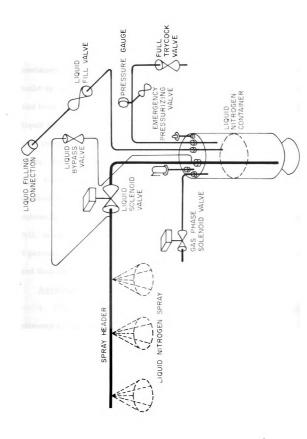
A more recent process is the flushing of the room with N_2 . This can be done in either of two ways:

- 1. The use of gaseous $N_{\boldsymbol{z}}$ to flush the oxygen from the room to obtain a rapid oxygen drop.
- 2. The use of liquid N_2 as a supplement to mechanical refrigeration in the precooling of the apples and at the same time to flush out the oxygen from the room.

The difference between these two methods is that in the first one gaseous N_2 from cylinders is used for flushing only, there is no cooling

effect, and in the second, liquid N_2 from cylinder is used for precooling and flushing and then gaseous N_2 is used from the same cylinder to regulate the atmosphere. There are different engineering problems with the gaseous and liquid N_2 involved. We will discuss only the liquid N_2 process and analyze the difference between the two only economically (Sec. 2J).

Smock and Blanpied (1965) conducted a small scale (1500 bu.) experiment using a modified version of the "Polastream" intransit refrigeration process of the Linde Division of Union Carbide Corporation (Kane 1961) (Fig. 2D2-1). For the cooling phase of the experiment they introduced liquid N2 through a ceiling mounted spray header set up in front of the blower on the evaporator. A thermostatic control in the liquid nitrogen line caused liquid nitrogen to be introduced into the room when the air temperature rose above 30°F. Since a great deal of nitrogen gas was introduced into the room during cooling, the pressure was released by opening the port hole in the gas tight door. After the cooling and oxygen flushing operations were finished, the unit was switched over to gaseous nitrogen introduction into the room. This meant that the liquid nitrogen had to go through a vaporizer attached to the storage tank prior to entering the room. An oxygen sensor was placed inside the CA room. When the oxygen level rose in the room above 3 percent concentration, the oxygen sensor caused a solenoid valve to open and nitrogen gas entered the room. Since this introduction of



PTg. _D_-1 _ Polestream | refrigeration system (Kine 1901)

 N_2 raised the pressure in the room, the excess pressure was released through a 2-in. pipe. The end of this pipe was immersed 1/2-in. in a container of water so that not more than 1/2-in. water pressure would build up inside the room. The CO_2 was controlled by running pipes to and from the CA room into a dry lime scrubber. The precooling with liquid N_2 was very efficient. The maintenance of the oxygen level with the automatic nitrogen supply also was very efficient in a "leaky" room. (Naturally the bigger the leak the bigger is the consumption of N_2 .) When the room was opened and half of the apples removed the desired oxygen level was reached a day after resealing using the automatic nitrogen supply. During the period that the room was half full, twice as much nitrogen was required per day to hold the O_2 at 3 percent. Smock and Blanpied (1965) summarized the advantages and disadvantages of nitrogen CA rooms:

Advantages:

- 1. Flushing out the oxygen in a CA room is very rapid when liquid nitrogen is used for cooling as well as flushing.
- 2. While flushing with liquid nitrogen, there is a cooling effect that can supplement refrigeration.
- 3. Very close, automatic control of the oxygen level was obtained by the use of the modified "Polastream" process.
- 4. No servicing of the equipment was required once it was installed and started up. There are no moving parts. Negligible

electricity is required for the oxygen sensor and to activate the solenoid valves.

- 5. There is no continuous flushing of the room. The apples are respiring and nitrogen is introduced into the room only to hold the oxygen at 3 percent.
- 6. The CA room can be opened and some of the fruit removed with quick regeneration of the atmosphere following resealing.

Disadvantages:

- 1. During liquid nitrogen cooling there is a slight danger of freezing the fruit since nitrogen vaporizes at -370°F but it could be avoided.
- 2. When the room is not full the flushing rate increases and this introduces the problem of the maintenance of a high enough CO₂ level.
 - 3. There is some loss of liquid nitrogen during long storage.

The economical study of this system is in Sec. 2J. As the experiment was done for a 1500 bu.-room, definite conclusions from the results have to be judged carefully for a larger room.

The addition of carbon dioxide

Another possibility for a combination of oxygen pulldown and precooling is the use of dry ice or liquid carbon dioxide. The rate of sublimation or heat absorption of dry ice (at the temperature of sublimation; -110°F) is too slow. The dry ice could be crushed to reduce

the particle size and expose more surface area to increase the refrigeration capacity, but the pulverizing operation reduces the overall efficiency therefore liquid carbon dioxide is more suitable for this purpose.

There are at present "in-transit" refrigeration units similar to the "Polastream" discussed, using liquid CO_2 instead of liquid N_2 . ¹ A similar modification as with the Polastream is possible. The big disadvantage is that high CO_2 level will be reached and extra scrubbing of CO_2 will be needed. However, this disadvantage is an advantage when high concentration of CO_2 is needed, over 20 percent as with cherries and black currants for example.

This operation is not suitable for apples and will not be discussed any further.

2D3. Hydrocarbon fuel burner

Another way to accelerate the natural reduction of oxygen by respiration, is to burn the oxygen of the storage atmosphere with gas. Gases with relatively low concentration of N₂ and CO₂ are the most practical sources for this purpose. Fig. 2D3-1 shows the volumetric relationship between O₂ and CO₂ that can be expected with a combustion system using air as a source of O₂ (Lannert 1964). Two gaseous fuels

¹Liquid Carbonic-Division of General Dynamic Porta-CO₂ LD--and Pureco CO₂ Blast Chilling--Pure Carbonic Division of Air Reduction Company.

are shown; natural gas, which is assumed to be methane-CH4 and propane-C₃H₈. Fig. 2D3-1 also shows an oval which embraces the O₂ and CO₂ concentrations commonly accepted in the CA apple storage. Since the curves do not intersect this oval, it is obvious that CO₂ must be removed from the room. From Fig. 2D3-1 if 3 percent O₂ and 5 percent CO₂ are desired, for example, we find that for combustion of the oxygen down to 3 percent the CO₂ generated will be over 10 percent, therefore, this excess has to be removed. The excess CO₂ produced is removed by an absorber as the room atmosphere is recirculated through it. By operation on a recirculatory basis the need is to convert only the 21 percent oxygen of the air in the room (after sealing the room) and the 21 percent oxygen of the air introduced to the room because of CO₂ scrubbing and leakage. When the rooms are made as tight as possible the use of the burner and in turn the absorber will be smaller which is desirable. A full storage room (low space factor) takes less time to pull down, than does a half-full room, as more of the air space is taken up by the apples. The apples act as a supplement to the burner operation. The burner can be adjusted to accommodate for the original oxygen present in the room, oxygen introduced because of leakage and oxygen introduced because of CO₂ removal.

Two companies, Tectrol Division of Whirlpool Corp., and Atlantic Research are using catalytic burners in their CA generating equipment

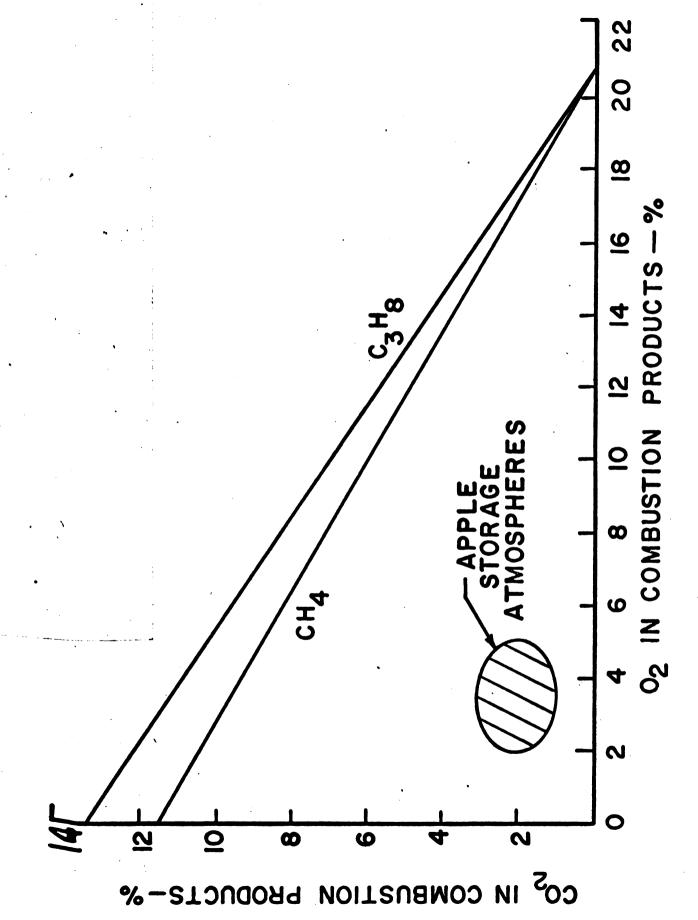


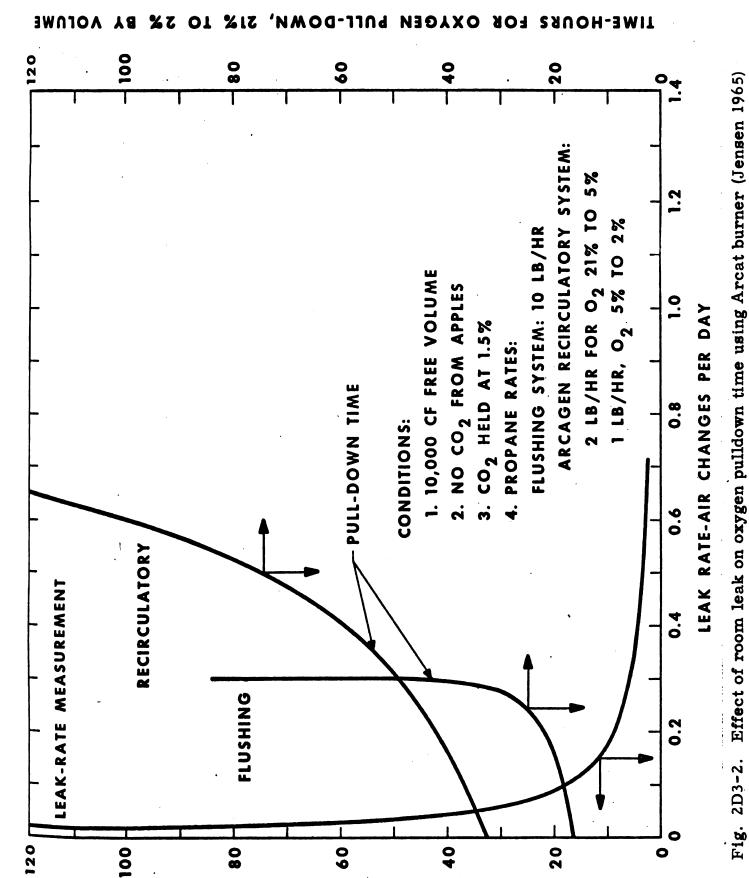
Fig. 2D3-1. Oxygen vs. carbon dioxide from combustion in air (Lannert 1964)

and Eaves and Lockhart (1964) introduced a simple low cost burner in their experimental "Oxygen controller."

The difference between the operation of the Tectrol burner and the Atlantic Research burner—Arcat is that the Tectrol burner is a part of the Tectrol complete externally generating system (Sec. 2E) using continuous flow of outside air and the Arcat is using the recirculating atmosphere and can operate in combination with an Arcosorb or as an independent unit (can be moved from one room to another). The Arcat is used during pulldown periods and whenever the air leakage is too high or after removal of part of the apples from the room (high space factor). It is not used once pulldown is achieved in a relatively tight full room. The Tectrol burner is discussed in Sec. 2E and the Arcat is discussed here as an example of a catalytic burner.

The catalytic burner. --Arcat (Fig. 2C4-2) converts oxygen to CO_2 and water vapor by burning liquid petroleum gas at temperatures and O_2 concentration far below those normally required for oxidation. The burner effluent then proceeds to a condenser where it is cooled and some of the water is removed assisting in the rehumidification of the process stream whenever necessary (as with MS adsorbers). By using a catalytic burner it is possible to maintain complete combustion at O_2 concentration ranging down to 1-2 percent.

Fig. 2D3-2 shows the pulldown time in hours needed for different leakage rates using the Arcat (Jensen 1965). A pulldown time is



33 hr. for every 10,000 cu. ft. of free air space for 0.05 air changes per day when 2.0 lb. of propane per hour and oxygen from 21 percent to 2 percent by volume with CO₂ level at 1.5 percent (without the assistance of the respiration of apples). The pulldown can be calculated easily also by using Eq. 2D1-4. The Arcat burner is using a maximum 2 lb. L. P. per hour during pulldown (for handling about 60,000 bu. apples) and one gpm of water is needed for cooling.

Within the design parameters of the Arcat, the entering oxygen content does not affect the performance of the equipment until approximately 5 percent O₂ is reached. At this point an adjustment is made in the fuel flow if lower oxygen levels are desired. The system is designed to oxidize only a portion of the inlet oxygen, not the entire amount, and in this way the availability of sufficient oxygen to oxidize the fuel is assured (Thomas 1965).

Catalytic oxidation is independent of the entering oxygen concentration and provides complete combustion through the whole range of inlet gas concentration. By careful design of the catalyst bed and the use of appropriate catalysts by-products of incomplete combustion are eliminated. The primary control problem is maintaining adequate temperature within the catalyst bed to assure a complete reaction, and this problem is independent of the inlet oxygen concentration (Thomas 1965). Eaves and Lockhart (1964) as mentioned, developed an extremely simple and inexpensive oxygen controller

(Fig. 2D3-3) which consists of a propane burner, a cooler condenser coil and an independent dry lime scrubber. Preliminary results indicated that the O₂ concentration was reduced to 3 percent within 24 hrs. They used a regular propane burner to burn the O2 of the recirculating atmosphere, and found that the toxic concentration of carbon monoxide accumulated in the storage was 2 percent. By disconnecting the return pipe to the burner the hazard from carbon monoxide was eliminated. In other words it was changed from a closed recirculating system to externally generated. In the future the air discharge pipe complete with valve will be put through an outside wall in a convenient location for operation thus eliminating any possible hazard from CO. Eaves (1965) did not find any known toxic combustion products, but as toxic gases are very dangerous checks had to be made regularly and further additional experimental results are needed. As the cost of the burner is less than 10 percent of the Arcat, its potential use is worth looking into.

Advantages of hydrocarbon fuel burner:

- 1. Fast oxygen reduction permits early opening of rooms when CA laws must be met.
- 2. Reopening and closing of the CA storage room, during storage season, is possible.
 - 3. Enables operation of partially filled room.
- 4. It is possible to keep oxygen level as low as 1-2 percent when desired.

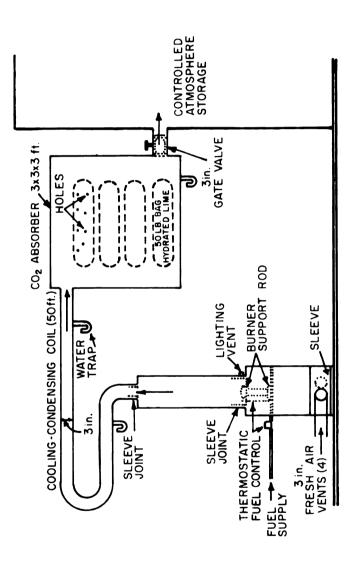


Fig. 2D-3. Oxygen controller for controlled atmosphere storages (Eaves 1964)

- 5. For a recirculating atmosphere the burner is only needed for the pulldown periods.
- 6. When the burner is operating, some air leakage can be tolerated.

Disadvantages of hydrocarbon fuel burner:

- 1. Excess CO_2 is formed and has to be removed.
- 2. Causes heat input into the room, therefore, more refrigeration is needed.
- 3. The constant change of fuel-oxygen ratio in the recirculating atmosphere (because of constant O₂ reduction) may present a problem of burner control.
- 4. Possible problems with toxic impurities—when the O_2 level drops below the stoichiometric level, unburned fuel and impurities will be present in the combustion product. This problem is important since during the pulldown the fuel-oxygen is constantly changed because the O_2 level drops continuously especially with the regular burner.

2D4. External gas generator

The oxygen reduction and the control of the atmosphere is made by introducing externally generated atmosphere into the room. This is discussed in Sec. 2E.

2E. External Gas Generator

The external generation of the atmosphere (EGA) for the CA storage of apples is a different approach to atmosphere control in a CA storage room. The desired atmosphere is produced outside the room and then introduced into the room. In this way the atmosphere is not as dependent on respiration as with the regular CA. There is no oxygen reduction here because the original atmosphere actually is replaced and equilibrium is reached with the respiring apples.

Tectrol Division of the Whirlpool Corporation in 1962 introduced their Tectrol (Total Environmental Control) system which is an externally generated atmosphere. Fig. 2E-1 diagrammatically represents the atmosphere control factors affecting the storage using their system. The storage atmosphere is a function of (1) air leakage in (2) atmosphere supplied by the generator (3) respiration of the apples (4) atmosphere leakage. This technique utilizes the CO₂ produced by the apples along with a constantly supplied generated atmosphere that will complement the air infiltration to provide the desired atmosphere. When the required atmosphere is to contain for example 3 percent O₂, the generator output must be somewhat below this value so that it will be complemented by the 21 percent O₂ in the infiltration air.

Fig. 2E-2 is a schematic of the Tectrol generator which produces

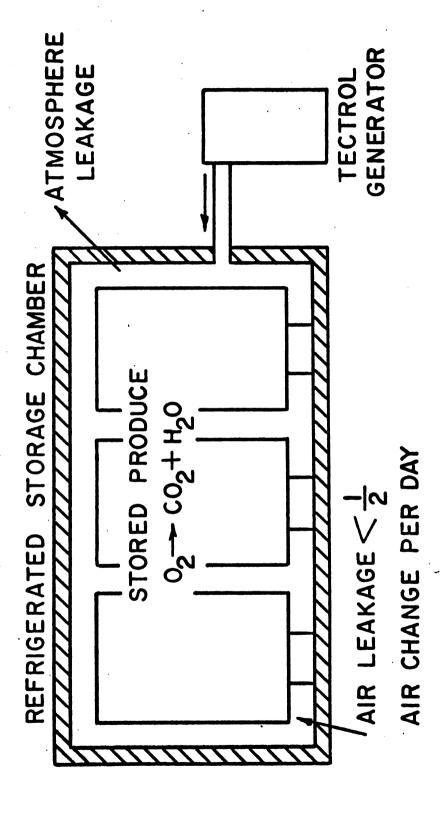


Fig. 2E-1. Atmospheric control factors affecting the storage (Lannert 1964)

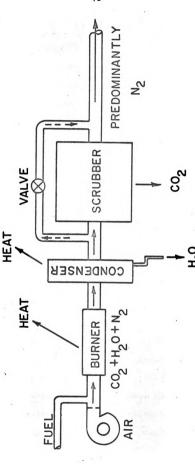


Fig. 2E-2. Tectrol atmospheric generator schematic (Lannert 1964)

the atmosphere that is supplied to the storage chamber. Hydrocarbon gas is used in the burner for the reasons described in Sec. 2D-3. Gaseous fuel and outside air mixed together in the proper proportions are fed into the burner constantly all season. The mixture is burned catalytically with the O2 in the air combining with the fuel to produce CO2 and water. This step is different from the one used in the Arcat where the burner is burning the O_2 in the recirculating atmosphere. Changes in the gaseous fuel input mixture result in a change in the O_2 content of the effluent (present an engineering problem for Arcat). As outside air and specific type of fuel is used (usually liquid petroleum-LP fuel as natural gas), there are only minor feed gas fluctuations and the effluent gas composition is steady. In this way there are no problems of traces of unburned or partially burned components when an atmosphere of O2 lower than 2 percent is desired due to insufficient O2 in feed gas.

The mixture is burned catalytically with the O_2 in the air combining with the hydrocarbon fuel to produce CO_2 and water. The burner effluent then proceeds to a condenser where it is cooled and some of the water is removed. The effluent then enters the scrubber section (probably MS type, see Sec. 2C-4) where most of the CO_2 is removed and the resultant effluent is then expelled from the generator to the storage room. A valve is arranged in parallel with the scrubber to control the CO_2 output by control of the amount of

effluent bypassing the scrubber.

The particular Tectrol generator Model 2197-G has a limit of 110,000 Btu/hr. and volumetric output of approximately 950 cu. ft. per hr., if combustion is stoichiometric. Cooling water must be available--3.5 gpm (70°F and 25 psig). The gaseous fuel flow will be approximately 44 cu. ft. per hr. of propane, or 110 cu. ft. per hr. of natural gas. This unit will take care of between 12,000 and 18,000 bu. depending on the leakage rate of the storage room. The pulldown period is about 3 days and the Tectrol generator can tolerate up to 0.5 air changes per day.

The use of the Tectrol generator has been on a lease basis only but now is offered for sale too.

