

THE UNIVERSITY OF MANITOBA

WASTEWATER RENOVATION BY  
NATURAL FREEZE-PURIFICATION IN LAGOONS

by

Robert David Sinclair

A THESIS  
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE  
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CIVIL ENGINEERING  
Winnipeg, Manitoba  
May, 1981

WASTEWATER RENOVATION BY  
NATURAL FREEZE-PURIFICATION IN LAGOONS

BY

ROBERT DAVID SINCLAIR

A thesis submitted to the Faculty of Graduate Studies of  
the University of Manitoba in partial fulfillment of the requirements  
of the degree of

MASTER OF SCIENCE

© 1981

Permission has been granted to the LIBRARY OF THE UNIVER-  
SITY OF MANITOBA to lend or sell copies of this thesis, to  
the NATIONAL LIBRARY OF CANADA to microfilm this  
thesis and to lend or sell copies of the film, and UNIVERSITY  
MICROFILMS to publish an abstract of this thesis.

The author reserves other publication rights, and neither the  
thesis nor extensive extracts from it may be printed or other-  
wise reproduced without the author's written permission.

Abstract

A study of the effectiveness of nutrient and microbiological removals from domestic wastewater using freeze-purification technology was carried out in laboratory simulations. The results of the study indicated that both the reservoir and layer freezing methods can effectively remove the major nutrients; carbon, nitrogen and phosphorus, as well as significantly reduce the microbial numbers. The removal efficiencies for both the reservoir and layer freezing tests ranged from 0 to 89 percent and 62 to 84 percent respectively for carbon, from >29% to 96% and >56% to 90% respectively for phosphorus and from 47% to 87% and 53% to 90% respectively for oxygen demand. The micro-organism concentration, as measured by the Most Probable Number and Standard Plate Count tests, demonstrate reductions of 100 to 1,000 fold and 0 to 10 fold, respectively.

Acknowledgement

The author wishes to express his appreciation to Dr. A.M. Lansdown, my personal advisor, and Dr. B.H. Topnik for their patience and support during the preparation of this study.

Thanks also to Judy Tingley for her help and recommendations during the laboratory work and to the Civil Engineering Technical Team, Ed Lemke, Brian Turnbull and John Clark for their help and suggestions in construction of the testing apparatus.

Financial support through the University of Manitoba Fellowship program is gratefully acknowledged.

Certainly, the most important acknowledgement must go to my wife, Arleen, who gave continuous moral support as well as very necessary typing and organizational capabilities.

## TABLE OF CONTENTS

CHAPTER		Page
1	TECHNOLOGICAL BASIS	1
	1.1. Introduction	1
	1.2. Purpose	3
	1.3. Scope of Study	3
2	LITERATURE REVIEW	5
	2.1. Introduction	5
	2.2. Theoretical Analysis of Freeze-Purification	5
	2.2.1. The States of Water	5
	2.2.2. The Structure of Aqueous Solutions	7
	2.2.3. Impurity Rejection from Ice Crystal Lattices	9
	2.2.3.1. Ionic Size and Charge	10
	2.2.3.2. Solubility	15
	2.2.3.3. Eutectic Point	17
	2.2.3.4. Rate of Freezing	18
	2.2.3.5. Pressure	19
	2.2.4. Impurity Rejection from the Ice Crystal Boundaries	19
	2.2.4.1. Gravity Drainage	22
	2.2.4.2. Pressure Expulsion	23
	2.2.4.3. Diffusion	25
	2.2.5. Freeze-Purification of Aqueous Dispersions and Suspensions	25
	2.2.5.1. Structure of Aqueous Dispersions and Suspensions	27
	2.2.5.2. Fundamental Processes in the Freeze- Purification of Aqueous Dispersions and Suspensions	28
	2.2.5.2.1. Colloid and Suspensoid Size and Shape	28
	2.2.5.2.2. Surface Charge	29
	2.2.5.2.3. Rate of Freezing	30
	2.2.5.2.4. Particulate Migration Within Ice	31
	2.6. Consequences of Subzero ( $^{\circ}\text{C}$ ) Temperature on Micro-Organism Viability	33
	2.6.1. Temperature and Duration of Freezing	33
	2.6.2. Intracellular and Extracellular Ice Formation	35
	2.6.3. Freeze-Concentration of Intracellular and Extracellular Solutes	37

## Table of Contents, Continued

CHAPTER		Page
2	2.7. Engineering Applications of the Freeze-Purification Process	38
	2.7.1. Reservoir Freezing	38
	2.7.2. Layer Freezing	41
	2.7.3. Spray Freezing	46
	2.8. Laboratory Applications of Freeze Purification	51
3	EXPERIMENTAL EQUIPMENT, PROCEDURE AND ANALYSES	55
	3.1. Introduction	55
	3.2. Reservoir Freezing Method	55
	3.3. Layer Freezing Method	60
	3.4. Analyses and Analytical Procedure	63
	3.5. Initial Wastewater Characteristics	64
4	EXPERIMENTAL RESULTS	68
	4.1. Introduction	68
	4.2. Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)	70
	4.3. Nitrogen	72
	4.4. Phosphorus	74
	4.5. Most Probable Number (MPN) and Standard Plate Count (SPC)	76
5	DISCUSSION OF RESULTS	77
	5.1. Introduction	77
	5.2. Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)	79
	5.2.1. Biochemical Oxygen Demand (BOD)	79
	5.2.2. Chemical Oxygen Demand (COD)	86
	5.2.3. Total Organic Carbon (TOC)	88
	5.3. Nitrogen	90
	5.3.1. Introduction	90
	5.3.2. Nitrate (NO <sub>3</sub> -N)	90
	5.3.3. Ammonia (NH <sub>3</sub> -N)	92
	5.3.4. Organic Nitrogen (Org-N)	94
	5.4. Phosphorus	96
	5.4.1. Introduction	96
	5.4.2. Total Phosphorus (TP)	96
	5.4.3. Organic Phosphorus (Org-P)	98
	5.5. Most Probable Number (MPN) and Standard Plate Count (SPC)	99
	5.6. Field Applicability of Freeze-Purification in Lagoon Environments	100