Advantages:

- 1. Fast O₂ reduction--allowing reopening and closing of the CA storage room during storage season.
- 2. Enables operation of partially full room--part of the fruit can be removed and room resealed and kept at the desired atmosphere.
- 3. It is possible to keep Q_2 level as low as 1-2 percent when desired.
- 4. Can tolerate some leakage because of slight gas pressure developed which enables possible construction cost saving and relatively easy conversion of existing refrigerated room to CA.
 - 5. Automatic control of constant atmosphere.

- 6. No odor build-up because of the continuous flushing and the use of MS type scrubbers.
- 7. Definite prevention of impurities and unburned fuel because of the use of outside air for the burner and the continuous flushing.
- 8. Available also on lease basis. The atmosphere is guaranteed and there is no operational responsibility. There is no capital investment nor expensive start up and the full cost is tax deductible rather than capital investment.

Disadvantages:

- 1. Excess CO_2 is formed and has to be removed.
- 2. Causes heat input into room, therefore, more refrigeration is needed.
- 3. The burner is working all season long and is not so flexible in use as the Arcat.
- 4. Does not utilize all the O_2 reduction provided by the apples respiration.

2F. <u>Complete Systems for the Control</u> of the Atmosphere

Every combination of a $\rm CO_2$ scrubber and oxygen reduction system is suitable as a complete system for CA, as shown in Table 2F-1 and in addition Arcagen, Tectrol and Eaves "Oxygen controller."

As an example of a complete CA system the Tectrol was

TABLE 2F-1. Possible combinations for complete system for the control of the atmosphere in a CA room

Oxygen reduction		ž	Liquid N ₂	Burner	€.
	naturai respiration	N ₂ flushing	flushing +	Recirculating atmosphere	Outside air
Scrubber					
Water	×	×	×	×	×
КОН	×	×	×	×	×
NaOH	×	×	×	×	×
K ₂ CO ₃	×	×	×	×	×
Na ₂ CO ₃	×	×	×	×	×
Ethanolamines	×	×	×	×	×
Dry lime	×	×	×	×	×
Molecular sieves	×	×	×	×	×
Selective membrane	X	×	×	×	×

described in Sec. 2E and the combination of liquid N_2 and dry lime in Sec. 2D2 and I will analyze here the general overall operation of the Arcagen and Eaves "Oxygen controller."

Fig. 2C4-2 is the flow diagram of Arcagen of the Atlantic Research Corporation. The room atmosphere passes through the Arcosorb (described in Sec. 2C4) and the CO₂ and water are extracted. The adsorbed CO₂ is exhausted to the atmosphere during reactivation and the dual tower design allows continuous fully automatic operation. A portion of the scrubbed gas then passes through the catalytic burner, Arcat (Sec. 2D3), where O2 is con- ${\tt verted}$ to ${\tt CO_2}$ and water using liquid petroleum gas as fuel. The excess CO₂ produced in the oxidation process is removed by the absorber as the room atmosphere is recirculated through the equipment. The water vapor produced assists in the rehumidifi-Cation of the process stream. The catalytic burner is bypassed When O₂ pulldown is not required; the regulation of the atmosphere is made easily by automatic operation of the scrubbing and the regulation of the percent of atmosphere going through the burner.

Fig. 2D3-3 is the diagram of "Oxygen controller" for CA, as was suggested by Eaves and Lockhart (1964). The apparatus essentially consists of a propane burner (Sec. 2D3) cooler condenser coil, and an independent dry lime scrubber for the removal of the CO₂ formed. Toxic carbon monoxide was formed when using

the burner on the closed recirculating atmosphere during the preliminary tests. By disconnecting the return pipe to the burner
this hazard was eliminated. In the future the air discharge pipe will
be put through an outside wall thus eliminating any possible hazard
from carbon monoxide. By circulating the atmosphere from the
burner through air cooled coils, heat is removed. The cooling coils
also remove the moisture produced by the propane combustion. The
excess CO₂ which is formed by the burner and apple respiration is
then absorbed in the dry lime absorber.

2G. CO₂ and O₂ Measurement and Control Systems

To control the composition of the atmosphere in the room we have to measure the carbon dioxide and oxygen concentration. There are three general measurement techniques used in the CA analysis:

Carbon dioxide and oxygen are successively adsorbed from the gas sample, and observations are made of the change of volume, or pressure. Example of the constant pressure and temperature and changing volume system is the Orsat apparatus. The Orsat type CO₂ and O₂ measuring apparatus is relatively inexpensive, and is of such construction and operation that it can be operated successively by storage operators of all training levels. It is the most common analyzer used today in CA storages. Smock and Blanpied (1960)

described the apparatus and its use in CA storages in detail. The constant-volume, changing pressure types are inherently more accurate but are more expensive in use. The chemical methods are time consuming and do not lend themselves to easy mechanization.

of the component to be analyzed. These methods are much faster than the chemical ones and easily mechanized for automatic operation.

Physical properties such as thermal conductivity and paramagnetic susceptibility are the most common properties used. Some other properties such as absorption of monochromatic radiation, speed of sound in the gas, changes of density and infrared have been used too (Fidler 1961b).

Thermal conductivity

Detecting changes of thermal conductivity (using either hot wires, or thermistors), is a potentially accurate method to measure CO_2 concentration. With change of carbon dioxide concentration, the thermal conductivity is changed and the instrument can be calibrated to read CO_2 . As an example Beckman Model 7C thermal conductivity type carbon dioxide analyzer will be described as used to measure the CO_2 in the CA room (Hunter 1965). This analyzer measures the concentration of one gas component in a mixture of gases, utilizing specific sensitive thermal conductivity filaments as detector for CO_2 in a mixture of CO_2 , CO_2 and CO_2 in our case. Since the thermal

conductivity of CO_2 is much greater than that of N_2 or O_2 , the presence of a small amount of CO_2 will be easily detected. One advantage of using this analyzer is that it can detect ammonia gas leakage from the refrigeration system. It happens that ammonia gas has also a high conductivity and the apparatus will act both as CO_2 analyzer and as an ammonia leak detector alarm system. In normal operation, the CO_2 concentration will not change rapidly, but the development of a small ammonia leak will cause the CO_2 reading to increase rapidly which will indicate that something is wrong in the room (Hunter 1965).

The thermal conductivity analyzer can be used to measure oxygen concentration also, with the addition of change over valves and a small carbon furnace. The procedure is first to observe the percentage CO₂ and then to operate a change-over valve, passing the sample through a carbon furnace. In the carbon furnace the O₂ in the sample is burned to CO₂, the sample then passing through the thermal conductivity analyzer again and a new reading is obtained.

The O₂ concentration is easily calculated (Mann 1960).

Paramagnetic susceptibility

Oxygen is unique among gases in being strongly paramagnetic.

Thus, by measuring the magnetic susceptibility of the CA gas its O₂

Content can be determined. No other gas in the CA atmosphere can

affect the reading significantly. When the gas sample containing

Oxygen is drawn into the test chamber, the magnetic force is altered,

when the proper equipment is available. The measurement is simple, accurate and fast. The difference among paramagnetic oxygen analyzers is in the sampling method (automatic or manual) and the possibilities to record the results. As an example the Beckman D2 indicating oxygen analyzer for 0-25 percent O2 range (\$295) for manual sampling, the C2, E2 can be arranged for continuous oxygen analysis of sample stream but not for recording (range \$660-1200) and F3 is available optionally with complete sampling systems, automatic control and recorders (the price of the complete system is over \$2,000). Hunter (1965) reported the successful use of Model F3 with sampling and recorder for 325,000 bu. apple storage.

3. Polarography (electrochemical method). An oxygen sensor was developed, which is basically a polaragraphic oxygen electrode. In this method, a measured small potential is impressed across a Pair of electrodes one of which is a non-polarizable reference electrode, the other a polarizable inert electrode. The magnitude of the Current which flows is proportional to the amount of oxygen present in the sample.

The Beckman model 777 and 778 process oxygen analyzers can be used to measure the oxygen in a CA room. The sensor's small size makes it ideal for installation in gland assemblies and thus

suitable also for control systems. A sealed gland assembly is available which permits the sensor to be inserted into each room if needed. The current produced is read out or can be arranged as output for potentiometric recorder or control system. The readout may be directly calibrated in oxygen partial pressure, or in percent oxygen.

The control of the gas level in the atmosphere

The control can be done in four ways:

- 1. Manual operation. Carbon dioxide and oxygen analysis is followed by manual operation of CO_2 scrubbers, air fan, O_2 or N_2 addition. In this case the CO_2 and O_2 analysis can be done by any method mentioned and the control is manually on a trial and error basis.
- 2. Programmed operation. Intermittent electric time clocks are used to program the operation of the scrubber, air fan, O_2 or N_2 addition. The CO_2 and O_2 analysis can be done in any method mentioned and the program is adjusted according to the gas analysis. The program will be different for the oxygen reduction period and for the storage after equilibrium of the atmosphere is reached. The adjustment is simple; if for example under any given schedule, the CO_2 tends to increase slightly from one day to the next, an increase of the operating time is needed and vice versa. The adjustment

of the operation of the air fan, O_2 or N_2 addition is made in the same way. Most of the scrubbers are operating on a programmed operation, today.

- 3. <u>Control of the atmospheric generator</u>. The control of the atmosphere generated by the Tectrol generator is made by adjusting the generator. The adjustment is based on the O₂ and CO₂ analysis of the storage room atmosphere.
- 4. Instrumental control of the CO₂ and O₂. Zahradnik (1964) mentioned the idea of complete instrumental system of indication and control of the CO₂ and O₂ levels in the CA room operation. The CO₂ indicator-controller controls the operation of the scrubber as required and the O₂ indicator controller controls the addition of air, nitrogen or oxygen to the room.

Control of the carbon dioxide level. The control of the constant CO₂ level as measured by thermal conductivity analyzer can be done in few ways namely; (a) using a mirror galvanometer and a photocell acting on relays. --When the cell is hit by the light spot, the relay opens a solenoid-valve which operates the CO₂ scrubbing unit. The scrubber operates until the CO₂ concentration drops just a bit below the value to be kept constant (Wolf and Kuprianoff 1961), and (b) when recorder is used--the recorder is provided with a retransmitting slide wire which can be used for control purposes.

Control of the oxygen level. The oxygen concentration is

measured by the paramagnetic oxygen meter or the polargraph O2 sensor and small relay and solenoid valve feeds the system with air, O_2 or N_2 or operate an O_2 burner, as desired. When the oxygen content becomes just a little lower than the desired value, an electrical impulse is given to open the solenoid valve, this valve is closed after the O2 content has raised sufficiently. The oxygen sensor is used in the modification of "Polastream" (Smock and Blanpied 1965) to introduce N_2 gas into the room when the O_2 concentration is too high. Fig. 2G-1 shows schematically the possible CO_2 and O_2 measurement and the control of liquid nitrogen system. Wolf and Kuprianoff (1961) developed an apparatus for the control of the storage and simultaneous measurement of the gas exchange of the stored **pr**oduce. This apparatus is a laboratory scale one, using independent automatic regulation of the concentration of the O2 and CO2 in the internal gas atmosphere. The CO2 concentration is measured by thermal conductivity analyzer which also controls the CO₂ level by **absorption** in a solution of potassium hydroxide; O_2 concentration is measured by a paramagnetic oxygen meter, which by means of small relays and solenoid valve feeds the system with oxygen flowing from a special gas container.

Discussion of CO₂ and O₂ measurement and control

The problem of CO_2 and O_2 measurement is whether to use $\mathbf{O_r}_{\mathtt{Sat}}$ or a combination of CO_2 and O_2 instrumental analyzers and

recorders system, and also, which size storage (how many rooms or measurements) will justify the use of expensive instrumentation.

Fig. 2G-1 is a schematic instrumentation system for multiple CA rooms. Any multiple system will require one O₂ analyzer, one CO₂ analyzer, at least one recorder and a sampling device for continuous atmosphere analysis. In addition a switching system is needed to operate the system and its price will depend on number of rooms.

An approximate analysis based on comparison of annual cost of operation of Orsat and the above system is given in Appendix 2-1.

The Orsat is time consuming measurement and the Orsat service life is relatively short (assumed to be 3 years) on the other hand the instrumentation system is expensive but is automatic. The instrumentation system price was approximated for a relatively simple system based on "local" design and also on a specific proposal from commercial contractor (Beckman Instruments, Inc.) for a complete system.

It was found that with more than 4 rooms with the "local"

System and more than 7 rooms with the commercial system the in
Strumentation system is more economical than using Orsat.

This calculation is based on the fact that we pay for the time
the Orsat measurement is made as regular work. Some operators,
especially small ones do not consider their time as money and
believe that an operator must be present anyhow. In this case the

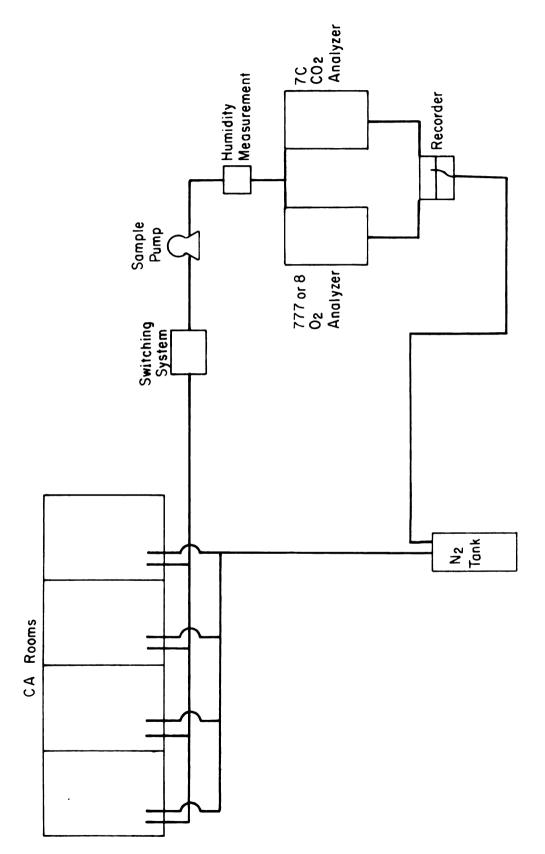


Fig. 2G-1. Schezzatic draming of CO₂ and O₂ instrumentation syntem for multiple CA rooms

above analysis is not correct. An analysis must be made according to the local circumstances.

The addition of a control system to the instrumentation system is quite simple and inexpensive (see Appendix 2-1). In our case (Fig. 2G-1) only the control of liquid N_2 was mentioned; it will need a specific and somewhat different design with the different atmosphere control systems.

2H. Humidity Control

The relative humidity (RH) in a CA storage should be high enough to prevent excessive weight loss of the apples but should, however, not be so high that the risk of microbiological spoilage is increased. RH between 90-95 percent is recommended (Smock and Blanpied 1960).

Humidity in the storage depends on a balance of losses and gains of moisture. The main loss is from condensation on cooling surfaces and absorption by containers and building materials and also from gas leakage from the room. Moisture is gained by evaporation from the apple, humidification device if provided, water absorber and evaporator during defrost. When store conditions of temperature and humidity are in equilibrium and there is no leakage of air into or out the space, the rate of condensation on the evaporator surfaces is equal to the water loss from the apples. These

conditions can be provided, only by equating the rate at which moisture is condensed on the evaporator surfaces with the rate at which it is evaporated from the apple, both factors are in part controlled by the relative vapor pressures. For the evaporator the weight of water condensed (W) can be expressed as W A x (Vp air - Vp evaporator surface) and for the apple the weight of water evaporated can be expressed as W B x (Vp apple - Vp air) where A and B are constants over a limited range of normally accepted storage conditions and Vp is vapor pressure (Mann 1954).

It is possible to provide large cooling surfaces which operate at a temperature close enough to that of the return air so that condensation is eliminated, or water may be sprayed into the air to offset condensation. It should be noted that even entire elimination of condensation on cooling surfaces does nothing to supply moisture that may be absorbed by containers, walls and ceilings. High humidity may usually be maintained at less expense by spraying water into the air to offset condensation and absorption. The disadvantage of the spray water is that much of the injected water will be collected on the refrigerated coils of the cooler unit, which will thus require more frequent defrosting (Mann 1960).

The Control of Relative Humidity in the Storage

There are two general ways of humidity control; the elimination of water evaporation and condensation, and direct humidification.

Elimination of evaporation and condensation

There are few methods for the elimination of water evaporation and condensation:

- 1. To obtain a high RH it is necessary to restrict the load on the cooler to a minimum by providing more than the theoretical minimum thickness of insulation to the storage structure, and by using high efficiency air circulating fans with speed control to reduce the heat produced by the fans. A vapor barrier (see Sec. 3) must be provided because when moisture is allowed to penetrate into the insulation from the warm face, condensation of water vapor in the insulation might occur, which decreases the insulation value and results in a greater heat load and low relative humidities.
- 2. Another way to control the humidity is by designing the cooler to affect the necessary heat transfer when operating a fraction of a degree above the desired air dew point temperature. This requires a large surface area and controlled uniform refrigeration evaporation temperature. Probably the most important factor controlling the humidity is the evaporator surface area. The refrigerant evaporation temperature is determined by the refrigerant

pressure within the evaporator coils. If, therefore, the refrigerant pressure is controlled within close limits, the evaporator surface temperature may be controlled at any desired level. This control is performed automatically by compressor speed control, or by back-pressure evaporator control (Mann 1955).

- 3. A change in air speed over the evaporator will have an effect on the humidity since it will cause an alteration in the heat transfer coefficient with a similar change in rate of water transfer. To increase air speed over the evaporator in order to increase the coefficient of heat transfer may not be economical because with increased air velocity the heat transfer coefficient will increase approximately as $v^{0.8}$ while the necessary fan power input will increase approximately as $v^{3.0}$ (Mann 1955).
- 4. Another aspect worth looking into is that the water transferred to the evaporator comes from the total weight of the stored apples. Because apples at 32° F only add very slightly to the total heat load this means that the weight loss on a percentage basis is practically inversely proportional to the weight of product in the room, provided, of course, the relative humidity remains constant. This is not quite so in practice as the RH will rise according to the total weight of the evaporating product and this may cause a less favorable ratio between heat and mass transfer to the air cooler. Nevertheless, a fully loaded room generally results in reducing the

loss of weight of the product (Geleynse and Stellenbosh 1962).

- 5. The wood usually used for boxes has an approximate equilibrium humidity of 62-65 percent. If, therefore, the boxes are put into a storage at 95 percent RH the wood will take up water, all of which must come from the apple. If, however, the boxes are wetted before loading into the room, they will lose a considerable proportion of the water during cooling down as condensate on the evaporator surfaces thus adversely affecting the duty of the coolers at a time when the highest performance is required. The method of overcoming this difficulty would be to wet the boxes at storage temperature as to be in equlibrium with the storage air but this is not a very practical solution. It does, however, raise the point that if the boxes could be precooled by immersion in cooled water, and then transferred into the room, a saving in weight of the apples could be affected (Mann 1954). Furthermore Philips et al. (1961) suggested the use of non-absorbent boxes.
- 6. The relative location of the fan and the evaporating coil in the refrigerating system has an effect on the RH also (Struz 1964). It can be seen (Fig. 2H-1) how, in the case of the draw thru application, the coil surface temperature would have to be lower to get the same amount of heat removal as shown for the blow thru application. This also affects the leaving air temperature which must be lower for the draw thru than for the blow thru. Therefore, the compressor

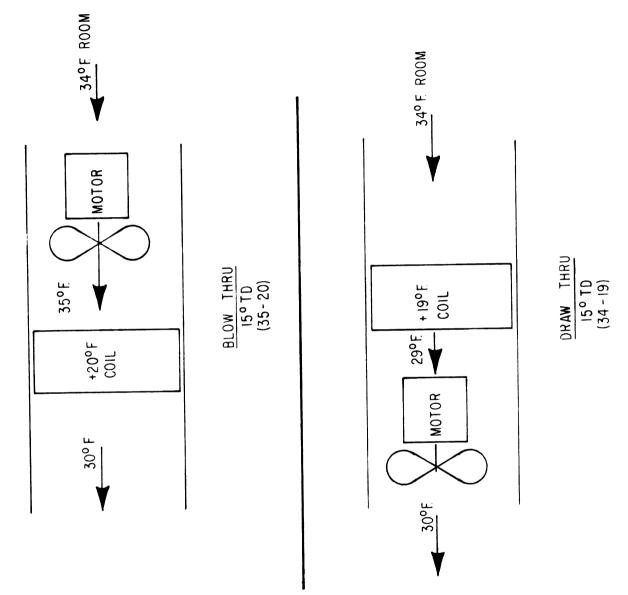


Fig. 2H-1. Blow toron and draw teron because 4640

capacity would have to be larger since it must operate at a lower suction temperature to produce a lower surface temperature that, in turn, produces the lower leaving air temperature. A blow thru application is better for maintaining a high humidity room condition than a draw thru application.

7. The Jacketed room system. In the jacketed system (Lentz 1959), the room is cooled by air circulating through a vapor-proof jacket entirely surrounding the room (Fig. 2H-2). Since the cooling air stream does not come into contact with the room air, RH, spatial temperature variations, and air velocity in the room are not directly dependent on the external heat load or on the operation of the refrigeration system. High RH is maintained by preventing moisture from leaving the room at a given temperature. The RH in the room is determined by the temperature of the coldest wall surface, and hence by the amount of air circulated in the jacket and also the direction of air circulation in the jacket. RH decreases from 98 percent at high rate of circulation to 89 percent with a low rate of flow in the top to bottom direction. The decrease was gradual with bottom to top circulation. With top to bottom circulation the relative humidity dropped sharply as the flow rate was reduced below 1200 cfm (Lentz 1955).

Another problem, associated with moisture in the CA storage is the accumulation of water in the insulation of the CA room, a

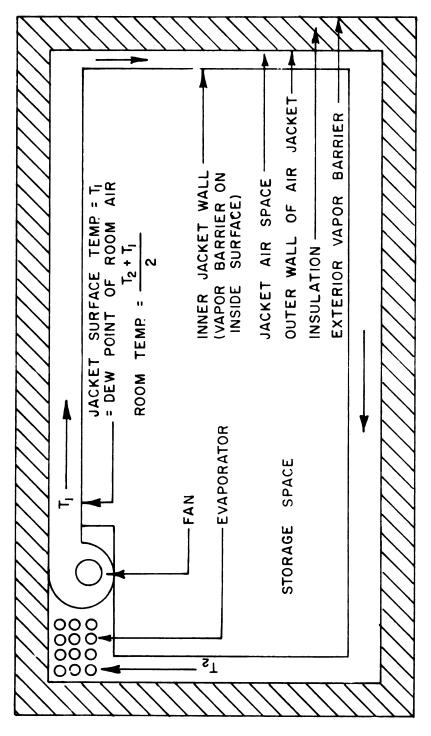


Fig. 2H-2. Schematic sketch of jacketed cold room (Lentz 1959)

problem aggravated by reversal of vapor pressure gradient (see Sec. 3). The jacket system is a solution for this problem in CA storages where a highly vapor-resistant lining is required on the cold side of the insulation (Lentz and Philips 1959). As moisture is not leaving the room there is a reduction or elimination of the defrosting problem.

Lentz and Philips (1959) showed that high RH, uniform temperature, and low uniform air velocity can be maintained in small storage without difficulty, but it would appear that special provision must be made for air circulation through the load in larger rooms. Another problem with the jacketed room is that this method is not effective where there is moisture absorption in the room by the boxes and packaging materials. Such absorption would not be a problem in a system in which high RH is maintained by moisture addition. The answer to the problem may be provided by a combination of the two systems (Lentz 1955).

Direct humidification

There are few ways of direct humidification:

1. Flooding the floor of the storage with condensate and/or water and relying on re-evaporation to improve the RH. This way is not entirely satisfactory as with the low air speed available over the water surface for evaporation and the vapor pressure difference is

insufficient. It is very essential that if this method is used there must not be any possibility of damage to floor insulation or the structure.

- 2. Providing an electrically heated water bath and regulating its temperature so that amount of water evaporated is sufficient to maintain the air moisture content at the required level. This method proved satisfactory in laboratory scale (Mann 1955) but it has the disadvantage of adding heat to the cold room.
- 3. The addition of water as a fine spray into the circulating air. It is essential, that the water introduced into the air stream should be as a very fine mist, and that the drops should evaporate fairly rapidly. Guillou and Richardson (1964) studied this problem and proposed as a standard system external-mixing pneumatic nozzles, directly connected to the regular water system and to an air compressor chosen to maintain suitable pressure while operating continuously.

High-pressure water systems need no air compressor but have some disadvantages like the danger of the plugging of the small orifice. Mechanical atomizers are self-contained and are good where the layout allows use of a few rather large units. Substitution of steam for spray is shown to impose a serious additional refrigeration load.

A system capable of adding one gallon of water per hr. for each ton of refrigeration, should be able to maintain up to 95 percent RH under any reasonable conditions (Guillou and Richardson 1964).

4. Defrosting methods as direct humidification. Two defrosting methods can be used for the purpose of direct humidification; water and antifreeze solution spray defrost systems.

Water defrost. Mann (1955) described a simple water defrost system in which the drain from the condensate tray was so arranged as to maintain a constant water level of 4-5 in. A small centrifugal pump was installed outside the storage with suction to condensate tray, the delivery from the pump being directed via perforated pipes to spray over the cooler surfaces. Bass (1964) described more complex method in which one of the steps, a water solenoid valve is opened supplying outside water or condensate water to spray over the coil or to a pan which allows water to drop uniformly over the coil. In this way it is possible to control the RH.

Antifreeze solution. A modification of the water defrost system for use at below freezing temperature is to spray the cooler coils with anti-freeze solution such as sodium or calcium chloride brine, or glycols such as ethylene glycol or propylene glycol in mixture with water (Mann, 1955; Lentz and Cook, 1955). Moisture absorbed by the solution is returned to the room as vapor by a continuously operating concentrator. Any RH up to saturation can be maintained by controlling the rate at which moisture is returned to the room from the concentrator. This system requires a considerable amount of additional equipment and maintenance work and therefore is more

expensive than the other defrosting methods (Bass 1964).

The Effect of CO₂ Removal and O₂ Reduction Methods on the Relative Humidity

There is no problem maintaining high RH using the wet CO₂ scrubbers (physical and chemical processes). The scrubbers in the room help to maintain high humidity more than the external ones.

Using dry lime scrubber, Eaves (1964) mentioned that he never encountered any problems of moisture loss and has repeatedly obtained 90-92 percent RH in the CA storage room. Smock and Blanpied (1964) on the other hand claimed that the use of dry lime scrubber tends to reduce the RH and recommended humidification with water spray.

The molecular sieve will absorb water, as a very strong polar compound, stronger than other components of the atmosphere, therefore rehumidification of the room is necessary. Rehumidification is provided with the Tectrol atmosphere generator and the Arcat part of the Arcagen. Rehumidification will also be necessary using selective membrane as proposed (Sec. 2C5). The water vapor which is produced when hydrocarbon fuel burners are used for the reduction of O₂ in the room, will assist in the rehumidification. This applies to Arcat, Tectrol and Eaves "Oxygen controller."

Flushing of the room with N_2 gas may lower the RH if a water trap is not provided. But using liquid nitrogen will not affect the RH

appreciably as relatively small quantities of cold N₂ vapor are used and there is no condensation, frosting and defrosting problems.

Relative Humidity Measurement and Control

Measurement of RH in the CA storage room is difficult because of the combination of low temperature and high RH (approximately 32°F and 95 percent RH). Fortunately a high accuracy is not of vital importance in CA storage practice.

There are three possible RH measurement systems commonly used in this range of temperature and humidities:

1. Wet and dry bulb-wick type. The dry wet bulb wick assembly consists of wet and dry bulb sensing elements, wet bulb fan which pulls air over a sensing element and enough water for the wet-wick assembly has to be maintained (Foxboro 1958, Wright 1961). RH is not recorded directly but can be determined by using a psychrometric chart. The disadvantages of this system are that a very small inaccuracy in the temperature measurement will cause large error in the RH at this range, a wick will become stiff and dirty and needs occasional replacement which is not possible in CA rooms and also there is no direct measurement of the RH. The humidity controllers have to be dual controllers, having two separate measuring systems each with its own control system for the dry and wet bulb temperatures. The dry-bulb control regulates the refrigerator and the wet

bulb controls the humidifying system through a relay switch (Foxboro 1958, Wright 1961). This method is not highly recommended for our use.

2. Dew point measuring system. This system consists of a humidity sensitive element, a power unit for furnishing the proper current to operate this element, and a temperature recorder, indicator or controller calibrated in dew point temperature. system measures the dew point of the surrounding atmosphere by measuring a temperature--the equilibrium temperature of an exposed solution of lithium chloride, which is a function of the atmospheric dew point. The range is 13 to 100 percent RH in our temperature range. The element is essentially a thin-walled metal tube with a conventional temperature bulb--either liquid expansion or electrical resistance in it (Foxboro 1964, Honeywell 1962, Hygrodynamics). Contrary to the wet and dry bulb system, accuracy is not affected by ambient temperatures, it does not depend upon controlled air temperature, nor does it require air circulation. As with the wet and dry bulb system two separate measuring and control systems are needed for the measurement and control of the dry bulb and dew point to control the RH. The sensing element can be mounted directly in the room but provision should be made to prevent saturation of the lithium chloride solution as the humidity approaches 100 percent. Another approach which is very convenient for multiroom storage is mounting

the element in a sampling chamber outside the room. Then a sample could be pumped from the room and heated to prevent condensation before being introduced into the sampling chamber. The system will read the actual dew point of the gas regardless of its temperature. One sensing element power unit and recorder can be used for multiple storage room system and this can be added easily to the complete CO₂ and O₂ instrumentation as described in Fig. 2G-1 with little expansion of the switching system, using 3 pen recorder and some other minor modification.

3. The hair hygrometer is used extensively for RH measurement but its normal working range is 15 to 96 percent RH which is not sufficient for our needs in CA storage rooms.

2I. Air Purification

Apples produce a wide range of organic volatile compounds during their normal ripening process. The most important gas produced is ethylene but other volatiles of greater molecular weight such as alcohols, ketones and esters are formed also (Meigh 1956, 1957). They will be called the non-ethylenic volatiles. The rate of production of ethylene is affected by the temperature and the composition of the atmosphere. At 38°F or lower temperatures neither ethylene nor ripe apples had any effect on the rate of respiration, nor the length of storage life of apples (Meigh 1957). Production of

ethylene is an oxidative phenomenon--it does not occur under anaerobic conditions. The lower the oxygen and the higher the CO2 level in the atmosphere the smaller is the production of ethylene (Fidler 1961a). The non-ethylenic volatiles production rate tended to increase in air storage, while in CA storage they tended to remain constant or decrease throughout the season (Meigh 1957). The nonethylenic have been credited with induction of superficial scald of apples. Air purification gave some scald reduction but never gave satisfactory control when scald incidence was severe, therefore air purification is not a dependable means of scald control and there are other dependable methods today (Smock 1961). As a conclusion, if the temperature of storage is below 38°F, then the probability of benefit from elimination of apples' emanation is negligible and air purification is needed only to prevent and remove foul odor from other sources such as storage building, wood boxes, rot and unburned fuel. Because of the great deal of controversy among investigators the purification of apples' emanation and odors will be analyzed. Fortunately enough most of the scrubbing and oxygen reduction methods used in the CA operations operate also as air purifiers to some extent. However, before analyzing their contribution to air purification two other methods will be analyzed:

1. Activated carbon. Air purification with activated carbon is the most common and has high retention per unit weight for

organic solvents. Performance of adsorbent beds depends upon their thickness, velocity of gas passing, mesh size of the adsorbent, and temperature of the vapor being removed (Turk 1955). Activated carbon reduces the non-ethylenic volatiles concentration in the room significantly but has very little or no effect on ethylene concentration (Johansson 1962).

2. Oil soluble volatile absorption column. Wolf and Kuprianoff (1961) used in their laboratory scale CA storage unit, oil soluble volatiles absorption column. Here, by contact with a large surface of a thin mineral oil layer on short pieces of polyethylene tube, used as filling, the oil soluble components of the emanation product of the stored apples were absorbed. The CO₂ was absorbed by KOH solution.

The Effect of the Use of Some of the CO₂ Removal Systems

Water scrubber: Water scrubbing prevented the continuous increase of the ethylene concentration and reduced the ethylene and the non-ethylenic volatile concentration. Water which has been used for some time seemed to be more effective in removing ethylene from the room than fresh water (Johansson 1962). There is danger of motor burning out in the CA room and the odor of burnt rubber insulation is hard to remove with water. Smock and Blanpied (1960) suggested having an activated carbon air purification unit in the room just in

case an odor situation develops. If it is not used at all the carbon should be reactivated only every 5 years.

NaOH scrubber: NaOH scrubbing had similar effect on the ethylene levels as the water scrubbing. The non-ethylene volatile concentration, however, increased after NaOH scrubbing. As with water, sodium hydroxide solution which had been used for some time seemed to be more effective in removing ethylene from the room than fresh solution (Johansson 1962). A combination of a NaOH scrubber and an activated carbon air purification unit will remove ethylene and non-ethylene volatiles. This combination was used in CA storages for a long time (Smock and Blanpied 1960).

Dry lime scrubbing: A result of a survey (Eaves 1964) of dry lime scrubber users showed that there were no measurable odor problems involved. Furthermore, a brochure distributed by one of the leading lime producers in Canada states that their product is useful also as a deoderant (?!).

<u>Carbonate solution and ethanolamines scrubbers</u> will have an effect similar to the NaOH scrubber.

Molecular sieves: The molecular sieves adsorbants show a high adsorptive selectivity. The MS used in the Arcosorb unit will also remove ethylene and other trace gases and eliminate the requirement for activated carbon filters (Thomas 1965).

The Effect of the Use of Some Oxygen Reduction Methods

Two general oxygen reduction methods support air purification:

- 1. Flushing of the atmosphere: Continual flushing of the storage atmosphere with N₂, CO₂ or externally generated atmosphere has the desirable effect of decreasing the concentration of volatiles in the environment. Smock and Blanpied (1965) pointed that there was no odor build-up using the liquid nitrogen system. Lannert (1964) mentioned that the concentration of ethylene in the storage environment produced by the Tectrol unit was found to be only one-fourth of concentration normally found in conventionally operated CA rooms.
- 2. The use of hydrocarbon fuel burner: With the air purification techniques discussed so far, the volatiles were physically or chemically removed. Burners can convert the volatiles to compounds which are not objectionable or that can be removed with greater ease than the volatiles present (but also to undesirable compounds such as carbon monoxide). Catalytic combustion is used to avoid the formation of impurities with the Tectrol and the Arcat units. Eaves'

 "Oxygen controller" uses regular burner in which there is the danger of CO production. Catalytic burners can be designed to convert a specific undesired compounds, by rather complete oxidation at control temperature levels.

Conclusions

Fortunately the low temperature (under 38°F) and relatively anaerobic conditions in the CA room suggest that the probability of benefit from elimination of the apples' volatiles is negligible. As there is still discussion on this statement the analysis was made and showed that except with some of the chemical absorption CO₂ scrubbing methods as NaOH, KOH, K₂CO₃, ethanol amine, all the methods discussed did not present any severe odor problems, and except for unusual circumstances the use of an additional air purifier is not needed.

2J. <u>Engineering Cost Analysis Study of Controlled</u> Atmosphere Storage Systems

The performance of different types of controlled atmosphere storage systems is very important. However, along with performance data, cost data are equally important in selecting equipment. The data that have been assembled on the relative initial and operational costs of the several types of controlled atmosphere storage equipment have been analyzed using the "Equivalent annual cost method" of Mayland (1956). The basic formula for this analysis is:

 $ACCR = (P - L_s)(CRF) + L_s i + operation cost$

ACCR = annual cost

P = initial cost

L = prospective salvage value

n = life, years

i = interest rate as a decimal

CRF = capital recovery factor (Mayland 1956)

The initial cost includes: first cost, shipment and installation. The operational cost includes: direct labor, utilities, taxes, insurance and maintenance. Annual costs were calculated for the several types of carbon dioxide scrubbing based on figures in Appendix 2-2 (Table 2J-1), methods of oxygen reduction based on figures in Appendix 2-3 (Table 2J-2), and practically all possible combinations of carbon dioxide scrubbing and oxygen reduction systems (Table 2J-3 and 2J-4). In addition, the annual costs of several complete systems are available (Table 2J-5) and estimated annual cost for liquid nitrogen system based on figures in Appendix 2-4 (Table 2J-6). Annual costs were calculated for: (1) three different volumes of apples, 15, 20 and 60 thousand bu.; 15 and 20 thousand bu. storages are common, the 60 thousand bu. size was used to represent a larger scale operation. (2) The costs were evaluated using a high and low utility rate which would be comparable to that received by the small and larger operator and high and low labor costs which would represent rural prices and urban price levels.

TABLE 2J-1. Annual cost for carbon dioxide removal (cents per bushel)

2.49	2.78	1.47		> 4.32	1.23	7.35	000,09
2.49	1 1 1	1.47		> 4.32	1.23	7.37	20,000
2.49	1 1 1	1.47		> 5.75 ^b	1.23	7.63	15,000
		ricity	Large operation, 1 cent/kwh electricity	operation, 1 c	Large		
4.65	3.52		1.29	> 4.85	1.59	7.62	000,09
4.65	1 1 1			> 4.85	1.59	7.61	20,000
4.65	1 1 1			> 6.45 ^b	1.59	7.89	15,000
		ricity	Small operation, 3 cents/kwh electricity	operation, 3 c	Small o		
MEA	Arco- sorb (MS)	Dry lime 3 cents/bu. const. cost (hired labor)	Dry lime 1.5 cents/bu. const. cost (local labor)	K2CO3	Water	NaOH	Volume bu. of apples

^aBased on initial price-suggested retail price in Europe without shipment and installation (Appendix 2-2).

based on the use of unit suitable for 20,000 bu.

^cBased on dry lime cost without resale or regeneration.

Annual cost for oxygen reduction (cents per bushel for 4 pulldown periods)^a TABLE 2J-2.

Liquid N ₂	iquid N ₂
flushing	flushing
& cooling	cooling.
Adjusted	Adjusted
flushing	flushing
37.5 cents/100 cu. ft. liq. N_2 54 cents/100 ft 3 liquid N_2	1. ft. liq. N2

Small operation, 3 cents/kwh electricity, 8.4 cents/lb. propane gas

4. 17 (3. 60) 2. 44 (1. 05) 5. 88 (5. 24) 3. 24 (2. 72) 2. 44 (1. 05) 4. 52 (4. 05) 1. 35 (0. 97) 2. 44 (1. 05) 4. 52 (4. 05)	ne gas	3. 82 (3.50) 1.34 (0.71) 5.36 (5.15) 2. 90 (2.64) 1.34 (0.71) 4.19 (3.96) 1.05 (0.90) 1.34 (0.71) 4.19 (3.96)
4. 17 (3. 60 3. 24 (2. 72 1. 35 (0. 97	s/lb. propa	3.82 (3.50 2.90 (2.64 1.05 (0.90
4.0 (0.4) 4.0 (0.4) 4.0 (0.4)	icity, 2.98 cent	5. 22 (1. 62) 5. 22 (1. 62) 5. 22 (1. 62)
4.8 (1.2) 4.8 (1.2) 4.8 (1.2)	nt/kwh electr	4.8 (1.2) 4.8 (1.2) 4.8 (1.2)
1. 2 (-1. 2) 1. 2 (-1. 2) 1. 2 (-1. 2)	Large operation, 1 cent/kwh electricity, 2.98 cents/lb. propane gas	2. 22 (-0. 18) 2. 22 (-0. 18) 2. 22 (-0. 18)
3. 2 (0.8) 3. 2 (0.8) 3. 2 (0.8)	Large	3. 2 (0.8) 3. 2 (0.8) 3. 2 (0.8)
15,000 20,000 60,000		15,000 20,000 60,000

^aNumbers in parentheses are the cost of one pulldown.

 $^{
m b}{
m The}$ liquid N $_{
m 2}$ flushing annual cost was adjusted because of possible saving on precooling cost-using combination of flushing and cooling (Appendix 2-3).

Annual cost for 15,000 and 20,000 bu. was based on the use of the 60,000 bu. Arcat burner.

dinitial cost of Tectrol generator for 20,000 bu. was assumed to be \$5000. Annual cost for 15,000 bu. was based on the use of the 20,000 bu. Tectrol generator.

TABLE 2J-3. Annual cost in cents per bushel for combinations of carbon dioxide removal and oxygen reduction

Small scale operation 3 cents/kwh, 8.4 cents/lb. propane gas, 37.5 and 54 cents/100 cu. ft. liquid N_2

Volume bu. of apples	O ₂ reduction	Natural respir- ation	Liquid N ₂ flushing (54 cents)	Liquid N ₂ ^a flushing adjusted (54 cents)
			One p	oulldown
15,000	Water	1.59	2.79	1.99
20,000		1.59	2.79	1.99
60,000		1.59	2.79	1.99
15,000	NaOH	7.89	9.09	8.29
20,000		7.61	8.81	8.01
60,000		7.62	8.82	8.02
15,000	K₂CO₃ ^b	>6.45	>7.65	>6.85
20,000		>4.85	>6.05	>5.25
60,000		>4.85	>6.05	>5.75
15,000 20,000 60,000	Arcosorb (MS)	 3. 52	 4.72	 3. 92
15,000	MEA	4.65	5.85	5.05
20,000		4.65	5.85	5.05
60,000		4.65	5.85	5.05
15,000	Dry-lime based on 3 cents/bu. const. cost	1.47	2.67	1.87
20,000		1.47	2.67	1.87
60,000		1.47	2.67	1.87
15,000	Dry-lime based on 1.5 cents/bu. const. cost	1.29	2.49	1.69
20,000		1.29	2.49	1.69
60,000		1.29	2.49	1.69

^aThe liquid N_2 flushing annual cost was adjusted because of possible saving on precooling costs using combination of flushing and cooling (Appendix 2-3).

b_{K2}CO₃ scrubbing cost is based on initial price-suggested retail price in Europe without shipment and installation (Appendix 2-2).