## Table of Contents, Continued

CHAPTER		Page
6	CONCLUSIONS	103
7	RECOMMENDED FUTURE RESEARCH	105
	References	108
	Abstract	ii
	Acknowledgements	iii
	Table of Contents	iv

## LIST OF FIGURES

FIGURE		
1	Diagrammatic representation of the structure of pure water near the freezing point.	8
2	The dependence of ionic mobility with fluidity values relative to water (after Podolsky, 3).	11
3	The effect of ionic radius and charge on the fluidity of water (after Podolsky, 3).	13
4	The phase diagram of ice as a function of temperature (T) and pressure (P), (after Glen, 10).	21
5	Idealized drawing of permeability network in ice.	24
6	The diffusion velocity of brine pockets in ice relative to the temperature gradient (after Hoekstra, et al,16).	26
7	Theoretical ice formation rates for Prairie winter conditions excluding influence of snow cover.	32
8	Desalination efficiency for layer freezing method (after Fertuck, 48).	45
9	Diagrammatic representation of reservoir freezing apparatus.	56
10	Diagrammatic representation of layer freezing apparatus.	61
11	Cost comparison for several feasible desalination processes.	101

## Table of Contents, Continued

Page

## LIST OF TABLES

## TABLE

1	Rates of ice formation on open water bodies for various ice surface temperatures (insulative values of snow has not been included).	20
2	Results of field studies of natural freeze-purification, winter of 1963-1964, Saskatoon, Saskatchewan.	40
3	Time required to purify ice blocks of various ice thicknesses and initial salinities.	42
4	Purification efficiencies for ice blocks of variable thicknesses and initial salinities.	43
5	Influence of layer thickness and salinity on purification times and percentage of initial volume collected at a TDS of 500 mg/l (after Spyker, 47).	44
6	Product quality and quantity for spray freezing field tests, Frontier, Saskatchewan, 1976-1977.	48
7	Product quality and quantity, for spray freezing field tests, Armley, Saskatchewan, 1976-1977.	49
8	Nutrient concentration in spring meltwater runoff in ice.	50
9	Nutrient concentration in spring meltwater runoff in ice.	51
10	Freeze concentration results for dilute aqueous solutions (after Baker, 55).	53
11	Recovery of <sup>14</sup> C-labelled compounds from distilled water using freeze concentration (after Kammerer and Lee, 56).	54
12	Initial wastewater characteristics for reservoir freezing analyses.	66



## Table of Contents, Continued

		<u>Page</u>
TABLE		
13	Initial wastewater characteristics for layer freezing analyses.	67
14	Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) concentrations for reservoir freezing simulations.	70
15	Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) concentrations for layer freezing simulations.	71
16	Nitrogen concentrations for reservoir freezing simulations.	72
17	Nitrogen concentration for layer freezing simulations.	73
18	Phosphorus concentrations for reservoir freezing simulations.	74
19	Phosphorus concentrations for layer freezing simulations.	75
20	Microbiological concentrations evaluated during reservoir freezing analyses using secondary effluent.	76
21	Effectiveness of BOD removal for both reservoir and layer freezing simulations.	82
22	Effectiveness of COD removal for both reservoir and layer freezing simulations.	87
23	Effectiveness of TOC removal for both reservoir and layer freezing simulations.	89
24	Effectiveness of NO <sub>3</sub> -N removal for both reservoir and layer freezing simulations.	91
25	Effectiveness of NH <sub>3</sub> -N removal for both reservoir and layer freezing simulations.	93

## Table of Contents, Continued

		<u>Page</u>
TABLE		
26	Effectiveness of Org-N removal for both reservoir and layer freezing simulations.	95
27	Effectiveness of TP removal for both reservoir and layer freezing simulations.	96
28	Effectiveness of Org-P removal for both reservoir and layer freezing simulations.	98

## LIST OF PHOTOGRAPHS

PHOTOGRAPH		
1	Reservoir freezing apparatus.	57
2	Layer freezing apparatus.	62
3	Colour variation among samples of initial wastewater underdrain effluent, and thawed ice.	78

WASTEWATER RENOVATION BY NATURAL  
FREEZE-PURIFICATION IN LAGOONS

Chapter I

Technological Basis

1.1. Introduction

The origin of many of our present concepts of wastewater management dates back to the time of the Greeks and Romans, however, it was the Europeans, who for reasons of widespread unsanitary conditions, first introduced sanitary wastewater handling on a broad scale. One of the earliest forms of effective wastewater handling was the construction of sanitary sewers. This eliminated the street-dumping of wastes and provided a period during which the air was odour free. However, once the volume of waste increased beyond the assimilative capacity of the receiving water, the whole situation became as bad and possibly worse than the period prior to the construction of sewers, as now, the drinking supply was often polluted. It was this general environmental problem which precipitated the advancement of wastewater treatment technology into the first half of the 20th century.

Since that time, there has been a second environmental problem; eutrophication, which has adversely affected our lakes and streams and certainly, in part, is attributable to domestic wastewater effluents. The natural aging of lake and river ecosystems has been accelerated by the addition of large amounts of nutrients, mainly in the form of phosphorus and nitrogen. This nutrient inflow has precipitated such events as algal blooms and the deterioration of fish stocks on

relatively wide scales, two common symptoms of eutrophication. To combat this problem, governmental agencies in the industrialized countries have started programs to limit the nutrient loads into the environment.

The reduction of nutrient concentrations has necessitated extensive amounts of research and process development for both municipal and industrial wastewaters. This research has included individual physical, chemical and biological processes as well as combinations of each. Furthermore, this research has also demonstrated that these processes have both application and environmental constraints. Similar wastewaters at separate locations may require very different nutrient-removal processes to obtain practical results. The philosophy of this research was that optimum results are more likely to come from research directed at the optimum uses of the physical environment at hand versus the construction of an artificial environment to utilize technology developed for significantly different environmental conditions.