TABLE 2J-3 (continued)

Liquid N ₂ flushing (37.5 cents)	Liquid N ₂ a flushing adjusted (37.5 cents)	Arcat burner	Eaves burner	Tectrol as a burner
One	pulldown		4 pulldowns	
2. 39	0.39	5.76	4.03	7.27
2.39	0.39	4.83	4.03	6.11
2.39	0.39	2.94	4.03	6.11
8.69	6.69	12.06	10.33	13.57
8.41	6.41	10.85	10.05	12.13
8.42	6.42	8.97	10.06	12.14
7.25	>5.25	>10.62	>8.89	>12.13
5.65	>3.65	>8.09	>7.29	>9.37
5.65	>3.65	>6.20	>7.29	>9.37
4.32	2. 32	See Arcagen Table 2J-5	5. 96	8.04
5.45	3.45	8.82	7.09	10.33
5.45	3.45	7.89	7.09	9.14
5.45	3.45	6.00	7.09	9.60
2. 27	0.27	5.64	See Eaves	7.15
2.27	0.27	4.71	O ₂ controller	5.99
2.27	0.27	2.82	Table 2J-5	5.99
2.09	0.09	5.46	See Eaves	6.97
2.09	0.09	4.53	O ₂ controller	5.81
2.09	0.09	2.64	Table 2J-5	5.81

 $^{^{\}text{C}}\text{Initial cost of Tectrol generator for 20,000 bu. was assumed to be $5000.}$

TABLE 2J-4. Annual cost in cents per bushel for combinations of carbon dioxide removal and oxygen reduction

<u>Large scale operation</u> 1 cent/kwh, 2.83 cents/lb. propane gas, 37.5 cents and 54 cents per 100 cu. ft. liquid N_2

Volume bu. of apples	O ₂ reduction	Natural respir- ation	Liquid N ₂ flushing (54 cents) One r	Liquid N ₂ a flushing adjusted (54 cents) oulldown
15,000	Water	1.23	2. 43	2.85
20,000		1.23	2. 43	2.85
60,000		1.23	2. 43	2.85
15,000	NaOH	7.63	8.83	9. 25
20,000		7.37	8.57	8. 99
60,000		7.35	8.55	8. 97
15,000	K ₂ CO ₃ ^b	>5.75	>6.95	>7.37
20,000		>4.32	>5.52	>5.94
60,000		>4.32	>5.52	>5.94
15,000 20,000 60,000	Arcosorb (MS)	 2.78	 3. 98	 4. 40
15,000	MEA	2.49	3.69	4.11
20,000		2.49	3.69	4.11
60,000		2.49	3.69	4.11
15,000 20,000 60,000	Dry-lime Based on 3 cents/bu. const. cost	1.47 1.47 1.47	2.67 2.67 2.67	3.09 3.09 3.09
15,000	Dry-lime Based on 1.5 cents/bu. const. cost	1.29	2.49	2.91
20,000		1.29	2.49	2.91
60,000		1.29	2.49	2.91

^aThe liquid N_2 flushing annual cost was adjusted because of possible saving on precooling cost using combination of flushing and cooling (Appendix 2-3).

^bK₂CO₃ scrubbing cost is based on initial price--suggested retail price in Europe without shipment and installation (Appendix 2-2).

TABLE 2J-4 (continued)

Liquid N ₂ flushing (37.5 cents)	Liquid N ₂ a flushing adjusted (37.5 cents)	Arcat burner	Eaves burner	Tectrol as a burner
One	pulldown		4 pulldowns	
2.03	1.05	5.05	2.57	6.59
2.03	1.05	4.13	2.57	5.42
2.03	1.05	2. 28	2.57	5.42
8.43	7.45	11.45	8.97	12.99
8.17	7.19	10.27	8.71	11.56
8.15	7.17	8.40	8.67	11.54
>6.55	>5.57	>9.57	>7.09	>11.11
>5.12	>4.14	>7.20	>5.64	>8.49
>5.12	>4.14	>5. 37	>5.66	>8.51
3. 58	2.60	See Arcagen Table 2J-5	4.12	6.67
3. 29	2.31	6.31	3.83	7.85
3.29	2.31	5.39	3.83	6.68
3. 29	2.31	3.54	3.83	6.68
2. 27	1.29	5. 29	See Eaves	7.17
2.27	1.29	4.37	O ₂ controller	5.66
2.27	1.29	2.52	Table 2J-5	5.66
2.09	1.11	5.11	See Eaves	6.65
2.09	1.11	4.19	O ₂ controller	5.48
2.09	1.11	2.34	Table 2J-5	5.48

CInitial cost of Tectrol generator for 20,000 bu. was assumed to be \$5000.

Annual cost in cents per bushel for several existing complete controlled atmosphere systems TABLE 2J-5.

		}					
Volume	Elec- tricity	Arca-	Tectrol (lease)	(lease)	Tectrol (purchase)	urchase)	Eaves O, controller
bu. ot apples	cents/ kwh	gen	Regular	Save	Regular	Save	(based on 6000 bu. room)
15,000	-	13.60 ^a	20.7	18.5	10.35	5.95	For 8.4 cents/lb.
	3	16.50 ^a	21.7	19.5	11.40	6.95	propane gas 4.02 cents/bu.
20,000	1	10.25 ^a	20.6	18.4	9.16	5.32	For 2.83 cents/lb.
	3	12.40 ^a	21.6	19.5	10.10	6.31	propane gas 2.92 cents/bu.
000,09	1	3.52	20.6	18.4	9.20	5.32	
	3	4.22	21.6	19.4	10.20	6.31	

 $^{\mathbf{a}}$ Arcagen costs are based on 60,000 bu. unit cost for all volumes.

b Tectrol (lease) regular costs based on information of general nature provided by the Tectrol Division of Whirlpool Corporation for lease and operation cost. ^cTectrol (purchase) regular costs based on a price of \$5000 for their 20,000 bu. generator and operation costs based on information of general nature provided by Tectrol Division of Whirlpool

d Tectrol saving costs based on saving of 40 cents/bu. on construction costs of storage when using Tectrol compared to regular gas tight CA rooms.

Estimated annual cost a in cents per bushel for a "polastream" modification and dry lime scrubbing as controlled atmosphere system for the whole season based on Smock (1965) TABLE 2J-6.

Flushing and scrubbing costs adjusted because of precooling cost saving	37.5 cents/100 cu. ft. liquid N ₂	13. 2	er 90 days	19.1
Flushing and adjusted because	$54 \text{ cents}/100$ cu. ft. liquid N_2	18. 2	ned and held anoth	28.9
Flushing, partial precooling and scrubbing costs	37.5 cents/100 cu. ft. liquid N ₂	15.8	days, one-half fruit removed, flushed and held another 90 days	23.2
Flushing, parand scrub	54 cents/100 cu. ft. liquid N ₂	22.4	days, one-half fr	33.1
Flushing and scrubbing	37.5 cents/100 cu. ft. liquid N_2	15.8	When room opěned after 90	21.7
Flushing an	54 cents/100 cu. ft. liquid N ₂	20.1	When roor	30.8

^aThe costs are based on estimation of 10,000 bu. storage, might be lower for volumes over 100,000 bu. apples.

Discussion of the Results of the Cost Study

CO₂ Removal

High utilities cost, local labor. The most economical carbon dioxide scrubbing system where utility costs are high and local labor is available are the dry lime and water systems. The Arcosorb (MS) is more expensive but much lower than MEA, K₂CO₃ and NaOH, at present the Arcosorb units are built for 60,000 bu.

Low utilities cost, expensive labor. The water system is the most economical; however, the difference between the cost of the water system and of the dry lime system is very small. MEA and Arcosorb are about twice as expensive as the water and dry lime system but are more economical than the K_2CO_3 and NaOH.

Oxygen Reduction

The development of the low oxygen atmosphere using the natural respiration of the fruit entails no out of pocket costs. However, the time delay in developing the atmosphere can cause a loss in quality of the fruit and therefore has, in reality, a negative cost or liability. There has been no attempt in this study to assign a dollar value to the loss in quality that may occur during the development of the low oxygen atmosphere using the natural respiration processes of the fruit in the storage.

Oxygen reduction costs with high cost utilities (liquid nitrogen, 54 cents per 100 cu. ft., propane 8.4 cents per lb.). The discussion will be divided into two parts: 1. One pulldown only--when it is not necessary to re-open the room during the storage period. 2. Four pulldowns--allowing three additional re-opening of the rooms during the season.

- 1. A combination of liquid nitrogen flushing and cooling is the most economical method. The liquid nitrogen flushing, the Eaves burner and the Arcat (at its optimum capacity--60,000 bu.) comprise the next most economical group. Introduction of a smaller Arcat burner would probably change the cost figures for 15 and 20 thousand bu. The Arcat is more economical than the Tectrol generator when the Tectrol is used only as a burner.
- 2. The Arcat when used at its optimum capacity is the most economical method. The Eaves burner is much more economical than the Arcat (for 15 and 20 thousand bu.), liquid nitrogen, and the Tectrol generator when it is used as a burner.

Oxygen reduction costs with low utilities costs (liquid nitrogen 37.5 cents per 100 cu. ft., propane 2.83 cents per lb.).

1. One pulldown only--a combination of liquid nitrogen flushing and cooling is the most economical method. Liquid nitrogen flushing, Eaves burner and Arcat (when used for a 60,000 bu.

operation) comprise the next group. The Arcat for 15,000 and 20,000 bu. is more economical than the Tectrol generator for this purpose.

2. Four pulldowns--the Arcat (for 60,000 bu.) and the Eaves burner are the most economical, followed by liquid nitrogen flushing and cooling. Arcat (for 15,000 and 20,000 bu.) and liquid nitrogen flushing are quite comparable and are more economical than the Tectrol generator when it is used as a burner.

Combinations of Scrubbing and Oxygen Reduction Systems

The results are summarized for high utilities cost (small scale operation) in Table 2J-3 and for low utilities costs (large scale operation) in Table 2J-4.

Small and large scale operations

The costs per bushel on the small scale operation are higher than that of the large scale operation except when using a combination of flushing and cooling with liquid nitrogen. In this case the saving on electricity in the small scale operation (because of the more expensive electricity for mechanical refrigeration), is higher than in the large scale operation using the same liquid nitrogen costs. The economical order of the different combinations within each group is

nearly the same. When the room does not have to be opened during the storage period, combinations of liquid nitrogen for flushing and cooling or flushing only, with dry lime or a water scrubber are the most economical. When re-opening is needed a combination of the Eaves burner with water (or "Oxygen controller") is more economical than the Arcat with water and dry lime scrubbing. The Tectrol generator used as a burner is less economical than the Arcat.

With the 60,000 bu. the only difference is that the Arcat combinations are more economical than Eaves' burner. Tectrol generator when used as a burner is more expensive than the other two methods.

Several Existing Complete CA Systems

The results are summarized in Table 2J-5. Arcagen for 60,000 bu. and Eaves "Oxygen controller" are much more economical than the Tectrol (lease) system, with and without saving on construction costs. (Externally generated atmosphere systems can tolerate higher gas leakage in the CA room than a regular CA system. Practically this is an advantage when a regular cold storage is converted to CA room or when a new CA room is too leaky). The introduction of the Tectrol generator on a purchase basis--\$5000 for the 20,000 bu. capacity generator (Pflug 1965), will bring Tectrol to a more competitive price position. Assuming a saving on construction costs the

Tectrol system costs are close to Eaves' and Arcagen for 60,000 bu. Even without the construction costs saving, Tectrol (purchase) costs for 15,000 and 20,000 bu. are more economical than the Arcagen. However, as the costs for the use of Arcagen for 15,000 and 20,000 bu. were based on the Arcagen initial cost for the 60,000 bu. unit, the costs are relatively high. The Atlantic Research Corp. is planning to come out with a smaller unit for 20,000 bu. which might be more economical for this volume. The calculations for the "Oxygen controller" are based on 6,000 bu. room but the figures are so low that a further look into this process is highly recommended.

Combination of "Polastream" Modification and Dry Lime Scrubber

This combination is used as a complete system of CA for the whole storage period and its annual cost is summarized in Table 2J-6. The combination of flushing and maintenance of the atmosphere all season long is not recommended especially when re-opening of rooms during season and operation with rooms which are not completely full. The use of liquid nitrogen for flushing and cooling only is very promising but is only in the experimental stage.

SECTION 3

GENERAL CONSIDERATIONS IN THE DESIGN AND SELECTION OF VAPOR BARRIER AND GAS SEAL MATERIALS

3A. Introduction

3A1. General

There is a large number of construction materials available for use in the specific areas of controlled atmosphere storage construction. Since there are a number of structural or outer surface materials plus insulation materials, plus gas seal and vapor barrier materials, and since the respective materials may be combined in many different ways, there is a large number of individual specific designs of floors, walls and roofs. The most common type of construction scheme in use is that using concrete block or tilt up concrete with board form insulation described by Pflug et al. (1957b), Pflug and Dewey (1959), plywood described by Zahradnik and Southwick (1958), and buildings constructed using prefabricated insulated panels by Poms (1965) and Dow Chemical (1965). In general, all of these designs have included some type of vapor barrier and a satisfactory gas seal material. In this discussion, the problem and possible solutions to the problem of water vapor transfer and CA gas tightness

will be considered as these two gas barriers are influenced by weather conditions, material used and different design procedures.

Controlled atmosphere storages require (1) gas tight wall construction so that the design oxygen-carbon dioxide levels can be maintained in the storage, and (2) prevention and elimination of moisture accumulation and condensation within the insulation or within the storage wall.

3A2. Water vapor barriers

Water vapor barriers are those materials which are recognized as retarding the transmission of water vapor with reasonable effectiveness under specified conditions. Water vapor barriers may be applied to the insulation to prevent accumulation of water within the insulation or they may be applied to the outside or inside wall to prevent moisture from migrating into the insulation. The objectives of the vapor barrier are (1) to keep the insulation dry and reduce the heat load requirements for the cooling system, (2) prevent structural damage that may occur due to rot, corrosion, or the expansion effect of freezing water.

The effectiveness of any vapor barrier system in preventing water accumulation in the walls and insulation depends upon its natural vapor barrier properties, the care and thoroughness in which it is installed and also its location within the insulated section. Vapor

barriers must be applied to the surface exposed to the higher water vapor pressure. For most applications, this will be the warm side. The vapor barrier problem is much more complicated when a reversal of the warm side takes place due to seasonal changes which is what exists in the CA storage wall. Work carried out by Lorenzen (1963) in New York State where the operating temperature of the storages was 32°F found that the warm side of the wall is on the outside for 8-9 months of the year and is at the inside for the remainder of the year. This problem is discussed in Sec. 3C. At this point it is perhaps well to recognize that there is no material installed by man under field conditions that can be considered a perfect vapor barrier.

3A3. Thermal insulation

Thermal insulation is used in cold storage walls to minimize the cost of refrigeration equipment necessary to remove the heat that flows through the walls and in addition thermal insulation is required to prevent surface condensation and therefore is a factor in the room humidity. Moisture must be kept out of insulation if the insulation is to remain effective. Any moisture that moves into the insulation area by diffusing or passing through the vapor barrier system should be able to pass through the system into the cold storage space. Some types of insulation are manufactured using a close cell system that will perform adequately without effective vapor barrier.

Although these materials can be used without a vapor barrier, a good vapor barrier is recommended for all refrigerated storage construction.

3B. Moisture Migration Through Materials

The basic migration of moisture through materials of the type used for building construction and insulation takes place by three mechanisms (Lorenzen 1963). (1) total volume transfer, accounts for rain, seepage, or infiltration of moisture bearing air, (2) hygroscopic action, accounts for the movement of moisture in intimate contact with solids, (3) diffusion of moisture as a vapor which is the mechanism of major significance and is due to vapor pressure differences.

Water vapor transmission through materials under the influence of a water vapor pressure gradient is called vapor diffusion. The designed equation commonly used to describe this is:

$$W = \mu A t \frac{\Delta P}{l}$$
 (3B-1)

where:

- W total weight of vapor transmitted, grains
- μ permeability, grain in./(sq. ft.)(hr.)(in. Hg vapor pressure difference)
- A area of cross section of flow path, sq. ft.
- t time of transition, hrs.

ΔP vapor pressure difference, in. Hg

length of flow path, in.

Or using the permeance coefficient M where $M = \frac{\mu}{l}$ perm or grains/(sq. ft.)(hr.)(in. Hg), Eq. 3B-1 will take the following form:

$$W = MAt\Delta P (3B-2)$$

Fortunately, in many cases consideration of water vapor pressure differences alone can be used to obtain a fairly accurate estimation of the water vapor flow.

The above equations can be used to explain the design possibilities where reversible vapor flow, flow paths which terminate within the material, and variable vapor pressures exist.

When the vapor flow path terminates within the wall, a wetting potential exists (ΔP is positive). This situation exists when the storage temperature is below the dew point temperature of the exterior air. The vapor flow path may originate within the wall and terminate outside the wall under which conditions a drying potential exists and the pressure difference is negative. This happens when the storage temperature is above the exterior dew point temperature. When the vapor flow path terminates within the wall an accumulation of moisture will take place. It is possible to store a limited amount of moisture in hygroscopic materials, the amount depending upon the equilibrium moisture content of the materials. Moisture storage capacity for a given amount of hygroscopic material is given by the equation:

$$W_{S} = [H_{1}(m_{1}^{"} - m_{1}^{"}) + H_{2}(m_{2}^{"} - m_{2}^{"}) + \cdots] 7000 \quad (3B-3)$$

where

W moisture storage capacity, grains

H dry weight of hygroscopic material, lbs.

m' initial equilibrium moisture content of material, lb./lb.

m" allowable equilibrium moisture content of materials, lb./lb.

3C. The Effect of Weather and Reversible Vapor Flow

It is necessary that both the annual and diurnal climatic variations be considered in order to design a CA enclosure using gas and vapor barrier materials properly located for a specific geographical area. Lorenzen (1963) in his extensive study provides the general environmental background on which a CA structure vapor balance system can be based. Lorenzen presents the average climatic conditions for the Rochester, New York area in the time series form. Lorenzen (Fig. 3C1) indicates the manner in which this time series climatic data can be used to define wetting and drying potential for the wall for a specific operating temperature of 32° F. If the potential outward movement of moisture is greater than the potential inward movement of moisture, then the wall will be comparatively dry. If the potential inward movement of water, then the wall will become water logged.

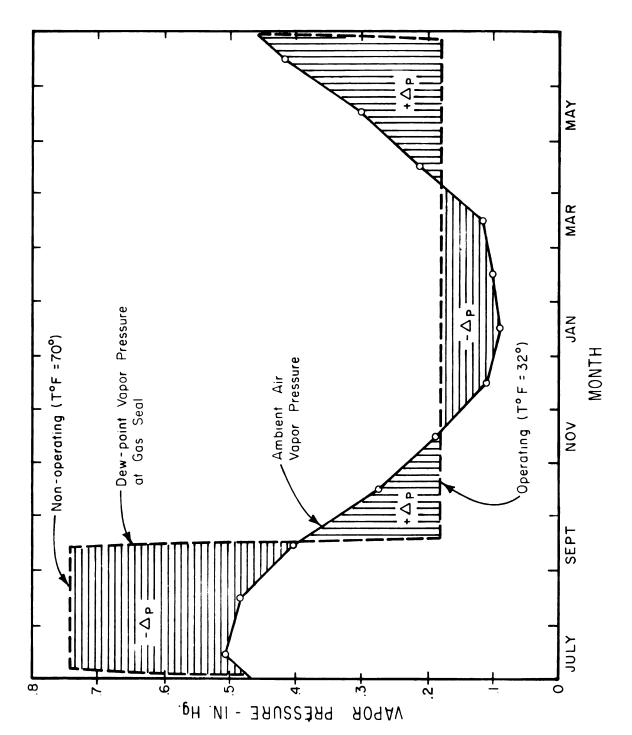


Fig. 3C+1. Wetting and drying potentials for CA storage structural components Rochester, N.Y. (Lorenzen 1965)

Diurnal climatic variations (Fig. 3C-2) are significant too and have to be taken into account. Vapor flows from a point of greater vapor pressure to a point of lesser vapor pressure. In Eq. 3B-1, $\Delta p = p_1 - p_2$ and $p_1 - p_2$ may be lesser pressures, resulting in $\pm \Delta p$, indicating that vapor flow may be in a positive or negative direction. In a structure Δp can be positive or negative, depending on the relative vapor pressures on the end of the external and internal environments. There is a reversal sign for Δp as effected by diurnal climate variation, by average climatic conditions and by interior environmental design conditions. Lorenzen (1963) analyzed this problem extensively, basing his examples on New York weather conditions and arrived at a "balancing technique for moisture control and structural components of CA storages" which will be discussed in Sec. 3E.

3D. Gas Sealing the CA Room

Smock (1962) has outlined specific recommendations for the location of the gas seal, the materials used in the gas seal, and the methods of applying the gas seal. Pflug and Dewey (1959) have worked extensively with gas sealing of CA storage rooms and have also made recommendations regarding the location and installation of gas seals. The purpose of the following discussion is to summarize the general principles involved in the gas sealing of controlled atmosphere storage rooms and to point to theoretical possibilities that can be adapted for use.