The technological basis of this study stems almost exclusively from research conducted on the natural freeze desalination of brackish water (approximately 15,000 to 20,000 mg/L Total Dissolved Solids). The fact that domestic wastewater is normally over 99% water makes it characteristically very similar to brackish water. The research on brackish water has shown that the salinity of brackish water can be effectively reduced from 75 to 95% using natural freeze-purification in lagoon systems. It was a consequence of these results that made the application of freezing technology look promising as a tertiary treatment method for lagoon wastewater.

## 1.2. Purpose

The purpose of this study was to demonstrate proof of concept of natural freeze-desalination for nutrient removal. Freeze-desalination coupled with irrigation could provide practical and cost effective recycling of nutrients into the environment in rural areas. At the present time, the only effective forms of tertiary treatment are costly and require relatively well trained personnel. Consequently, in these rural areas such as in Western Canada where the lagoon is the major form of wastewater treatment, the incorporation of nutrient removal can be expected to be difficult and expensive. For nutrient removal to be practical, it will be necessary to evaluate other forms of tertiary treatment technology. This research, on the effectiveness of natural freeze-purification of wastewater for nutrient removal is one alternate method that has the potential, when the climatic conditions of the Prairies are considered, of being both environmentally appropriate and cost-effective for lagoon operations.

## 1.3. Scope of Study

The research conducted in this study was limited to a laboratory analysis. Work done by the Saskatchewan Research Council on freeze-purification of brackish waters demonstrated that the laboratory studies correlated well with their field studies and provided the important first step in the evaluation of these processes.

This laboratory study investigated the treatment capability of the freeze-purification process for carbon, nitrogen, phosphorous, and micro-organisms using the reservoir and layer freezing techniques.

Reservoir freezing is the natural form of freezing, from top to bottom, typified by lakes, ponds, dugouts, etc. Layer freezing requires that successive flooding occur once the previous layer has frozen sufficiently. Layer freezing is therefore, more labour intensive than reservoir freezing but has the one main advantage that a much greater thickness of ice per unit of land area is possible.

## Chapter 2

### Literature Review

#### 2.1. Introduction

The main emphasis in the renovation of domestic wastewater is directed toward the reduction of dissolved and suspended solids, including microorganism concentrations. For this reason, the emphasis of the following chapter was directed towards an evaluation of the effect of the freezing of wastewater on these different factors. This included the basic theory of phase change as well as an analysis of low temperature microbiology, now part of the field of cryobiology. In addition, laboratory and field studies of the freeze-desalination process were evaluated.

#### 2.2. Theoretical Analysis of Freeze-Purification

##### 2.2.1. The States of Matter

Freeze-purification is a phase change phenomenon, that is to say, it occurs as a consequence of the physical and chemical changes that take place in the states of matter, in this case, liquids and solids as they change from one phase to another. These states or phases are a function of the electronic and nuclear structure of the component ions, atoms, or molecules. In a gas, the individual components have little if any attractive forces and for this reason can maintain a highly energized state. If unconfined, the individual gas particles would move away from each other in a random, chaotic pattern. Liquids are representative of particles having significant stronger nuclear

and electronic bonding. The energy of motion is primarily translational with a minor vibrational contribution. The atoms, ions, or molecules of a solid cannot move about freely. They are limited to vibration motion about fixed positions and represent the lowest energy form of the states of matter. In crystalline solids, the structure is arranged in an orderly, long-range pattern.

In broad terms, the major difference between the states of matter is the energy level. The differences in energy level are directly related to changes in atomic structure which in turn affects the degree or strength of bonding and therefore the state or phase (1). A consequence of this atomic theory is that matter can move from one phase to another by the addition or removal of energy. For most applications of phase change, this energy is in the form of heat (temperature,  $T$ ) and/or pressure ( $P$ ). Temperature ( $T$ ) and pressure ( $P$ ) are the independent variables for equations of state and are, therefore, the parameters ultimately controlling changes from one state to another. In freeze-purification theory, the equations of state become more complicated than those for single compounds or elements as two and sometimes three phases are in or moving toward equilibrium at the same time. It is the two-phase mixtures of solids and liquids that are of prime interest in this study. The term for these mixtures are the solution (dissolved solids) and the suspension (suspended solids). The structure of these mixtures is intimately related to the freeze-purification process and is discussed in some detail in the following sections.



### 2.2.2. The Structure of Aqueous Solutions

In comparison to most other liquids, water has a relatively open structure. That is to say, the internal bonding strength of the water molecule is somewhat less than most other liquids. If water molecules were as closely packed as most liquids, the density would be nearly twice that observed. This open structure results from the polar nature of the water molecules (see Figure 1) and facilitates the dissolution of a large number of different substances or solutes.

The whole concept of solubility in water or any other solvent for that matter, is derived from the atomic structure and electronics bonding theory briefly mentioned in the previous section. A substance is soluble in water only if the energy level of the water molecules is sufficient to break the bonding of the solute. This is why heating a solution often increases the rate of dissolution. The water molecules are more highly energized and impart more energy per molecular collision and this, coupled with the increase in vibrational energy of the solute, results in faster and increased solubility. The limit of solubility is theoretically the point at which the dissolved species becomes so numerous that interspecies collisions and subsequent rebonding with the resulting insolubility, is in equilibrium with dissolution events. Insoluble substances are theorized to have durable bonding, that is, uninfluenced by the translation energy imparted by a collision of a water molecule regardless of the temperature or pressure (2).

One of the most common types of solutions in environmental engineering is the non-volatile, electrolytic solution. The dissolved minerals in surface and ground-water are typical examples.