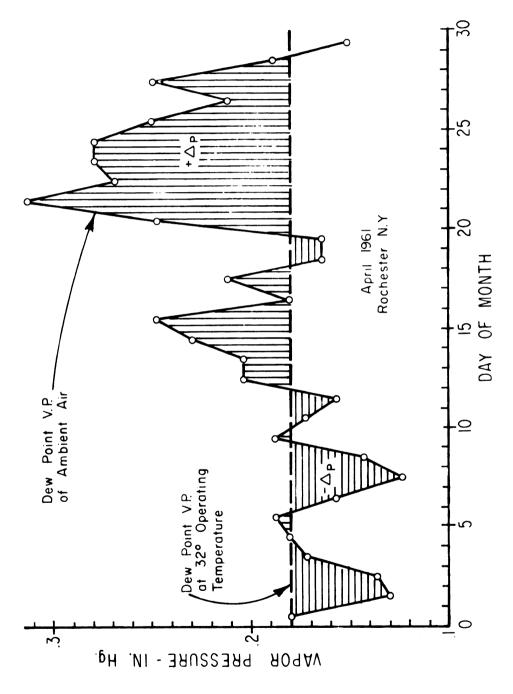


Fig. 3C-2. Histogram of diurpal everage vapor pressures (Lorenzen 1963)

The gas barrier is critical for the successful operation of the CA storage. It must be relatively impermeable to oxygen, nitrogen, and carbon dioxide. Pflug (1960) calculated the rate of leakage of CA storages that can be tolerated and still permit development of the desired atmosphere, as a function of the fullness of the room and the rate of respiration of the fruit. The maximum leakage allowable for a fruit generated CA room may be as low as 0.028 air changes per day. The gas seal must maintain this low leakage rate against continuous pressure differentials that may be as high as 0.1 in. of water gage (Zahradnik et al. 1958). When externally generated atmospheres are being used, there is only an economic limit to the rate at which leakage of the atmosphere through the room can be permitted.

Up to this point, we have been treating the gas barrier separately from the water vapor barrier in the CA storage. We must now recognize that the CA gas barrier is in the final analysis a water vapor barrier and is in reality a nearly perfect water vapor barrier; in fact, it is a much more perfect vapor barrier than anyone can afford to put in a storage for a vapor barrier purpose alone.

Theoretically, the best place for placing a vapor barrier is at the warm side of the wall which is the outside for 32°F refrigerated storages. The gas barrier basically must be placed on the inside wall of the CA storage which is the cold wall. Simply, the reasons for placing the gas barrier at the inside wall are that the gas barrier

must be near perfect, it must be accessible to repair from year to year because if the gas barrier is not adequate, then all is lost.

Essentially we are saying that we cannot tolerate a poor gas barrier; however, we can tolerate a poor vapor barrier.

The fact that we locate the gas barrier on the cold side of the wall precludes the possibility of having one membrane serve both as a gas barrier and as a vapor barrier. The combination of a gas barrier on the inside and a vapor barrier on the outside form a wall structure from which moisture escapes with difficulty. The vapor barrier is usually more permeable than the gas barrier; therefore, the gas barrier functions to retard the movement of moisture out of the wall. Vapor enters the wall at a much larger rate than it can escape from the wall and the accumulation of moisture takes place inside the wall usually close to the gas barrier; in some cases it may migrate to and condense on the back side of a metal gas barrier.

It is necessary that the gas seal be accessible for maintenance and testing. Because of this requirement, the most practical location of the gas seal is at the interior surface of the storage room. When a gas barrier is present at the inside of a wall structure, the vapor can no longer pass through the wall. If the gas barrier is at the cold side of the wall, the pressure differential is positive. The moisture will diffuse into the wall until it reaches a point of storage, the maximum penetration being the gas barrier. If the gas barrier

side of the wall becomes the warm side, the pressure differential is negative and a diffusion process will transfer moisture out of the wall. The moisture which is diffused out of the storage room wall will usually be stored as hygroscopic moisture until the wall materials reach the saturation point. After saturation is reached, the moisture will run off as free water. A CA storage wall with the gas barrier on the inside can be designed to facilitate a favorable moisture balance within the wall, according to Lorenzen (1963).

Some of the moisture accumulating problems of a CA storage wall would be eliminated if the gas barrier could be located on the warm side of the wall, the greater part of the year, where a single barrier would serve both as a gas barrier and a vapor barrier.

3E. <u>Analysis of Design Principles</u> and Possibilities

3E1. One direction vapor flow

When the vapor is flowing in the structure only in one direction because of favorable weather and operating conditions, the basic design principle is to avoid vapor condensation within the structure; this is the flow-through principle. The flow-through principle (BRAB 1963) "moisture which flows into the insulated system should not be allowed to become trapped therein, but should continue to flow completely through the system." Several commercial designed procedures are based on this principle. For example:

- 1. <u>Fail safe concept</u> of Lotz (1964). A fail safe system is one that provides a highly efficient vapor barrier on the warm side with a porous insulation and a porous interior finish. This allows any vapor that does penetrate the vapor barrier to pass through the wall to the inside without any intermediate vapor dams to cause condensation within the insulation system.
- 2. The mechanical system. This system is based on the principles that (a) the best vapor barrier economically available is used on the warm side; (b) an insulation with a moderate water vapor permeability (4 perm per in.) plus a relatively low air permeability is desirable; (c) a cold side finish that is highly permeable to vapor; (d) eliminate vapor dams on the cold side of the vapor barrier.

 McGarvey (1964) gives a detailed description of the materials and construction procedure.

An adoption of these methods for CA construction would require that the gas and vapor barrier both will be the same barrier and located on the warm side.

3. <u>Dow Chemical method</u>. The Dow Chemical method uses exterior aluminum finish as the gas and vapor barrier on the warm side (Dow 1965).

3E2. Reverse flow

When reverse flow conditions are expected to exist in a wall for extended periods of time, then the economics, temperatures, dew points, and the duration of the reverse flow cycles should be studied to determine which one of the following possible practical solutions to the problem of moisture accumulations in the wall will be chosen.

Possible Reverse Flow Solutions

- system. Unless the vapor pressure gradient reversal is particularly severe, a single vapor barrier and gas seal may be located to restrict vapor movement under the most severe conditions with some condensation being tolerated when the vapor pressure reversal occurs (Lotz 1964, Hutcheon 1958). The Dow Chemical Co. is using 15 mil embossed aluminum with a baked on enamel as the outside covering for their new design of insulated panel for CA apple storage construction in Michigan (Dow 1965). The aluminum skin on the outside of the panel plays a triple role--it provides the weatherability of the side walls themselves, and serves as the vapor seal and gas seal. The panels are constructed around Styrofoam insulation which is sandwiched between sheets of 1/4 in. thick exterior grade plywood.
- 2. <u>Seal both sides of non-permeable insulation</u>. Theoretically it is a good solution to seal both sides of a non-permeable insulation,

one vapor barrier on the warm side, and one vapor barrier on the cold side. Since the commercial installation of vapor barriers is usually relatively poor, and the warm side vapor barrier is more difficult usually to apply than the cold side, in the practical end, a poor warm side barrier is installed with a moderately good cold side of the barrier. In this case, the cold side barrier serves as a vapor trap and maintains and holds the vapor that moves into the wall preventing its escape and allowing it to be present because of deterioration of the wall. Only when the insulation is hermetically sealed in the wall it is a good solution. However, the high cost coupled with severe technical fabrication problems make this solution undesirable as far as controlled atmosphere storages are concerned.

3. Install a vapor and gas barrier in the insulation with adequate insulation on each side of the vapor barrier to prevent condensation.

There is a design trend to use ventilation to prevent condensation of water within the enclosed wall. There are several different methods using ventilation to prevent condensation. These methods are analyzed below:

- 4. Lorenzen's (1963) balancing technique for moisture control.

 Three factors are considered for vapor balance within the CA storage walls.
 - (a) The environment within and outside the storage and its

wetting and drying effect on the wall.

- (b) Potential moisture capacity of the wall.
- (c) The movement of moisture into and out of the wall and the resistance to the movement of moisture into and out of by varying materials and types of construction.

The amount of vapor which may be allowed to be transmitted into the wall for storage within the wall is limited by the moisture storage capacity of the wall.

$$MAt\Delta P = [H_1(m_1'' - m_1') + H_2(m_2'' - m_2') + \cdots] 7000 \quad (3E-1)$$

The vapor pressure of the ambient air at the end of the drying period will determine the maximum equilibrium moisture content available for a given hygroscopic material. The safe moisture content should be realized with a vapor pressure just below the dew point vapor pressure for the ambient air temperature with a relative humidity of about 95 percent. The hygroscopic moisture storage potential of the wall will be exceeded if a vapor barrier with too great a permeability is installed. If a vapor barrier with too great a resistance to vapor flow is installed, the full drying potential of the drying period will not be realized. When the full natural drying potential of the wall is not realized, mechanical drying of the wall may become a necessity.

Generally, if the area of drying potential (when ΔP is negative) exceeds

the area of wetting potential (Fig. 3C-1), a dry wall may be maintained naturally. When wetting potential exceeds the drying potential, then a wall compartment ventilation system becomes a necessity (Fig. 3E-1). This ventilation system must be designed to take advantage of any periodic drying potential. Automatic controls would operate when actual vapor pressure reversals occur; these vapor pressure changes would be sensed by dew point indicators. A thermostat set at the controlled atmosphere operating temperature could also be used to control the system. When a drying potential exists, dampers will open and ventilation will start. When a wetting potential exists, dampers will be closed and ventilation will stop. The capacity of the ventilating system will be determined by the rate and quantity of air movement required to achieve a favorable drying effect. Vapor will pass through the insulation and condense on a surface, such as the back of the gas barrier which should be separated from the insulation and major framing material so that condensed moisture will drain away without saturating these materials.

The summer non-operational period is a period of drying potential which has to be taken into consideration. The length of this potential drying period will vary. It can be extended when the room is put into operation later in the fall and also when the room is opened and the fruit is removed earlier in the spring (Fig. 3C-1).

The rate of vapor transmission into and out of the wall can be

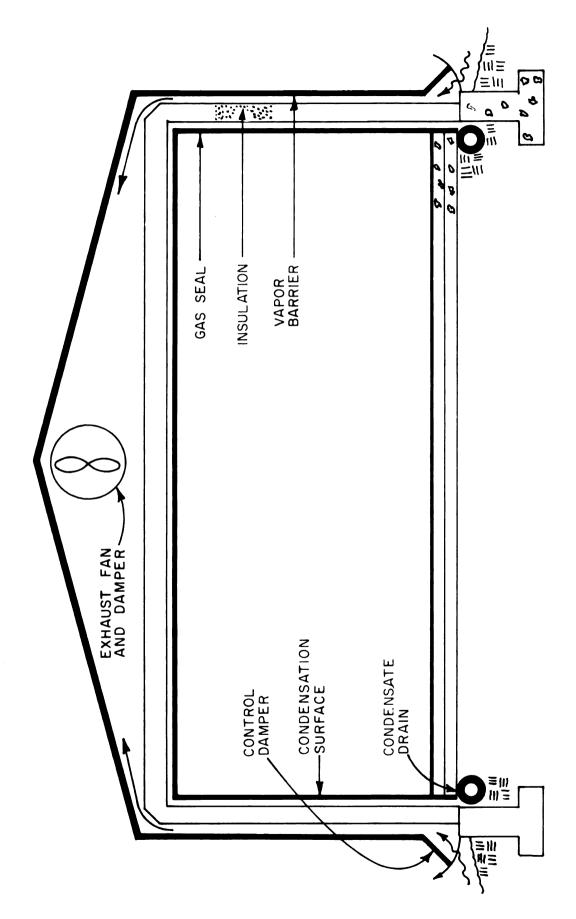


Fig. 3E-1. Features of design for moisture control within CA storage structural components (Lorenzen 1963)

also regulated by the permeability of the wall. The control of this permeability can be achieved by inserting a vapor barrier with the desired resistance to vapor flow. If a wetting potential exceeds the drying potential, it may be desirable to have an outer vapor barrier of varying permeability. This will allow fast drying and also slow wetting of the wall under certain conditions. This variable permeability may be achieved by inserting vent ports in the vapor barrier system and using forced ventilation under certain conditions. These vent ports and the forced ventilation would take place when a drying potential exists.

5. The jacketed cold storage. In the jacketed cold storage construction, an insulated room is constructed and then a jacket, usually a metal lining is installed inside the room in such a way that the refrigerated air is circulated between the wall of the structure and the jacket. The fruit is placed inside the jacket. Air may circulate through the jacket as well as around the jacket during the pre-cooling period; however, during the CA storage season, the jacket is sealed and all cooling takes place by heat flow through the jacket (Fig. 2H-2).

In the jacketed cold storage, the vapor barrier would be placed on the outside or warm side; the cold air circulating in the space between the wall and the jacket would allow any moisture that found its way through the vapor barrier to move into this air and to condense

on the evaporator. The vapor and gas impervious jacket would maintain the necessary high humidity and gas concentration in the storage and in reality would act as a vapor barrier on the warm side since the interior of the jacket would be slightly warmer than the air surrounding the jacket.

- 6. The dehydration system. In the dehydration system, dry, cool air is circulated through grooves formed usually in the last 2 in. of insulation next to the cold zone. The gas seal can be used on the inside of the room (Anon 1959).
- 7. Shuman (1961) proposed that the exterior walls and roof be made entirely independent of the cold storage space. The cold storage space would be provided with its own enclosing vapor barrier system.

 Under these conditions closer control of vapor flow should then be possible.
- 8. <u>Inside out design</u>. In the inside out design (Meyer 1964) the load bearing structure is within the refrigerated space, separated from the outside framing which contains the insulation and a vapor barrier, by an air space. The vapor barrier is accessible from the outside for convenient maintenance and repair.

SECTION 4

OPERATIONAL FACTORS AFFECTING GAS LEAKAGE IN CA ROOM PERFORMANCE

4A. Pressure and Temperature Cycles in the CA Storage Room

According to Pflug and Dewey (1955) CA storage rooms are subject to pressure differentials arising from several sources.

- (1) Changes in atmospheric pressure.
- (2) External air movement (wind forces).
- (3) Temperature changes in the storage usually due to temperature cycling.
- (4) Air movement in the storage.
- (5) The absorption or removal of gas from the storage.
- (6) The carrying in or carrying out of air or gas through the flow of fluids either in the defrost system or in an absorption system due to faulty trapping.

The effect of these individual elements will be discussed in detail below.

1. <u>Changes in atmospheric pressure</u>. Changes in atmospheric pressure will cause air to move into and out of the storage room as

the barometric pressure rises and falls due to normal weather cycles. The continuous external pressure cycling may cause leaks to develop in extremely tight rooms if expansion devices are not used. However, Pflug and Southwick (1954) found that the oxygen gain from atmospheric pressure fluctuations was small compared to leakage from other causes. The leakage resulting from atmospheric pressure fluctuations can be approximated from weather data.

The effect of barometric pressure cycles on the actual oxygen level of CA storage rooms is small because the barometric pressure cycle is long (for example six days from peak to peak in Amherst, Mass., October to March 1953). While the length of the cycle is long and its effect on oxygen is small, the magnitude of the pressure change is of the average of 8.58 in. of water. This pressure change can produce terrific stresses on the building if it was sufficiently hermetic and the pressures would not equalize as the external pressure changed.

2. External air movement. The average leakage into and out of CA storage rooms due to external air movement will be negligible under normal weather conditions but can reach significant proportions during times of high wind. The effect of the wind is to create areas of positive pressure on the windward side of the building and a vacuum on the leeward side. It is the experience of CA storage operators that during periods usually more than one day of continuous high wind, the controlled atmosphere storage room oxygen level will rise

by 1 or 2 percent with a drop in carbon dioxide level. While the room will almost appear out of control during the high wind period, it will return to the normal oxygen and carbon dioxide levels as soon as the wind has reduced to normal velocity levels.

3. Temperature changes in the storage. When the temperature in the storage changes, the specific volume of the air in the storage will change. A vacuum will be formed when the temperature decreases below the mean level with a positive pressure developing when the temperature is above the mean level. These specific volume changes will occur whenever an on-off temperature control system is used and will be proportional within limits to the absolute temperature changes. These pressure conditions occur during each temperature cycle. air leakage pattern into the controlled atmosphere storage room due to temperature fluctuation is a cycle of great amplitude and short duration. Therefore, its effect can be somewhat reduced with the use of a breather bag (Sec. 4B). The magnitude of the pressure and vacuum cycles will be a function of the variation of temperature in the storage room from the mean. Therefore, the reduction in the differential of the thermostat will reduce the magnitude of these pressure cycles and in general will reduce leakage. In general, thermostats with wide differentials will cause long cycles with high pressures and low vacuums and as the temperature differential of the thermostat is reduced the cycles will become more frequent but

the magnitude of the pressure and vacuum portion of the cycle will be decreased. When a proportional type temperature control system is installed in which cooling is continuous, these pressure cycles will be eliminated.

The defrost cycle contributes a type of temperature cycle; however, there are major differences. During a prolonged defrost cycle, a substantial temperature increase can occur which will cause a large volume change. In a long defrost cycle, considerable gas can flow out of the CA storage through the minute leakage points. A secondary factor that occurs during the defrost cycle is that the evaporator is heated and the vapor pressure in the evaporator area becomes very large considering the normal vapor pressure creating a vapor area in and around the evaporator. At the end of the defrost cycle, the room rapidly cools to the control temperature which results in a decrease in gas volume. Therefore, any vapor around the evaporator area is quickly condensed, further reducing the volume. These two actions, that of condensing vapor and cooling the gas, can result in critical pressures sufficient to pull the gas seal off the wall since this vacuum situation is produced in a very short time.

The effect of cooling the atmosphere in the room and condensing the vapor in the air due to the defrost cycle can result in a high vacuum that develops very rapidly since cooling after defrost usually takes place very rapidly. The vacuum is sufficient to, in some cases, pull

the gas seal from the wall, or, in other cases, to pull the gas seal and insulation off the wall. When the defrost is done using water, the amount of vapor diffusing into the room is a function of water temperature; water temperatures above 50°F are not recommended because of their high vapor pressure compared to the normal saturation vapor pressure in a 32°F room.

4. Air movement in the storage. The circulation of air in the storage of a room by fans or blowers will cause pressure variation within the room. In general, the pressures in a room will be smallest when the room is near empty or when there is plenty of circulation space for the air. When propellor type fans are used, the pressures are usually lower than when centrifugal fans are used; however, the exact variation will depend on the design of the refrigeration air circulation system. The pressure variation due to air movement will be greatest in a very tightly stacked room in which the air is led from a centrifugal blower to the far end of the room in a duct and forced to flow back through the fruit to the air intake of the blower. In this case a low pressure area in the vicinity of the evaporator and a high pressure in the vicinity of the end of the duct is expected. Under these conditions, when the evaporator is located near the door or other room opening, trouble is often encountered because of the difficulty in obtaining an adequate seal in door and opening area. In some cases, two speed blower fans have been used to reduce this air

leakage; however, this is not a recommended solution. The recommended solution would be to increase the tightness of the room (see also Sec. 5).

5. The removal of carbon dioxide or other gases by absorption. The removal of carbon dioxide will cause air to leak into the room to replace the gas that has been removed by the absorption process. A substantial vacuum may be developed in a tight room if provision is not made for replacing the removed volume of gas. The oxygen gain of a room due to the absorption of carbon dioxide will be approximately 21 percent of the carbon dioxide removed.

The gas removal rate when a water or dry lime type absorption system is used is relatively small and the rate is continuous over many hours. However, when caustic soda is used to absorb carbon dioxide the rate of carbon dioxide removel is extremely high during the initial 15-30 min. of operation. If the loading and starting of a carbon dioxide absorber coincides with a defrost cycle where water is the defrost agent and perhaps abnormally high water temperatures are used, the result is a vacuum in the room due to a combination of both carbon dioxide removal and the defrost situation as outlined above. The stress under this type of situation is much more severe than for either one agent operating alone.

6. Gas flow in and out of the CA storage room due to water flow. Improperly designed liquid traps will allow large quantities of

air to be added or removed from the CA storage room. A trapping problem is involved any time storage room atmosphere and liquid come in contact. When water-type defrost refrigeration evaporators are used, a severe trapping problem exists where the water leaves the storage room, and when water-type or caustic soda-type carbon dioxide absorption systems are used, trapping problem exists, usually at the outlet of the trap system. In general, if water is being pumped from a deep tank designed so the pump does not draw air, no air will be added as the water flows into this scrubber or into the evaporator. As this water freely flows out of the absorber or out of the evaporator, it is necessary to provide a trap that will separate air from water allowing the CA room atmosphere to remain in the room and allowing the water to move out of the room. To separate air from water in a positive manner, it is necessary to have a water-air separation area where the downward velocity is sufficiently low that entrapped bubbles of gas can rise to the surface. If the downward velocity is greater than the upward velocity of the gas bubbles; the gas bubbles will be carried through the trap system. The multi-trap unit designed for water type carbon dioxide scrubbers for example, is shown in Fig. 4A-1.