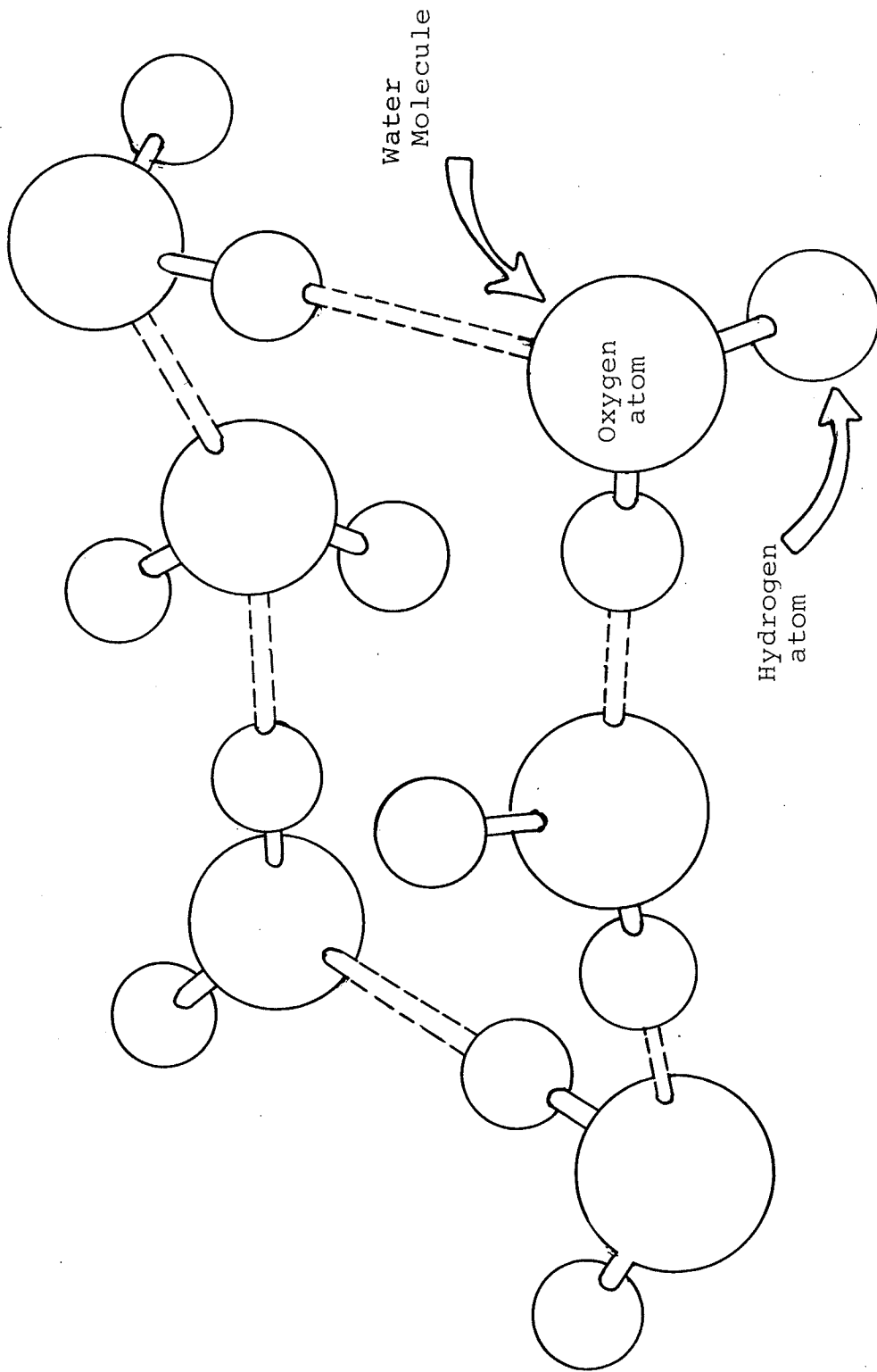


FIGURE 1. Diagrammatic representation of the structure of pure water near the freezing point.

Electrolytes when dissolved in water, break up to form positive and negative ions, cations and anions respectively. These ions are in reality, minute solids in the submicron or angstrom range and actually displace water molecules rather than fitting between them. These small charged particles disturb not only the tetrahedral structure of the water but also the normal charge distribution. These molecular and electronic disturbances cause changes to a large number of water's physical properties, namely density, conductivity, vapour pressure, freezing point, boiling point, optical density, specific heat, thermal conductivity and fluidity.

Of all these changes, the most important one in terms of this study is the fluidity, even more so than changes in the freezing point or specific heat. Changes in fluidity of water have been linked to the compatibility of specific ions to meshing into the tetrahedron water crystal. Ions that move into the crystal lattice, can be shown to either increase or decrease the structural integrity or bonding strength of the tetrahedron.

It is a similar phenomenon to that of increased strength of steel by addition of cobalt or molybdenum or the exchange phenomenon that occurs in clays. This effect is therefore, an indirect method of measuring how strongly, specific ions are held in the water crystal lattice. This phenomenon is of great importance in freeze-purification theory and is discussed in the following sections which deal with factors influencing ion separation during freezing.

### 2.2.3. Impurity Rejection from Ice Crystal Lattices

The freeze-purification process, to be effective is dependent on

two different but equally important phenomena. The first of these is the removal of impurities from the crystal structure to the crystal boundary and the second is the removal of the impurities from the boundary region out of the ice mass as a whole. The effectiveness of these two steps has been shown to be dependent on the physical and chemical properties of the impurities and ice as well as some environmental factors. The main factors influencing the first step of this process, namely impurity rejection from the crystal lattice itself, are the ionic size, ion charge, solute solubility, eutectic points, temperature (T), pressure (P), as well as the rate of freezing.