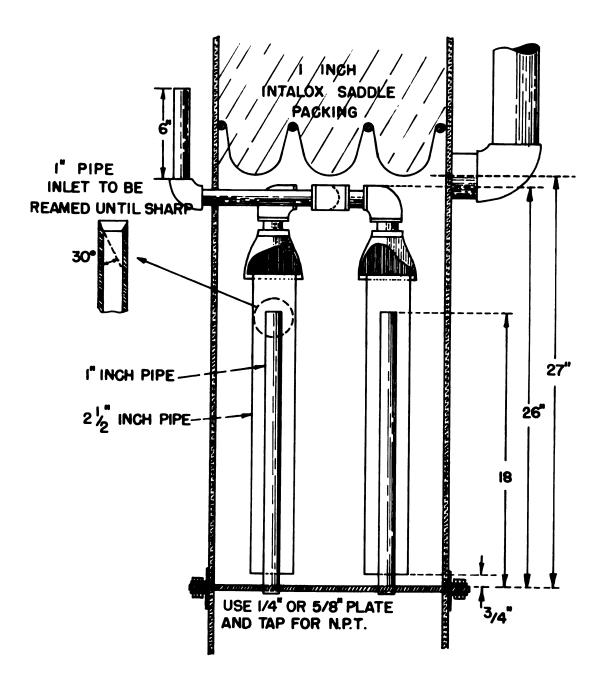


Fig. 4A-1. Trap that allows water to flow from absorption section to desorption section without gain or loss of storage room gas (Pflug 1961)

4B. Eliminating Pressure Changes and Devices To Prevent Room Damage due to Pressure Changes

There are two ways to solve the CA storage pressure cycle problems: (1) elimination of the cause of the pressure cycle, or (2) incorporating a safety device that will prevent the build up of excessive pressure differences across the storage room walls.

- 1. Pressure cycles can be reduced or substantially eliminated by:
 - a. Use of temperature controls with more narrow differentials and the locating of the temperature controls at a point in the room where it more accurately reflects the room temperature conditions.
 - Reduction in the flow rate and temperature of water used in water defrost systems or the use of a different system such as continuous antifreeze spray defrost system (Sec. 2H).
 - e. Improve design of air circulation.
 - d. Use of externally generated atmospheres.

A manometer is a valuable guide in controlled atmosphere storage room operation and the correlation of manometer readings and room operation is useful in ascertaining the causes for excessive pressure or vacuums in the CA storage rooms.

2. Safety devices to restrict the maximum pressure differences

across the wall should be incorporated in every room.

- a. Pressure release valves. A pressure release valve of a type that will let either positive or negative pressure be discharged will prevent the rupture of the gas seal. A pressure release valve is a simple device, a safeguard against this difficulty. One type has been suggested by Dewey and Pflug (1965) Fig. 4B-1. Smock at Cornell University and Hunter at Food Industries Research are using a single pipe with a low spot as shown in Fig. 4B-2 for large storage rooms. This system has the capacity to release or add large quantity of gas and is a recommended type for large storage rooms.
- b. Breather bag. Temperature cycling of the storage room causes the specific volume of the atmosphere in the room to change and thereby creates positive and negative pressures during the cooling off and warming up portion of the temperature cycle. Since the structure of the CA storage room is rigid but not hermetic, the room will breathe with each temperature and pressure cycle. It was concluded by Pflug (1956) that if the atmosphere did expand and contract, an appropriate contraction and expansion chamber might be used to permit the room to breathe and to control and insure that the gas that flowed in and out during this breathing cycle was not lost.

A breather bag serves as a reservoir for a confined volume of atmosphere of the storage room and functions by giving up this air to the storage room during the cooling part of the temperature cycle. It

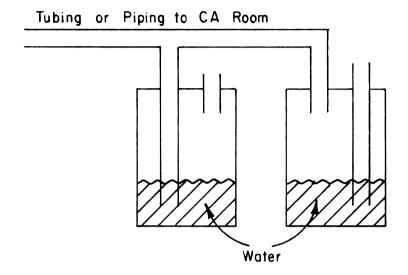


Fig. 4B-1. Safety device to prevent excessive pressure in the CA room (Dewey and Pflug 1965)

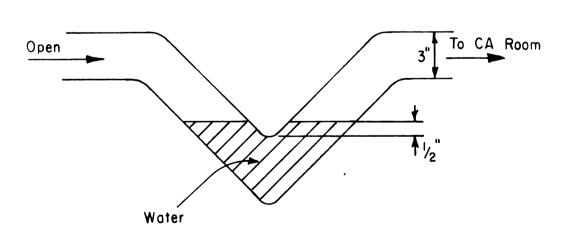


Fig. 4B-2. Relief valve to prevent excessive pressure in CA room (Smock and Blanpied 1960)

operates in parallel with the leaks in the storage room; therefore, to be effective, it must apply and recover air with very small pressure differentials. A breather bag acts to reduce air leakage due to temperature cycling and at the same time acts as a safety device for the room. In general, a properly designed breather bag may reduce the leakage from temperature cycle by 50 percent. However, the breather bag will not reduce leakage from pressure differentials induced by fans, winds or changing barometric conditions. The breather bag provides a good guide to the pressure condition in the room. A constantly deflated bag indicates that air is being continuously pumped from the room whereas the constantly inflated bag suggests air is constantly being added to the room. Oxygen gain due to carbon dioxide removal is also due to the control of the breather bag since the volume of CO₂ scrubbed out of the room must be replaced by air from outside the storage room before an equilibrium can be reached.

The breather bag will improve the operation of a tight room but will do little for a leaky room. The greatest benefit of the breather bags is in small rooms which tend to be subject to rapid changes in temperature and often have a large space factor.

4C. Measuring the Gas Tightness of CA Storage Rooms

Two general methods of measuring the gas tightness of CA storage rooms have been used and those may be appropriately referred

to as rate of leakage tests and the pressure drop test.

Rate of leakage test. In the rate of leakage test method of CA storage rooms, air is metered into the room at a constant rate, for example, 25 cfh, until the differential pressure across the wall reaches a constant value. At this point, air is leaking out of the room at the same rate as it is being added to the room. Therefore, the manometer reading is the differential pressure producing 25 cfh of leakage. Following the initial determination, the rate of flow is increased and the entire procedure repeated for a second flow rate. The final result is a graph relating pressure differential with rate of leakage.

Rate of leakage type tests are important in externally generated gas systems where a certain amount of atmosphere must be exhausted from the room per hour. However, in fruit generated storage rooms, the rate of leakage test has limited practical value because the normal pressures that the fruit generated CA room operates under are so low that micro-manometers are necessary to measure the pressure differentials. If the rate of leakage type test is carried out, variables such as changing temperature and barometric conditions can cause greater effects on the pressure than the air flow rate being evaluated.

Theoretically, rate of leakage tests can provide a great deal of information on the behavior of the CA storage room. For practical

purposes the rate of leakage tests require too long a time and too complicated equipment for general use in CA storage room evaluation.

Pressure difference CA storage room test. In the pressure difference CA storage room test, the room is sealed and the pressure inside the CA storage room is raised to 1 in. of water gauge by means of a small centrifugal fan or pressure type vacuum cleaner. When the desired pressure of 1 in. of water gauge has been reached, the fan is turned off, the room sealed and the time recorded and pressure differential recorded at 10 or 15 min. intervals during the next 1-2 hours. If a pressure of 0.1 in. of water gauge remains after 25 min., the rooms in most cases are sufficiently tight to operate well as CA storage rooms. In general, for a given pressure test result, the performance of the room will vary directly with the size in that large rooms will perform well and small rooms will perform less well. In general, rooms of less than 10,000 bu. capacity should require 60 min. for the pressure to drop from 1 in. of water gauge to 0.1 in. of water gauge.

SECTION 5

PRECOOLING AND AIR DISTRIBUTION IN A CA APPLE STORAGE ROOM

5A. Introduction

The present day designs of refrigerated storage rooms using, in some cases, ceiling mounted evaporators with propellor fans, in other cases, floor mounted evaporators with centrifugal fans, sometimes with ducts, sometimes without ducts, may appear to be haphazard; however, a great deal of time and energy has gone into attempts to improve the general performance of the storage room. The product is usually brought in from the orchard in pallet boxes and these boxes are moved into the storage directly from the loading dock. The boxes are stacked neatly in the storage room; in some cases by design, space is left between the boxes; in other operations again by design, the boxes are stacked as closely as possible. In all storage room designs, the objective is to have uniform air flow throughout the room and a uniform temperature throughout the room. Unfortunately, in large storage rooms it is extremely doubtful if these objectives are ever met.

When boxes are stacked in a large room and the air is rather

grossly circulated throughout the room, the problem is indeed quite complicated. Some of the complicating factors stem from practical situations; for example, the cold air is normally distributed at the top of the room, the cold air will normally move toward the floor of the room due to its density; however, air, as it flows through the stack and becomes warm, tends to rise which in some circumstances we may find that the natural convection forces are offset by the density effect of the mechanical circulating system. As the point in the room is farther from the evaporator discharge, evaporator inlet or duct discharge, the area is more subject to natural forces than to the mechanical forces; whereas then near the evaporator discharge or duct outlet or near the evaporator inlet the flow pattern depends more strongly on these mechanical effects and the forces generated by these devices.

Many researchers have studied the flow paths of air in specific types of rooms and under special types of loading and operating conditions. The type of box arrangement has been studied extensively and specific recommendations were presented by Sainsbury (1961, 1962) regarding the distance between rows of boxes and between the last row of boxes and the wall of the storage room. Gray and Smock (1955) have studied the air distribution from ducts. Hukill and Smith (1946) studied air distribution and precooling rates and designed a reverse flow system that permitted lower air temperatures and faster

cooling in a rather unique system. In all of these systems there has been a tendency to develop the system around practical guide posts.

Outlined below is a method of operation designed to obtain maximum use of the natural forces and supplemental mechanical forces.

5B. General Design of New Method of Storage

In this new approach to the problem of the storage room, its air distribution and precooling rates, all of the spaces between the pallet boxes will be closed and the stacking will be arranged in such a way that the air will be forced to flow only through the void spaces between the apples in the pallet boxes. In this way it will be possible to obtain a maximum cooling surface. After the air has moved upward through the stack of apples, it will move along the ceiling and wall, after which it will be cooled, allowed to move down toward the floor of the storage room where it can again move upward through a stack of product as shown in the schematic drawings in Fig. 5B-1 and Fig. 5B-2. Suction fans distributed uniformly on the false ceiling will be used to move the air through the system and give even distribution in the stack. To make possible the upward flow of air through the stacks of pallet boxes, a specially designed pallet box will be required in which the bottom has about 50 percent voids (about the same as in a pallet box full with apples). To prevent air from moving horizontally through the channel form by the stringers under the pallet box, an extra bottom or pallet (with 50 percent voids) can be

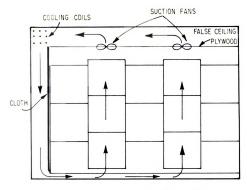


Fig. 5B-1. Schematic drawing of "packed bed" room--side view

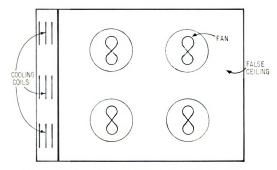


Fig. 5B-2. Schematic drawing of "packed-bed" room--top view

placed under alternate stacks so that the pallet openings are staggered, as shown in Figs. 5B-1 and 5B-3. To prevent air from moving back into the top of the boxes, a cloth baffle is hung vertically over the front of the boxes as shown in Fig. 5B-1. This "packed bed" approach, can be efficiently used for the prevention of short circuited air flow during precooling during the loading period (Fig. 5B-4). Using only those suction fans in the area in the room where the room is loaded plus the placing of baffles in strategic locations will force the air to move up the stack of fruit as shown in Fig. 5B-5. To prevent channeling in the stack itself, the fans can be used alternately for drawing and blowing the air.

5C. General Outline for Analytically Determining the Value of the Variables in the "Packed Bed" Type Storage Room Operating System

In developing this analysis it is assumed that there is one continuous box of apples extending from the floor of the room to the ceiling. Or, in the chemical and mechanical engineering terminology, a "packed bed" of spheres, where in practical sense the spheres will be apples or other food products. In considering the flow of air through this packed bed, the initial design criteria will be the temperature and air velocity through the bed to give the desired cooling rate. Once the desired velocity through the stack has been determined, it is considered that the apples in the box will cool at the same rate

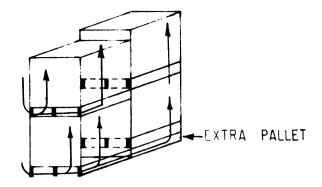


Fig. 5B-3. The use of an extra pallet every second row to prevent horizontal air channeling

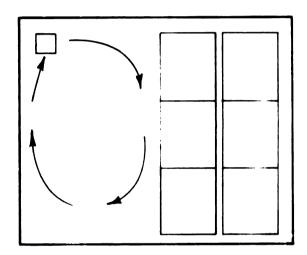


Fig. 5B-4. Short circuit air flow in regular room precooling during loading period

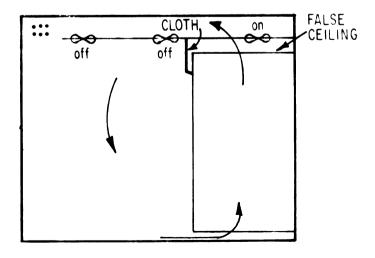


Fig. 5B-5. Precooling during loading—"packed-bed" approach

as an individual apple exposed to the same air velocity. This will allow the use of the experimental data available from single fruit cooling experiments of Kopelman et al. (1964). Using the "packed bed" principles, the pressure differential necessary to produce the desired air velocity through the boxes of apples will be calculated. The quantity of air necessary will be the product of the void area times the velocity. Once the quantity of air required and the pressure differential has been determined, the fans can be sized directly. Knowing the cooling rate data, the quantity of heat to be removed, the refrigeration capacity can be determined as soon as the heat removal rate has been evaluated.

5D. The Method To Calculate Design Data for the "Packed Bed" Room--Precooling and Air Distribution

The best conditions for the "packed bed" cooling-air distribution problem will be calculated now, involving the following variables:

- t time
- T_1 temperature of cooling media
- T initial temperature of the apple
- T temperature of the apple
- h film coefficient
- v air velocity
- Δp needed to get a velocity v
- Q heat to be removed

Transient state cooling of spheres, in a packed bed arrangement, generating heat (respiration heat which is a function of the temperature of the apple), under a constant flow of cold air, is assumed. As the air is circulating constant air temperature is assumed.

5D1. The approximate calculation of T_1 and h

To establish the exact cooling curve (T versus t) the first approximation of T_1 and h must be known. The easiest way to approximate h and T_1 is to assume cooling of a sphere without generation of heat using the method suggested by Pflug and Blaisdell (1963). The procedure for this approximation will be as follows:

The relationship between the f value and the air temperature is given by Eq. 5D1-1.

$$lg(T - T_1) = t/f + log j(T_0 - T_1)$$
 (5D1-1)

$$j = \frac{T_a - T_1}{T_0 - T_1}$$
 (5D1-2)

Assuming that it is desired to cool the apple in t hours from T_0 to T there are three unknowns T_1 , j and f. But if f is assumed $N_{\rm Bi}$ is found in Fig. 2 of Pflug et al. (1965), and j (Jc, Jm or Js as needed) in Fig. 3, 4 and 5 of Pflug et al. (1965). h is calculated from $N_{\rm Bi}$ and then T_1 is calculated from Eq. 5D1-1.

5D2. Calculation of the "exact" cooling curve

Assumptions and boundary conditions

1. It does not have to be assumed that the whole sphere is at the same initial temperature, a more realistic approach is that the temperature distribution in the sphere assuming equilibrium conditions is:

$$T = T_{OS} + b^2 \left(\frac{a^2 - r^2}{6}\right)$$
 (5D2-1)

where

$$b^2 = \frac{Q_R}{\rho C_S}$$
 (5D2-2)

- 2. The sphere loses heat to its surroundings at a rate proportional to the temperature excess above the surface.
- 3. Heat flow is uniform so that the temperature is a function of the radial coordinate r, and independent of angular coordinates. The fundamental cooling equation for a sphere generating heat (constant $\mathbf{Q}_{\mathbf{R}}$) is:

$$\frac{dT}{dt} = \frac{\alpha}{r^2} \frac{d}{dr} \left(r^2 \frac{dT}{dr} \right) + b^2$$
 (5D2-3)

taking a new variable u = rT this becomes

$$\frac{du}{dt} = b^2 r + \frac{d^2 u}{dr^2}$$
 (5D2-4)

The solution of the differential equation with the assumptions and boundary conditions mentioned (Awbery 1927) is:

$$T = T_1 + \frac{(a^2 - r^2)b^2}{6\alpha} + \frac{kab^2}{3h\alpha} + \frac{1}{r} \sum De^{-\phi^2 \alpha t / a^2} \sin \frac{\phi r}{a}$$
 (5D2-5)

where

$$D = \frac{2a^{2}hF}{\phi} \frac{\left[\phi^{2}k^{2} + (ha - k)^{2}\right]^{\frac{1}{2}}}{\phi^{2}k^{2} + (ha - k)}$$
(5D2-6)

$$F = (T_{os} - T_1) - \frac{kab^2}{3h\alpha}$$
 (5D2-7)

$$\tan \phi = \frac{k\phi}{k - ha} \tag{5D2-8}$$

The sphere temperature at any desired point within the sphere is a function of the heat of respiration, surface heat transfer coefficient, initial surface temperature, temperature of the surrounding air and time (Eq. 5D2-5).

However, it has to be kept in mind that this was calculated for a constant $\mathbf{Q}_{\mathbf{R}}$. In order to overcome the problem that $\mathbf{Q}_{\mathbf{R}}$ is changing with the temperature a numerical method will be applied at this point.

The relationship of the heat of respiration with apple temperature based on the data¹ in (U.S.D.A. 1954) for the Jonathan variety was found to be, for the second polinomial degree (T = °F).

$$Q_{R} = 3.59T^{2} - 248T + 5024$$
 (5D2-9)

Program E2 UTEX LSCFWOD--"Least square curve fitting with orthogonal polynomials" of the CDC 3600 computer of MSU was used to calculate Eq. 5D2-9. At this stage a finite difference numerical

¹The data are not enough therefore this equation is only approximate.

analysis will be applied. It will be assumed that during a very short $\frac{\text{time }Q_R}{Q_R} \text{ is constant and the temperature T of the sphere can be}$ found by Eq. 5D2-5. The new T will be used now to calculate a new $Q_R \text{ with Eq. 5D2-9 and the new }Q_R \text{ to calculate new T, etc. The}$ error can be controlled by adjusting the Δt .

In this way the relationship T versus t can be found. It is obvious that the last step can be most efficiently calculated using a computer.

To get accurate results Δt can be made as small as needed and as many roots for the tan ϕ as needed can be used.

The advantage of this numerical solution is that it will be easy to use the same procedure (program), change the variables; sphere size, initial apple temperature, air temperature, h and time, to get information about the effect of each variable and get the valuable design information needed for any specific case.

It is now clear that the h and T_1 found by Pflug's method (Eq. 5D1-1), ignoring the heat generated, have not influenced the results based on the "exact" method to evaluate T versus t. If t is found to be too long T_1 or h will be changed in order to obtain the desired T.

With the "exact" method the theoretical T versus t will be obtained and the use of f, j as with Pflug's method (Eq. 5D1-1) is not needed. It should be kept in mind that Pflug's method was developed with the assumption that when the time function is large, the curve

becomes coincident with the straight line asymptote. However, in this case, cooling of apples in rooms, the cooling process is relatively long and the effect of the heat of respiration is especially important at the beginning where the temperature of the apple is high. As Pflug's method is much easier to use it may be possible to find a correlation between the two methods. In other words, it might be possible to find apparent f,(f') that will include the effect of heat of respiration.

As the apple is cooled $\frac{\Delta T}{\Delta t}$ becomes smaller and smaller and Q approaches a constant value therefore, t will have to be definite in the program. As t $\rightarrow \infty$, T approaches equilibrium temperature where Q_R = constant, and the surface temperature exceeds the temperature of the surrounding by $\frac{kab^2}{3h\alpha}$. This is the steady state stage or the regular storage period.

5D3. The determination of the air velocity v needed and Qcfm

A large amount of experimental information on heat and mass transfer in packed bed has been analyzed to arrive at the following empirical correlations (Bird et al., page 411, 1965).

$$j_{H} = 0.91 \text{ Re}^{-0.51} \psi$$
 (when Re<50) (5D3-1)

$$j_H = 0.61 \text{ Re}^{-0.41} \psi$$
 (when Re>50) (5D3-2)

Here the Colburn factor (j_H) and the Reynolds number (Re) are defined by

$$j_{H} = \frac{h}{\overline{C_{PA}}G_{O}} \left(\frac{\overline{C_{PA}}^{\mu}}{k}\right)^{2/3}$$
 (5D3-3)

$$Re = \frac{G_o}{a_S \mu_f \psi} = \frac{\rho v}{a_S \mu_f \psi}$$
 (5D3-4)

In this equation the subscript f denotes properties evaluated at the "film temperature"

$$T_f = \frac{1}{2} (T_S + T_1)$$
 (5D3-5)

 ψ is an empirical coefficient that depends on the particle shape. For a sphere a value of ψ = 1 was found. Since the desired h is known (calculated in Sections 5D1 and 5D2), J_H is found from Eq. 5D3-3. The Re is calculated using Eq. 5D3-1, or 5D3-2, depending on the range of Re numbers. v is then found from Eq. 5D3-4. Knowing v, the quantity of air to be circulated can be found from Eq. 5D3-6.

$$Q_{cfm} = v A \epsilon \qquad (5D3-6)$$

where A is the cross section area of the stack and ϵ the void fraction.