#### 2.2.3.1. Ionic Size and Charge

The work of Podolsky (3), as mentioned previously, has shown that the size and charge of ions are very important in controlling the mobility of specific ions in aqueous solutions. He showed that ions which increased the strength of the molecular bonding would be detected by a decrease in the fluidity of the liquid. Similarly, increased fluidity was rationalized by a decreased bonding strength causing increased ion mobility. The plot shown in Figure 2 (after Podolsky) shows this relationship between ionic mobility and fluidity for a large number of ionic solutes. The most highly negative values are indicative of ions which greatly increase the molecular integrity of the water tetrahedron and are consequently hardest to remove from the crystal structure. The highest relative values (positives) reduce the molecular bonding and increase the fluidity and are therefore the most mobile and most easily excluded from the crystal structure. From this figure, it can be seen that the mobility of the charged cations

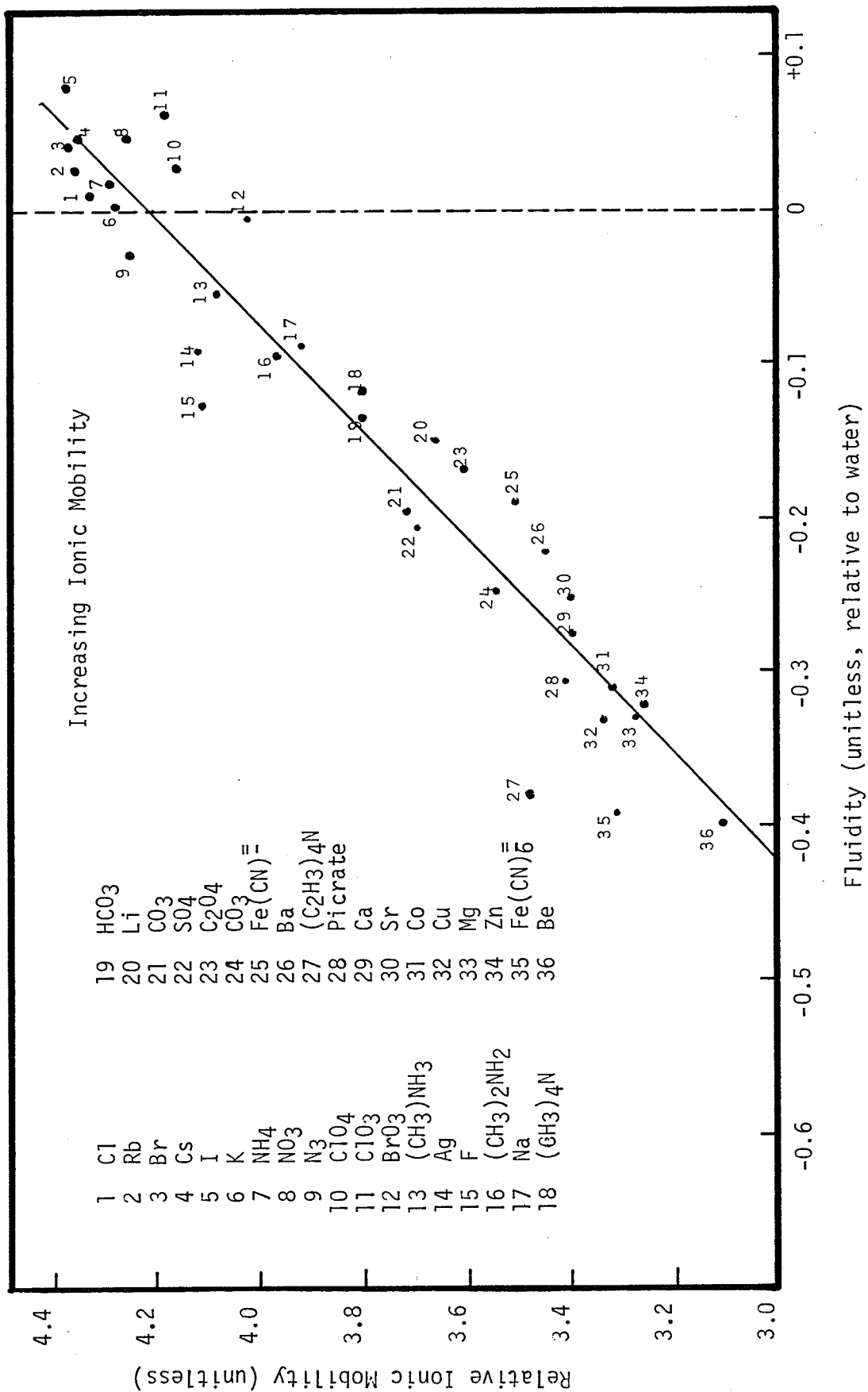


FIGURE 2. The dependence of ionic mobility with fluidity values relative to water (after Podolsky, 3).

and anions decreases with increasing charge (positive or negative). For example, sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ ) are much more mobile than calcium ( $\text{Ca}^{++}$ ) or magnesium ( $\text{Mg}^{++}$ ) and nitrate ( $\text{NO}_3^-$ ) is more mobile than sulphate ( $\text{SO}_4^{--}$ ) or carbonate ( $\text{CO}_3^{--}$ ).

The significance of ionic charge and radius on the relative fluidities is presented in Figure 3 (after Podolsky). This figure demonstrates the decreased fluidity for the higher charged anions and cations as well as for the ions with radii below  $1.5\text{\AA}$  and above  $3.2\text{\AA}$ . Ions above the zero line have difficulty in leaving the water crystal while those below it move in and out quite freely.

Luyet was able to extend this theory from the crystal structure of water to that of ice by x-ray diffraction studies (4). This work showed that the crystal lattices of ice and water are essentially the same. The major difference is the fact that ice has a continuous orderly structure while that of water is more short range. In terms of freeze-purification theory, this difference has not been found to be significant as the molecular structure and size for both solid or liquid is the same. The specific migration rates or velocities for ions in ice, as would be expected with the lower temperature and energy, are lower than in the liquid, however, the relative rates for the ions remains the same. It is important to note that this relatively theoretical analysis by Podolsky (3) has been substantially corroborated by studies of freeze-purification efficiency in Russia.

A comparison of these two very different sources of data demonstrates a surprisingly good correlation. Vaslov and Chernyshev calculated "inclusion factors" from studies of ice freezing on Selenga Lake in Russia (5). They froze a number of samples of lake water and

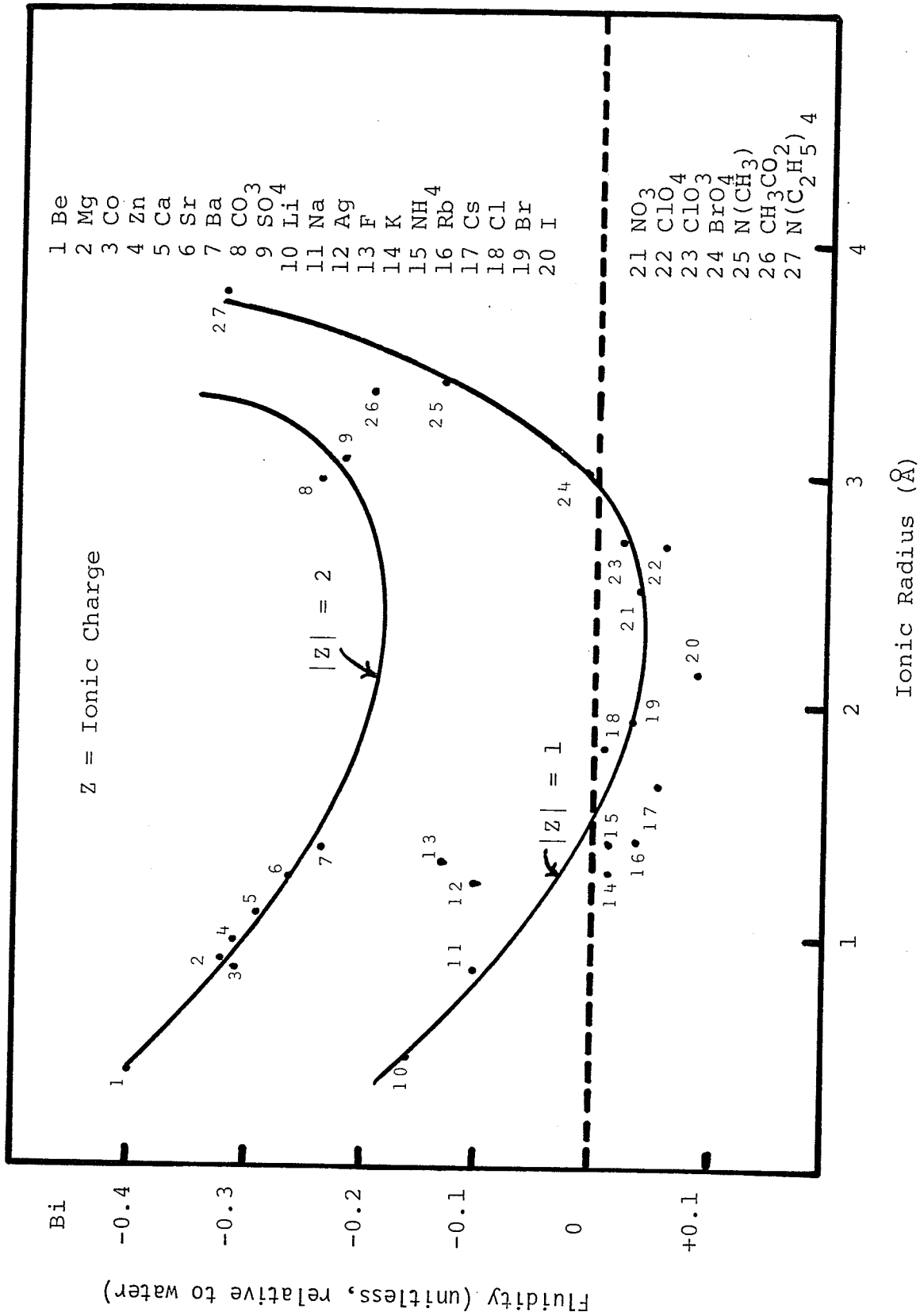


FIGURE 3. The effect of ionic radius and charge on the fluidity of water (after Podolsky, 3).

centrifuged the samples in the frozen state. They assumed that ions which were most strongly held in the ice lattice would be the most difficult to desalinate by freeze-purification. The relative desalability was based on the concentration of the ions in the fluid centrifuged out of the ice. They found that the order of preferences of inclusion was  $\text{Ca}^{++}$ ,  $\text{SO}_4^-$ ,  $\text{CO}_3^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{++}$  and  $\text{K}^+$ . If these values are compared to Podolsky's fluidity values for the same ions, the order is exactly the same with exception to the  $\text{Mg}^{++}$  ion. The  $\text{Mg}^{++}$  ion, based on the fluidity data, would be expected to be at the other end of the scale. It is possible, however, that the  $\text{Mg}^{++}$  ion results of Vaslov and Chernyshev were influenced by other factors. Other studies found  $\text{Mg}^{++}$  to have a much higher preference for inclusion than their study showed. Kervan for example, showed that  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  were much more difficult to remove from the ice than either  $\text{Na}^+$  or  $\text{K}^+$  and that  $\text{Mg}^{++}$  was the most difficult to remove of the four (6). Furthermore, ion exchange phenomena, a somewhat similar process also demonstrates  $\text{Mg}^{++}$  to be between  $\text{Ca}^{++}$  and  $\text{Na}^+$  in terms of order of replacement. These factors indicate that the placement of  $\text{Mg}^{++}$  on Vaslov's and Chernyshev's list of ion "inclusion factors" is quite likely incorrect.

It is interesting to note that the work of Podolsky (3) produces results that are remarkably similar in both theory and operation to the basic concepts of cation exchange in clay mineralogy (7). The clay minerals are composed essentially of aluminum silicate sheet structures which consists of a negatively charged repetitive structure. These negatively charged sites are most often occupied by singly and doubly charged cations with  $\text{Na}^+$ ,  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  being the most common.