5D4. The determination of maximum ΔP_B needed for air distribution

Using the "packed bed" approach (Bird et al., page 196, 1965)

the ΔP_B needed for the desired v can be calculated.

The correlations to calculate ΔP_B are based on data from experiments with perfect spheres which were smaller than an average apple, therefore, the present procedure can only give an

approximation or trend and will have to be checked thoroughly experimentally.

The general Ergun (1952) equation which is suitable for a large range of Re numbers is suggested to determine the ΔP_B

$$\frac{\Delta P_{B}^{\rho}}{G_{O}^{2}} \left(\frac{2a}{H} \right) \left(\frac{\epsilon^{3}}{1 - \epsilon} \right) = 150 \frac{(1 - \epsilon)}{D_{P}G_{O}/\mu} + 1.75 \qquad (5D4-1)$$

where

$$G_0 = \rho \epsilon v$$

Preliminary calculations of ΔP_B using Eq. 5D4-1 showed that a very low ΔP_B is required: to obtain velocities of 5-100 f.p.m. the pressure drop ΔP_B , was found to be .001-0.3 in. water gage.

The air flowing along the ceiling, walls and floor is subject to friction forces; the fans have to be designed to overcome this friction in addition to the friction of the flow through the apple boxes. This difference in pressure ΔP_D will be calculated assuming air flow through a duct with a rough surface. Lentz and Nakano (1961) described a method of predicting air friction pressure losses in shallow ducts. This method can be used for our purposes.

The fan has to be designed for a total pressure drop, $\Delta P_{_{\mathbf{T}}}$, of

$$\Delta P_{T} = \Delta P_{B} + \Delta P_{D}$$
 (5D4-2)

5D5. Evaluation of the total refrigeration load

The maximum refrigeration load will be calculated for the first day of precooling (full room) when the temperature drop and the heat of respiration are largest. The total general heat balance is:

sensible heat heat of respiration
$$MC_{PS}(T_0 - T_d) + M \int_{T_d}^{T_0} (3.5 gT^2 - 248T + 5024) dT$$

$$+ Q_{fans} + Q_{leakage} = Q_{cfm} C_{PA} (T_1 - T_2)$$

The sensible heat, heat of respiration, heat produced by the fans and heat leakage into the room, are removed by the air at temperature T_1 and velocity v. The heat of respiration is calculated by integrating Eq. 5D2-9 for one day. The refrigerant temperature, T_2 , can be found using Eq. 5D5-1. Another important calculation will be the calculation of the surface temperature of the apple. By substituting r = a in the "exact" method, the surface temperature versus time will be found. This is important because the air temperature can be lowered as long as there is no danger of freezing the apple and during this period of time to obtain faster cooling with the same ΔP_T and v.

5E. Advantages, Disadvantages and Discussion of the New Approach

Advantages

- 1. As there are no spaces between the boxes more apples can be stored in the same size room, therefore:
 - (a) There is a possible saving on storage construction costs

 per bushel
 - (b) Space factor z ($\frac{ft.^3}{bu}$) (Sec. 2D1), is smaller (the amount of air (oxygen) in the room is smaller), therefore, the time to reduce the oxygen level in a regular CA room is shorter and the gas consumption using burner units to reduce the oxygen is smaller.
- 2. Since the air circulation is based on the minimum air movement;
 - (a) Infiltration will be reduced because of reduced air velocities.
 - (b) Less heat is added by the fans, therefore, the refrigeration load will be smaller.
 - (c) Smaller fans will be required and the energy consumption will be reduced.
 - 3. Because of the unique air distribution:
 - (a) A promising possibility for even distribution of air.
 - (b) Excellent air distribution where precooling of room during loading is needed.

Disadvantages

- 1. The need for standard size pallet boxes and rooms and especially designed pallet boxes.
 - 2. Stacking of boxes in the room is more complicated.
- 3. There is a danger of short circuiting air in case of poor stacking.
- 4. Insulation protection is not adequate because curls and bumper rails will interfere with the required spacing of the boxes.

This study was based on theoretical analysis without any experimental work and at this stage it is only a speculation of a new air distribution method. A general outline was given on how to calculate the various design factors for a storage room. A complete program to solve this complicated problem was beyond the scope of this thesis and results of experimental work to prove the advantages of this method are needed.

SECTION 6

DISCUSSION AND CONCLUSIONS

Controlled atmosphere (CA) storage is a method of keeping living fruit longer by refrigeration, reduced oxygen and higher than normal carbon dioxide concentration in a gas tight insulated room. There are a large number of construction materials available in use in the specific area of CA storage construction. The most common type of construction scheme in use is that of using concrete block or tilt up concrete with board form insulation, or prefabricated insulated panels. In most of the CA rooms today galvanized sheet steel (28-gage) on the inside is used to provide the gas seal, and vapor barrier at the outside surface of the building is used to prevent vapor transmission into the area. The room has to be gas tight and the gas tightness is a very critical factor determining the satisfactory operation of CA room as will be discussed below.

There are a number of alternative systems to control the atmosphere in the CA room. The simplest one is restricted ventilation in which the sum of the oxygen and carbon dioxide concentrations is always 21%, but that does not meet our present need of low oxygen and carbon dioxide.

The control of the atmosphere to achieve the desired ${\rm CO_2}$ and ${\rm O_2}$ levels is done in either of two ways.

1. By removal of the excess CO_2 by physical absorption (water), chemical absorption (NaOH, K_2CO_3 , MEA or dry lime) and by using molecular sieves, and reduction of oxygen in the room by the fruit itself, addition of liquid or gas N_2 or CO_2 , or by burning the oxygen in the room atmosphere.

Mile Company of the C

2. By external gas generator. The control of the atmosphere is made by introducing an externally generated atmosphere into the room.

As there are many alternatives to reduce the CO_2 and O_2 , many different combinations of carbon dioxide scrubbers and oxygen reduction systems can be used to control the atmosphere. In order to choose the best method for control of the atmosphere, some critical factors have to be considered:

very tight every combination of carbon dioxide scrubbing and oxygen reduction system can be used. In this case precautions against possible damage to the room because of pressure changes have to be considered. The possible damage can be reduced by eliminating the cause of pressure cycles or incorporating a safety device that will prevent the build-up of excessive pressure in the room. If the room is not very tight (0.5 air changes per day or more), combination of

water scrubbing and natural respiration cannot be used and the use of nitrogen flushing and liquid nitrogen are not desirable. Although there are methods to control the atmosphere in a leaky room using an externally generated atmosphere or combinations of commercial burners with scrubbers on a recirculatory basis, the operation of a tight room is easier and more effective. The time required to reduce the oxygen level in the room is shorter and the gas consumption using a burner to reduce the oxygen level is smaller than with a leaky room. Therefore, it is recommended that when building a CA enclosure it be made as tight as possible. However, in case a severe gas leakage develops because of failure in building construction or sealing, a combination of burner to reduce the oxygen with a CO₂ scrubber, or external gas generator is needed.

2. <u>Management practices</u>. It is necessary to know if the CA storage room is designed for single or multiple opening during season. <u>Single opening</u>. -- If it will not be necessary to re-open the room during the season, only one pulldown of oxygen will be needed (except for emergency). In this type of operation any combination of carbon dioxide scrubber and oxygen reduction system as mentioned before can be used. For such an operation, dry lime and water scrubbing were found to be the most economical carbon dioxide removal methods. A combination of liquid nitrogen for flushing and cooling appears to be potentially the most economical way to reduce

the oxygen level in the room and the burners comprised the next most economical group.

3. <u>Multiple opening</u>. If multiple opening of the rooms during the season is desired, practically all the combinations of scrubbing with natural respiration are not desired. Therefore, only combinations of scrubbers, with burners and liquid nitrogen are desired. The operation of a <u>partially filled room</u> will eliminate all the combinations of scrubbing with natural respiration and nitrogen gas or liquid (because too much liquid nitrogen is needed to operate a partially filled room economically). Only carbon dioxide scrubber combinations with burners are suitable. For such an operation, dry lime is the most economical carbon dioxide removal method and the burners are the most economical oxygen reduction systems.

Comparison of annual costs of carbon dioxide removal methods, oxygen removal methods, various combination of carbon dioxide scrubbing and oxygen reduction methods and commercial complete methods to control the atmosphere, are given in Tables 2J-3, 4, 5 and 6, for different volumes of storage utilities and labor prices.

The comparison of the results in Tables 2J-3, 4, 5 and 6 shows that combinations of scrubbing and oxygen reduction systems for a specific volume and utilities price level might be more economical than using one of the complete systems. As a typical example a combination of an Arcat burner with a water or dry lime scrubber for

60,000 bu. is more economical than the most economical complete system for this volume of fruit (which for both large and small operations is the Arcagen).

In a small scale operation the annual cost of water and dry lime scrubbing (based on 3 cents per bu. construction cost) is similar. In a large scale operation the annual cost of water and dry lime scrubbing (based on 1.5 cents per bu. construction cost) is also similar. Therefore, the choice between water and dry lime scrubbing or a possible change from water to dry lime scrubbing should be based on local conditions and prices. The advantage of water scrubbing for maintaining high relative humidity should also be taken into account.

For operation of filled and tight rooms and especially rooms which are not opened during the season, the combination of flushing and cooling or flushing only with liquid nitrogen shows promise. However, this combination is in the experimental stage and depends on the liquid nitrogen cost. The use of liquid nitrogen for maintaining the atmosphere during the season is much more expensive.

The Eaves "O₂ controller" was used on a small scale only, but is very promising economically and is worth looking into for a larger scale system. The use of Arcagen is economical for 60,000 bu. or multiples of 60,000 bu. An introduction of a smaller unit may be economical for a smaller scale system. The use of a Tectrol generator on a purchase basis (\$5000 per generator for 20,000 bu. was

assumed) is much more economical than on a lease basis.

Every combination of carbon dioxide scrubber and oxygen reduction device is suitable as a complete system for the control of the atmosphere. In order to choose the most suitable system, some preliminary elimination of these methods can be made easily according to the degree of gas tightness of the room and the management practices as mentioned before. After this elimination step, the most economical combination among the remaining can be chosen from Tables 2J-3, 4, 5, and 6 (which are cost data for CA unit operation) according to the volume of storage and utilities and labor prices of the particular case.

The problem of carbon dioxide and oxygen measurement in a CA room is whether to use Orsat or a combination of carbon dioxide and oxygen instrumental analyzers and recorders and also, which size storage (how many rooms or measurements) will justify the use of expensive instrumentation.

An approximate analysis based on comparison of annual costs of operation of Orsat and the instrumentation system showed that with more than 7 storage rooms, a commercial instrumentation system is more economical than using Orsat. When a relatively simple instrumental system based on "local" design and installation is used, it was shown that with more than 4 rooms this sytem is justified.

The mechanical refrigeration precooling of apples in the room

is a rather expensive method and an improvement of the air distribution method in the room during precooling is still needed. Recently liquid nitrogen was tried experimentally to serve both for partial cooling and for flushing the oxygen from the room. The use of liquid nitrogen is advantageous because there is a peak of refrigeration load at the first few days of the storage season when the field heat has to be removed. The refrigeration load calculation for sizing a mechanical refrigeration system is based on the maximum load during the precooling time. However, the precooling may be also done by a combination of a liquid N₂ and smaller mechanical refrigeration system. The mechanical system will be designed to hold the apples at the desired temperature after the precooling period only.

Approximate calculation for precooling apples from 65 to 35°F with mechanical refrigeration showed that the annual operative costs per year were 4.18 cents per bu. based on 1 cent/kwh and 5.2 cents per bu. based on 3 cents/kwy. Precooling (65-35°F) and flushing using liquid N₂ gave costs of 3.5 cents/bu. when the price of liquid N₂ was 54 cents/100 cu. ft. N₂ gas and 2.4 cents/bu. when liquid N₂ was 37.5 cents/100 cu. ft. N₂ gas, which shows that liquid N₂ precooling and flushing is more economical than using mechanical refrigeration only to precool. The use of liquid N₂ was only checked experimentally on small scale basis (1500 bu.) and has to be checked on a larger scale. It is too expensive to control the temperature and

the gas levels in the room for the whole season and especially when the room is not filled with apples, but is a potentially promising solution for precooling and oxygen reduction when only a single opening of the room is needed.

Another approach to precooling and air distribution in a CA storage room has also been presented. In this new approach, all the spaces between the pallet boxes will be closed and the stacking will be arranged in such a way that the air will be forced to flow only through the void spaces between the apples in the pallet boxes. In this way it will be possible to obtain a maximum cooling surface. After the air has moved upward through the stack of apples, it will move along the ceiling and wall after which it will be cooled, allowed to move down toward the floor and then again upward through the stack. Suction fans distributed uniformly on the false ceiling will be used to move the air through the stack. The most important advantage of this method to CA operation is that there are no spaces between the boxes in the room and more apples may be stored in the same size room. There is a possible saving on storage construction costs per bu. and the space factor Z (cu. ft./bu.) is smaller, i.e. the quantity of air (oxygen) in the room is lower. The time to reduce the oxygen level in the room is shorter than in a regular CA room and the gas consumption using burner units to reduce the oxygen is lower. This approach is only a speculation of a new air distribution method.

APPENDICES

APPENDIX 2-1

Comparison of Annual Cost of Operation of Orsat and the Instrumentation System Described in Fig. 2G-1

Annual measurement costs--one room per season using Orsat

Initial cost of Orsat: \$85

Service life: 3 years

Measurement of one room: 15 min.

Wages: \$1.5/hr.

Season: 200 days

CRF: capital recovery factor (see Sec. 2J) (3 years 5 percent

interest): 0.36721

Operation cost per season: $\frac{15}{60} \times 1.5 \times 200 = 75

Annual cost = P(CRF) + operation cost

= $85 \times 0.36721 + 75 = 106 per room per season

Approximate costs for the instrumentation based on "local" design and assembly work (up to 15 rooms)

Assumptions:

Service life: 10 years

CRF (10 years, 5 percent interest): 0.12950

Operation time: 0

Calibration time will be the same as Orsat checking and repair therefore will be ignored.

For the whole system

Beckman Model 778 - oxygen analyzer	\$	475
Beckman Model 7C Thermal Conductivity Analyzer (CO ₂ analyzer)		890
Two pen recorder		1300
Sampling devices		110
	\$ 7	2775

For each room sampling and switching system—(time switch, sole-noids, piping valves installation, etc.) where n is number of rooms: \$150 n

Total instrumentation cost for measurement and recording:

Therefore:

The additional costs of control of liquid nitrogen for example will be \$20 + \$45n therefore the total instrumentation cost for measurement,

recording and control will be approximately

$$(2775 + 150n) + (20 + 45n) = 2795 + 195n dollars$$

Cost of commercial instrumentation system based on proposal from Beckman Instruments, Inc. (1965)

Assumptions:

Service life: 10 years

CRF (10 years 5 percent interest): 0.12950

Operating time: 0

Cost of system

	For 15 rooms	For 7 rooms
Beckman 778 oxygen analyzer	\$ 475	\$ 475
Beckman 7C thermal conductivity analyzer (carbon dioxide analyzer)	\$ 890	\$ 890
Automatic stream selector	\$ 925	\$ 633
Sample handling system, unassembled	\$ 1570	\$1170
Panel including mounting of instruments	\$1265	\$ 1265
Baily two pen circular chart recorder	\$1300	\$1300
Total	\$6435	\$5733

Therefore, based on 15 room system cost,

Orsat operation costs	Total instrumentation measurement and recording for 15 rooms			Operation cost	
106n	=	6435 × 0.1295	+	0	
n	=	8			

There is some saving on automatic stream selector for smaller than 15 number of rooms (automatic stream selector 10 points - \$633) and on the sample handling system (for one room less than 15 subtract \$50 per room from \$1570). Therefore, the total cost of a system for 7 rooms will be as shown above and based on 7 room system cost

$$106n = 5737 \times 0.1295 + 0$$
 $n = 7$

With more than 7 rooms the commercial system is more economical than Orsat.

APPENDIX 2-2

CO₂ Removal Costs

Arcosorb for 60,000 bu.

Initial cost: \$9500

Shipment to Michigan: \$100

Installation: \$350

Years in service: 10

Salvage value: 10%

Operational costs

Power costs 1 cent/kwh: \$220

Power costs 3 cents/kwh: \$660

Water: \$14.3

Labor, 8 hr. per room per season \$1.5/hr.: \$36

Taxes and insurance (2%): \$190

K_2CO_3 - Sulzer Brothers Winterhur Switzerland

Initial suggested retail cost in Europe for 400 ton (19,500 bu.): \$5,650

Years in service: 10

Salvage value: 10%

Operational costs

Power

1 cent/kwh 20,000 bu.: \$ 51.7

60,000 bu.: \$155.1

3 cents/kwh 20,000 bu.: \$155.1

60,000 bu.: \$465.3

Labor, 8 hr./room/season when \$1.5/hr.

20,000 bu.: \$12

60,000 bu.: \$36

Taxes and insurance (2%)

20,000 bu.: \$113

60,000 bu.: \$339

<u>Water</u>

Initial cost based on \$1400 for 20,000 bu. unit

Years in service: 10

Salvage value: 10%

Operational costs

Power 1 cent/kwh: \$35.8 per 20,000 bu.

3 cents/kwh: \$107.0 per 20,000 bu.

Labor: 8 hr./room/season

Taxes and insurance (2%): \$28 per 20,000 unit

Dry lime

Initial cost (average)

based on local labor: 1.5 cents/bu.

based on hired labor: 3 cents/bu.

Years in service: 12

Salvage value: 10%

Operational costs

Dry lime cost: 1 cent/bu., based on price without resale or

regeneration

Labor: 12 hr. per room per season

Taxes and insurance: (2%)

Monoethanolamine (MEA)

Approximate initial cost: 1/3 more expensive than water

Scrubber: \$1865 for 20,000 bu.

Years in service: 10

Salvage value: 10%

Operational costs

Power 1 cent/kwh:

\$217 for 20,000 bu.

3 cents/kwh: \$650 for 20,000 bu.

Labor: 8 hr./room/season

Taxes and insurance: (2%)

<u>NaOH</u>

Initial cost: \$1650 for 20,000 bu.

Years in service: 7

Salvage value: 10%

Operational costs

NaOH cost: \$1000 for 20,000 bu.

Power 1 cent/kwh: \$25.24 for 20,000 bu.

3 cents/kwh: \$75.72 for 20,000 bu.

Labor: 1/2 hr./day/room, \$150 for 20,000 bu.

Taxes and insurance: (2%)

APPENDIX 2-3

Oxygen Reduction Costs

Eaves burner for 6000 bu. room

Initial cost: \$250

Years in service: 10

Salvage value: 10%

Operational costs

Fuel cost for 4 pulldowns

based on 8.4 cents/lb. propane: \$100

based on 2.83 cents/lb. propane: \$33.7

Labor, 8 hr./season: \$1.5/hr.

Taxes and insurance: (2%)

Tectrol generator as burner for 20,000 bu.

Initial cost: \$5000

Installation, 3 cents/bu.: \$600

Years in service: 10

Salvage value: 10%

¹The Tectrol unit includes the carbon dioxide scrubber that can be used, for the same basic cost for the pulldown period.

Operational costs for 4 pulldowns

Power 1 cent/kwh: \$4

3 cents/kwh: \$12

Water: \$5.6

Fuel 2.83 cents/lb. propane: \$32

8.4 cents/lb. propane: \$90.2

Labor: 8 hr./season/room

Taxes and insurance (2%): \$100

Arcat for 60,000 bu.

Initial cost: \$3350

Shipment to Michigan \$ 100

Installation \$ 200

Years in service: 10

Salvage value: 10%

Operational costs for 4 pulldowns

Power 1 cent/kwh: \$7.2

3 cents/kwh: \$21.6

Water: \$1.0

Fuel 2.83 cents/lb. propane: \$78.5

8.4 cents/lb. propane: \$233.0

Labor: 8 hr./season/room

Taxes and insurance (2%): \$67

Liquid N₂

Based on projected estimated costs for 10,000 bu. room (Smock, 1965). The adjusted price for flushing with the liquid N_2 and flushing and cooling combination is based on comparison of the liquid N_2 operation costs with the estimated mechanical refrigeration precooling (from 65 to 35°F) cost of 4.18 cents per bu.