The net negative charge is due to unsatisfied valences on edge of the structured units.

The ability of clays to retain these cations is as was Podolsky's fluid factors related to ionic charge and radius (8). Ions with higher net charge smaller radii are generally the most tightly bound. They have the highest surface charge per unit area. A listing of the more common ions in order of decreasing surface charge per unit area is as follows:  $H^+$  >  $Sr^{++}$  >  $Ba^{++}$  >  $Ca^{++}$  >  $Mg^{++}$  >  $Rb^+$  >  $K^+$  >  $NH_4^+$  >  $Na^+$  >  $Li^+$ . These orders are similar to those of Podolsky, however, there are several ions out of order by 1 and as much as 2 places. However, there is a reasonable correlation in terms of ionic charge and radius.

#### 2.2.3.2. Solubility

The influence of solubility can be very significant in the freeze-purification process where precipitation of a solid occurs while the solute is slowly being concentrated. Vaslov and Chernyshev found that  $Na_2SO_4 \cdot 10 H_2O$  would precipitate in the ice indicating that its limiting solubility concentration had been surpassed (5). They were able to determine those solutes that precipitated by centrifuging the ice samples. They found that nearly all the dissolved solids that were still in the ice were located in brine pockets that would migrate out of the ice under the high gravitational potential of the centrifuge leaving the precipitated solids in the ice. The theoretical aspects of this phenomenon are discussed in the following sections.

As mentioned previously, the solubility of a substance in water is governed by the bonding strength of the solute and the energy state of the water solution. A solute will be soluble as long as the energy imported by a water molecule collision is sufficient to break the bonding energy. The limit of solubility is also governed by the solute bond energy. A solution becomes saturated when the density of solute is sufficiently high that each bond that is broken by a water-solute collision is equilibrated by rebonding during an anion-cation collision. This phenomenon was identified by the ionization theory developed by Svante Arrhenius in the 1880's and further justified by more recent analyses using molecular statistical theory (9).

The ionization theory states that all acids, bases or salts dissociate into ions when placed in water. The degree of dissociations is a consequence of the bonding energy which in itself may be influenced by such factors as pH, Eh, temperature and pressure. A general mass action equation for the ionization phenomenon is presented below:

$$\frac{(\text{Anion}) \cdot (\text{Cation})}{\text{solute}} = K \quad (\text{ionization constant for given temperature})$$

( ) = molar concentration

At the start of the freeze-purification process, the solutes normally form dilute solutions with concentrations well below the saturation level as determined by the K value. However, as the freezing process continues both the anion and cation concentration will increase while the dissociation constant K, typically decreases with temperature. As cooling continues, therefore, the solution may become saturated causing the precipitation of all additional freeze-

concentrated solute and thereby limiting the effectiveness of the process.

#### 2.2.3.3. Eutectic Point

As with the changes in dissociation constant, the freezing point of the solution drops as the concentration of the ions increases. For each different solute, there is a specific temperature at which no further freeze-concentration occurs. This temperature is the eutectic point, below which the liquid will freeze with the ions remaining in the ice crystal structure.

In the natural freeze-purification process, the eutectic point is of major significance in the previously frozen ice above the freezing, or ice-water interface. In this upper region the ice temperature can drop as low as  $-35^{\circ}\text{C}$ , especially near ice surfaces during Prairie winters. These temperatures can immobilize many of the small brine pockets in the ice by freezing them into a solid. As a consequence, the drainage of these brine pockets does not occur until the spring thaw raises the ice temperature above the eutectic temperature. The result is that the cleansing potential of the winter months by gravity movement is lost. This subject is discussed more fully in the following section on the removal of brines from the crystal boundary. The eutectic point is of little consequence at the freezing interface because the temperature rarely, if ever, drops below  $-5^{\circ}\text{C}$ .

#### 2.2.3.4. Rate of Freezing

The rate of freezing has been found to be very important in the development of the ice crystal structure (4). Luyet has found that water molecules will form well ordered ice structures if they are given sufficient formation time. With increasing cooling rates, the elements of the hexagonal symmetry are more regularly lost with voids often present or there is replacement by irregular crystals such as dendrites. It is under these conditions that the freeze-purification process at the ice-water interface is rather ineffective. The voids and gaps in the crystal structure provide locations for impurities to accumulate and remain as well as increase the porosity and possibly the permeability as well. In lagoon systems, rapid freezing is generally not a problem because the seasonal change is gradual and the ice and snow accumulations provide good insulation. Estimates of the rates of freezing in lagoons can be made, however, by heat flow-analysis.

Once the initial sheet of ice forms over a lagoon, conduction becomes the major mode of heat transfer from the water mass. The Fourier Law heat conduction shown below, defines the flow of heat by conduction (9, 10):

$$q = kA \frac{dT}{dx}$$

where  $q$  = heat transferred by conduction, cal/hr;

$k$  = thermal conductivity of material, ice in this case  
cal/hr cm<sup>0</sup>C;

$A$  = cross-sectional area normal to direction of heat flow, cm<sup>2</sup>;

$\frac{dT}{dx}$  = temperature gradient °C/cm.

This initial sheet of ice forms after the water at the surface has reached  $0^{\circ}\text{C}$ . The water at the bottom of the pond may still be at  $4^{\circ}\text{C}$  depending on the degree of natural mixing. In any case, the heat of fusion, released as the ice front advances is the major energy factor used to determine the rate of ice accumulations. Movement of energy into or out of the soil and that energy stored as sensible heat above  $0^{\circ}\text{C}$  are small (approximately 5%) when compared to the heat of fusion (80 cal/gm) for water (12). Table 1 shows the theoretical depth of freezing with time for a range of ice surface temperatures.