APPENDIX 2-4

Complete Systems Annual Costs

Tectrol - annual cost based on lease and operation costs

The cost information provided by the Tectrol Division of Whirlpool Corporation is of a general nature and should be treated as such. It is based on 6 month operation, 2.5 cu. ft. storage volume per bushel, electrical power at 1 cent or 3 cents per kwh, propane gas at 2.83 cents/lb (12 cents/gallon), and four rooms with 15,000 bu. in each room. The Tectrol service charge is 15 cents/bu./6 months. There is a first year installation and room leak test charge of approximately 3 cents/bu. The Tectrol service includes: six months service, four pulldowns, warantee, parts and on-call service, technical assistance and annual leak test.

Costs for 60,000 bu. CA room

Installation: \$1800

Operational costs

Service charge: \$9000

Power 1 cent/kwh: \$300

3 cents/kwh: \$900

Water: \$427

Fuel: 12 cents/gallon propane, \$2400

Labor: 4 down periods a season, 8 hr. total

Taxes and insurance: none

The cost was also calculated assuming 40 cents/bu. saving on construction costs. For example, for 60,000 the saving is \$24,000. The actual annual saving is $$24,000 \times 0.05 = 1200 based on annual interest of 5%.

Tectrol - annual cost based on purchase and operation costs

The annual cost was based on a \$5000 possible initial cost of the Tectrol generator for 20,000 bu. (Pflug 1965) and the installation and operational costs provided by Tectrol Division of Whirlpool Corporation.

Costs for 60,000 bu. room

Initial cost \$15,000

Installation costs, 3 cents/bu. \$ 1,800

Years in service: 10

Salvage value: 10%

Operational costs

Power 1 cent/kwh \$ 300

3 cents/kwh \$ 900

Water \$ 427

Fuel, 12 cents/gallon propane	\$ 2,400
Labor, 4 down periods a season	\$ 36
Taxes and insurance	\$ 300

Arcagen for 60,000 bu.

Initia	al cost	\$11	900
	Shipment to Michigan	\$	150
	Installation	\$	500

Years in service: 10

Salvage value: 10%

Operational cost, based on 4 pulldowns

Power, Arcat	l cent/kwh:	\$7.2
	3 cents/kwh:	\$21.6
Power, Arcosorb	1 cent/kwh:	\$208
	3 cents/kwh:	\$624
Water Arcat		\$1.04
Arcosorb		\$13.5
Fuel, 12 cents/gallon	propane	\$78.5
Labor, 20 hr. per sea	ason	\$ 35
Taxes and insurance ((2%)	\$238

Eaves "Oxygen controller" for 6,000 bu.

Initial cost: \$250

Years in service: 10

Salvage value: 10%

Operational costs based on 4 pulldowns

Fuel costs 8.4 cents/lb. propane: \$100

2.83 cents/lb. propane: \$33.7

Dry lime cost-because of extra load on scrubber 1.5 cents/bu.

was assumed: \$90

Labor: 8 hr./room

Taxes and insurance (2%): \$10

Liquid N₂

Based on projected estimated costs for 10,000 bu. room (Smock 1965). The adjusted price for flushing is based on 4.18 cents per bu. annual cost precooling 30°F with mechanical refrigeration.

LITERATURE CITED

- Angelini, P. 1956. A study of CO₂ absorption equipment for CA fruit storages. M.S. Thesis, Michigan State University, East Lansing, Michigan (unpublished).
- Anon. 1959. Smith complete another cold store for Birds eye. Insulation Review (London) Feb. p. 24.
- Astarita, G. G. Marrucci and F. Gioia. 1964. The influence of carbonation ratio and total amino concentration on CO₂ absorption in aqueous MEA solutions. Chem. Eng. Sci. <u>19</u>, 95.
- Awbery, J. H. 1927. The flow of heat in a body generating heat. Phil. Mag. (7), 4, 629.
- Bass, R. 1964. Defrosting methods used on blower evaporators. Proc. Food Eng. Conf. p. 67, April 1964, M.S.U.
- Benson, H. E., J. H. Field and W. P. Haynes. 1956. Improved process for CO₂ absorption uses hot carbonate solutions. Chem. Eng. Progr. 52, 433.
- Bird, R. B., W. E. Stewart and E. N. Lightfoot. 1965. Transport phenomena. 5th printing. John Wiley & Sons, New York.
- Blum, H. A., L. F. Stutzman, and W. S. Dodds. 1952. Absorption of carbon dioxide by sodium and potassium hydroxide. Ind. Eng. Chem. 44, 2969.
- BRAB. Building Research Advisory Board. 1963. Cold storage facilities; A guide to design and construction. National Academy of Sciences-National Research Council No. 1098.
- Buck, B. O., and A. R. S. Leitch. 1958. Carbon dioxide removal from natural gas. Petrol. Refiner 37, 241.
- Clarke, J. K. A. 1964. Kinetics of absorption of CO₂ in MEA solutions at short contact-time. Ind. Eng. Chem. Fundamental <u>3</u>, (3), 239.
- Clarke, R. G. 1964. Gels and methods of making. U.S. Patent 3, 191, 729.

- Comstock, C. S. and B. F. Dodge. 1937. Rate of carbon dioxide absorption by carbonate solutions in a packed tower. Ind. Eng. Chem. 29, 520.
- Cooper, C. M. 1945. Gas-scrubbing apparatus, U.S. Patent 2, 398, 345.
- Cooper, C. M., R. J. Christland L. C. Peery. 1941. Packed tower performance at high liquor rates. Trans. Am. Inst. Chem. Eng. 37, 979.
- Cryder, D. S. and J. O. Maloney. 1941. The rate of absorption of carbon dioxide in diethanolamine solutions. Trans. Am. Inst. Chem. Eng. 37, 827.
- Deed, D. W., P. W. Schutz, and T. B. Drew. 1947. Comparison of rectification and desorption in packed columns. Ind. Eng. Chem. 39, 766.
- Dewey, D. H. and I. J. Pflug. 1965. Suggestions for the management and operation of your CA storage. Dept. of Horticulture and Food Science, Michigan State Univ., E. Lansing, Mich.
- Dow Chemical Company. 1965. Dow insulating panels for controlled atmosphere apple storage. Plastics Dept., Midland, Mich.
- Eaves, C. A. 1964. The effect of the chemical and physical properties of lime on scrubbing efficiency. Univ. of Mass. Amherst, Mass. Extension publication 422, 16.
- . 1965. Kentville Nova Scotia. Personal correspondence.
- Eaves, C. A. and C. L. Lockhart. 1964. Oxygen controller for CA storage. Ann. report--Nova Scotia fruit growers' Assoc.
- Eckert, J. S., E. H. Foote, and R. L. Huntington. 1958. Pall rings-new type of tower packing. Chem. Eng. Progr. <u>54</u>, 70.
- Ergun, S. 1952. Fluid flow through packed columns. Chem. Eng. Prog. 48, 89.
- Fidler, J. C. 1961a. Physiological activity of volatile organic compounds produced by fruits. Intern. Inst. Refrig. Annex 1961-63, p. 379.
- _____. 1961b. The measurement of carbon dioxide and oxygen concentration. Inter. Inst. Refrig. Comm. 4, 241.

- Foxboro Company, Foxboro, Mass. Feb. 1958. Wet and dry bulb humidity instrument-wick types. Instruction sheet 3-110.
- Foxboro, Mass. May 1964. Dew point-recorders and controllers. Bull. 11-11D.
- Fujita, S. and T. Hayakawa. 1956. Liquid-film mass transfer coefficients in packed towers and rod-like irrigation towers. Chem. Eng. (Japan) 20, 113.
- Furnas, C. C. and F. Bellinger. 1938. Operating characteristics of packed columns. Trans. Am. Inst. Chem. Eng. 34, 251.
- Geleynse, J., W. P. F. R. I. Stellenbosch. 1962. Relative humidity-measurement and control in coldstores. The Deciduous Fruit Grower 12, (5).
- General Electric Research Laboratory, Schenectady, N.Y. 1964. Artificial gills are not for fish. Chem. Eng. 71 (24), 94.
- Gray, H. E. and R. M. Smock. 1955. Farm refrigerated apple storages. Cornell Univ., Agr. Exp. Sta. Bull. 786.
- Greenwood, K. and M. Pearce. 1953. Removal of CO₂ from atmosphere air by scrubbing with caustic soda in packed towers. Trans. Inst. Chem. Eng. (London) 31, 201.
- Gregory, L. B. and W. G. Scharmann. 1937. Carbon dioxide scrubbing by amine solutions. Ind. Eng. Chem. 29, 514.
- Gregory, S. A., P. B. Herbert, and J. J. Lane. 1963. The removal of carbon dioxide by molecular sieve absorbent. Symposium on less common means of separation. (Inst. Chem. Eng.).
- Guillou, R., H. B. Richardson. 1964. Humidity control in fruit cooling and storage. Univ. of Calif. Davis Agr. Ext. Serv. Nov. 1964.
- Hall, J. E. 1957. New scrubber for gas stores. Mod. Refrig. 60, 322.
- Harte, C. R., E. M. Baker, and H. H. Purcell. 1933. Absorption of carbon dioxide in sodium carbonate-bicarbonate solutions. Ind. Eng. Chem., 25, 528.
- Hersh, C. K. 1961. Molecular sieves. New York, Reinhold Publications Inc.

- Honeywell Regulator Comp. Minneapolis, Minnesota. 1962. Dew Probe sensors. Specification data 90-1716.
- Hoogendoorn, J. C. 1963. A comparison of some carbon dioxide removal processes. Trans. Inst. Chem. Eng. 41, 264.
- Hukill, W. V., and E. Smith. 1946. Cold storage for apples and pears. U.S. Dept. Agr. Circ. 740, February.
- Hygrodynamics, Inc., Silver Spring, Maryland. Humidity instrumentation and systems. Catalog SF-1B.
- Hunter, D. L. 1965. A doctor for the apple. The analyzer, Scientific and Process Instruments, Beckman Instruments, Inc. April.
- Hutcheon, N. B. 1958. Vapor problems in thermal insulation. ASHAE J. August.
- Jeffreys, G. V., and A. F. Bull. 1964. The effect of glycine additive on the rate of absorption of CO₂ in sodium carbonate solutions. Trans. Inst. Chem. Engrs. 42, 118.
- Jensen, W. F. 1965. New principles improving the CA system. Produce Marketing, April.
- Johansson, J. 1962. Concentration of volatiles in CA storage and their relation to some storage operation. Proc. Amer. Soc. Hort. Sci. 80, 137.
- . 1963. Use of molecular sieve as a CO₂ adsorbent in experimental CA chambers. Am. Soc. Hort. Sci. 83, 172.
- Kane, J. J. 1961. Multi-stop delivery of frozen foods using liquid nitrogen refrigeration. Linde, Cryogenic Products Development Department (Unpublished).
- Kendenburg, F. V. Jr. 1959. CA refrigerated storages a boon to fruit warehouses. Ind. Refrig., 137, (2), 22.
- Koch, H. A., L. F. Stutzman, H. A. Blum, and L. E. Hutchings. 1949. Gas absorption-liquid transfer coefficients for the carbon dioxide-air-water system. Chem. Eng. Progress, 45, 677.
- Kohl, A. L. 1956. Plate efficiency with chemical reaction-absorption of carbon dioxide in Monoethanolamine solutions. Am. Inst. Chem. Eng. J. 2, 264.

- Kondo, R., and K. Fukuba. 1958. Absorption of CO₂ by MEA solutions in packed columns. Chem. Eng. (Japan) 22, 610.
- Kopelman, J., J. L. Blaisdell and I. J. Pflug. 1964. The influence of fruit size and collant velocity on the cooling of Jonathan apples in water and air. To be submitted at ASHRAE semi annual meeting, Houston, Texas January 1966.
- Lannert, J. W. 1964. Tectrol atmospheric control. Agr. Eng. 45, 318.
- Lentz, C. P. 1955. Humidification of cold storages: The Jacket System. Can. J. Technol. 33, 265.
- _____. 1959. The Jacketed system for cold rooms. Proc. 10th Intern. Congr. Refrig. 3, 298.
- Lentz, C. P., and W. H. Cook. 1955. Comparison of two types of high humitidy cold storage systems. Proc. 9th Intern. Congr. Refrig., 2, p. 5.039.
- Lentz, C. P., and U. Nakano. 1961. Predicting air friction pressure loss in shallow ducts. ASHRAE J. 3, February. p. 32.
- Lentz, C. P., and C. W. R. Philips. 1959. Use of the jacketed room system for fresh fruit and vegetable storage. Proc. 10th Intern. Congr. Refrig. p. 309.
- Leva, M. 1953. Tower packing and packed tower design, 2nd ed. U.S. Stoneware Co., Akron, Ohio.
- . 1955. Gas absorption in beds of rings and saddles. Am. Inst. Chem. Eng. J. 1, 224.
- Lorenzen, R. T. 1963. A balancing technique for moisture control in structural components of CA storages. Winter meeting Am. Soc. Agr. Eng. Paper No. 63-905. December, Chicago.
- Lotz, W. A. 1964. Vapor barrier design for cold storage application. ASHRAE J., 6, Dec. p. 46.
- Mann, G. 1954. The control of relative humidity in cold stores. 1. The loss of water from perishable produce during storage. The Inst. Refrig., London. 1953-54 Session March 16.
- Proc. 11th Intern. Congr. Refrig. Comm. 4.

- Mod. Refrig. 61, 990.
- Inst. Agr. Eng. 16, October.
- Mayland, B. J. 1964. Removal of carbon dioxide from gaseous mixtures. U.S. Patent 3, 144, 301.
- Mayland, H. B. 1956. Industrial engineering handbook. p. 7-84. McGraw-Hill Book Co.
- McGarvey, A. R. 1964. Wrap your cold storage room in a vapor barrier. ASHRAE J. 6, Dec. p. 42.
- Meigh, D. F. 1956. Volatile compounds produced by apples. 1. Aldehydes and Ketones. J. Sci. Food Agr. 7, 396.
- esters. J. Sci. Food Agr. 8, 313.
- Meyer, A. 1961. Sulzer CO₂ washing plant for the cold storage of fresh fruit. Intern. Inst. Refrig. Comm. 4, p. 267.
- Meyer, C. S. 1964. Inside out design developed for low temperature building. ASHRAE J. 6, April, p. 50.
- Nelson, K. E., R. Guillon. 1960. Highly marketable grapes maintained by controlled humidity. ASHRAE J. 2, 57.
- Palmer, R. 1959. Special report to CA storage operators. Am. Fruit Grower, 79, (8), 20.
- Perry, J. H 1963. Chemical engineering handbook. 4th ed. McGraw-Hill, New York.
- Phillips, W. R., C. P. Lentz, E. A. Rooke and W. M. Rutherford. 1961.

 The use of jacketed room system for the storage of apples. Canadian Refrig. Air Conditioning. Dec.
- Pflug, I. J. 1956. Breather bag for CA fruit vegetables storages. Agricultural Engr. 37, (7), 476.
- _____. 1960. Oxygen reduction in CA storages: A comparison of water vs caustic soda absorbers. Mich. State Univ. Agr. Exp. Sta. Quart. Bull. 43, 455.

- _____. 1961. Design of water type carbon dioxide absorption system for fruit storage. ASHRAE J. 3, 65.
- _____. 1965. Mich. State Univ. Personal Communication.
- Pflug, I. J., and J. L. Blaisdell. 1963. Method of analysis of precooling data. ASHRAE J. 5, November, p. 33.
- Pflug, I. J., and D. H. Dewey. 1955. Controlled atmosphere storage. Agrigultural Engr. 35, (3), 171.
- _____. 1956. A theoretical relationship of the variables affecting the operation of CA storage rooms. Mich. State Univ. Agr. Exp. Sta. Quart. Bull. 39, 353.
- Agr. Eng. 40, (2), 80.
- Pflug, I. J., and F. W. Southwick. 1954. Air leakage in controlled atmosphere storage. Agr. Eng. 35, (9), 635.
- Pflug, I. J., P. Angelini, and D. H. Dewey. 1957a. Fundamentals of CO₂ absorption as they apply to CA storages. Mich. State Univ. Agr. Exp. Sta. Quart. Bull. 40, 131.
- Pflug, I. J., M. W. Brandt and D. H. Dewey. 1957b. An experimental tilt up concrete building for the controlled-atmosphere storage of apples. Mich. State Univ. Agr. Exp. Sta. Quart. Bull. 39, 505.
- Pflug, I. J., D. H. Dewey and M. W. Brandt. 1957c. An absorber for the removal of carbon dioxide from CA storage. Mich. Agr. Expt. Sta. Quart. Bull. 40, 131.
- Pflug, I. J., J. L. Blaisdell and J. Kopelman. 1965. Developing temperature-time curves for objects that can be approximated by a sphere, infinite plate, or infinite cylinder. ASHRAE Transactions 31.
- Poms, A. I. 1965. Controlled atmosphere enclosures. Koppers Company. Panel dept. Detroit, Mich. February.
- Richards, G. M., G. A. Ratcliff and P. V. Danckwerts. 1964. Kinetics of CO₂ absorption-3. First order reaction in a packed column. Chem. Eng. Sci. 19, 325.
- Robb, W. L., Manager, Chemical Process Studies. General Electric Company. 1964. Personal correspondence.

- Sainsbury, G. F. 1961. Cooling apples and pears in storage rooms. U.S. Dept. Agr. AMS 474, September.
- August. 1962. Cooling apples in pallet boxes. U.S. Dept. Agr. AMS 532,
- Sherwood, T. K. and F. A. L. Holloway. 1940. Performance of packed towers-liquid film data for several packing. Trans. Am. Inst. Chem. Eng. 36, 39.
- Sherwood, T. K. and Pigford, R. L. 1952. Absorption and extraction. McGraw-Hill, Inc. New York, N. Y.
- Shulman, H. L. and J. J. DeGauff, Jr. 1952. Mass transfer coefficients and interfacial areas for 1-inch Rashing rings. Ind. Eng. Chem. 44, 1915.
- Shuman, E. C. 1961. Private communication to BRAB cold storage committee 1961.
- Smock, R. M. 1960. Water scrubbing in CA rooms. Cornell Univ. Dept. of Pomology, Mem. 5-508.
- Sta. Bull. 970, October.
- _____. 1962. Gas sealing the CA room. Cornell Univ. Dept. of Pomology, Mem. S-528.
- . 1965. Personal communication.
- Smock, P. M. and G. D. Blanpied. 1960. Handbook for CA rooms. Cornell Univ. Dept. of Pomology. Mem. S-504.
- Smock, R. M. and G. D. Blanpied. 1964. Lime scrubbing, water scrubbing and externally generated atmospheres compared in CA storage. Univ. of Mass. Amherst, Mass. Extension publication 422, p. 22.
- . 1965. The use of nitrogen for cooling, flushing, and maintaining atmosphere in CA rooms. Proc. 1965 Annual Meeting, New York State Hort. Soc.
- Smock, R. M. and VanDoren, A. 1941. CA storage of apples. Cornell University Agr. Exp. Sta. Bull. 762.

- Southwick, F. W. and J. W. Zahradnik. 1958. CA apple storage. Univ. of Mass. Amherst, Mass. Extension Bull. 322.
- Spector, N. A. and B. F. Dodge. 1946. Removal of carbon dioxide from atmospheric air. Trans. Am. Inst. Chem. Eng. 42, 827.
- Strutz, W. 1964. Evaporator coils and humidity in fruit and vegetable storages. Proc. Food Eng. Conf. p. 53. April 1964. M. S. U.
- Teller, A. J. and R. E. Ford. 1958. Packed column performance of carbon dioxide-monoethanolamine system. Ind. Eng. Chem. 50, 1201.
- Tepe, J. B. and B. F. Dodge. 1943. Absorption of carbon dioxide by sodium hydroxide solutions in a packed column. Trans. Am. Inst. Chem. Eng 39, 255.
- Thomas, O. O. Atlantic Research Corporation. 1965. Personal correspondence.
- Turk, A. 1955. Air purification in refrigerated storage in the U.S. A review. Proc. 9th Intern. Congr. Refrig. Paris, p. 41.
- U. S. Dept. Agr. 1954. The commercial storage of fruits, vegetables, and florist nursery stocks. Agr. Handbook, 66.
- Walter, J. F. and T. K. Sherwood. 1941. Gas absorption in bubble-cap columns. Ind. Eng. Chem. 33, 493.
- Wolf, J. and J. Kuprianoff. 1961. Apparatus for control of storage and simultaneous measurement of the gas exchange of the stored produce. Intern. Inst. Refrig. Comm. 4, p. 34.
- Wright, N. 1961. A program controlled environmental plant growth chamber. Univ. Ariz. Agr. Exp. Sta. Tech. Bull. 148.
- Yoshida, F., and T. Koyanagi. 1958. Liquid phase mass transfer rates and effective interfacial area in packed absorption columns. Ind. Eng. Chem. <u>50</u>, 365.
- Zahrandnik, J. W. 1964. Functional specifications for CA instrumentation controlled atmosphere storage. Univ. of Mass. Amherst, Mass. Extension publication 422, p. 5.

- Zahradnik, J. W. and F. W. Southwick. 1958. Design details and performance characteristics of a Douglas fir plywood apple storage. Univ. of Mass. Amherst, Mass. Exp. Sta. Bull. 505.
- Zahradnik, J. W., F. W. Southwick, and J. M. Fore. 1958. Internal atmosphere movement in CA apple storage. Agr. Eng. 39, (5), 288.