#### 2.2.3.5. Pressure

For natural freeze-purification systems, small changes in pressure have little effect on the efficiency of solute removal. At high pressures, however, the process would be subjected to changes in removal efficiencies for each of the different ions in solution due to the fact that the ice crystal structure as well as the crystal size changes. The phase diagram and densities of ice at different pressures as shown in Figure 4, indicate the range of the different ice forms.

The fact that the crystal structure changes with pressure indicates that variations in the crystal dimensions and charge distribution could be expected. As a consequence, the mobility of specific ions could be expected to be different for each of the ice forms. The degree and type of change for specific ions is unknown.

#### 2.2.4. Impurity Rejection from the Ice Crystal Boundaries

In the previous section, the factors influencing the expulsion of brines from the crystal proper into the boundary region or into

Ice Thickness (cm)	Surface Temperature °C											
	-5°C		-10°C		-20°C		-30°C					
	Hours	Days	Hours	Days	Hours	Days	Hours	Days	Hours	Days	Hours	Days
5	10.65	0.4	5.3	0.2	2.7	0.1	1.8	0.07				
10	42.6	1.8	21.3	0.9	10.6	0.4	7.1	6.3				
25	266	11	133	5.5	67	2.8	44.3	1.8				
50	1066	44.4	533	22.2	266	11.1	178	7.4				
100	4260	178	2130	89	1065	44	710	30				
150	9584	400	4792	200	2396	100	1597	67				
200	17040	710	8520	355	4260	178	2840	118				

TABLE 1. Rates of ice formation on open water bodies for various ice surface temperatures (insulative values of snow has not been included).

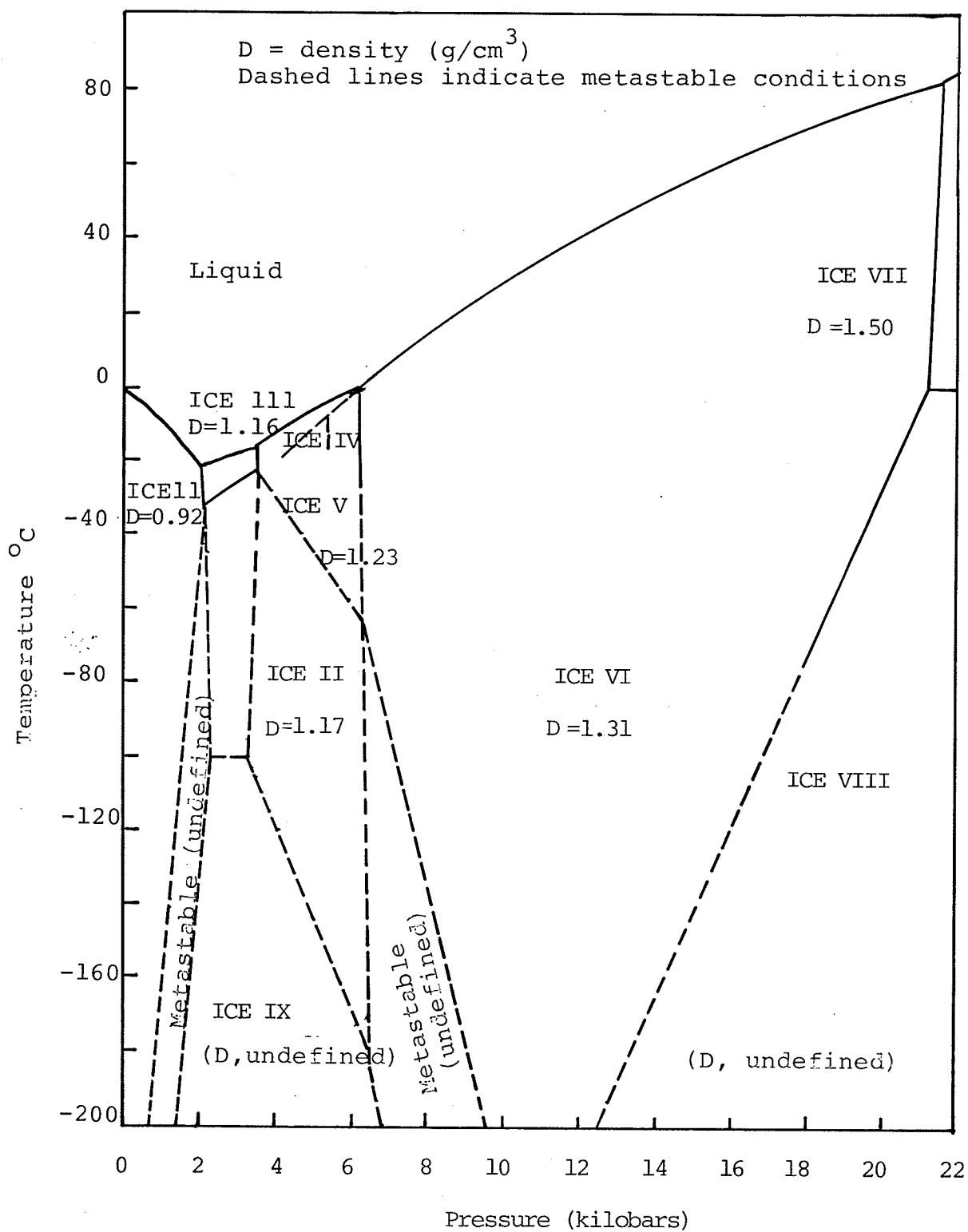


FIGURE 4. The phase diagram of ice as a function of temperature (T) and pressure (P) (after Glen, 10).

voids were evaluated. In this section, the modes of natural removal of the fluids from the locations outside the crystal are discussed. The modes of major interest are gravity drainage, pressure expulsion, and to a much lesser degree, diffusion.

#### 2.2.4.1. Gravity Drainage

Gravity drainage is the most important factor influencing the removal of saline inclusions or pockets from ice. Gravity drainage provides for brine removal over long distances while diffusion and pressure expulsion are more localised phenomenon responsible for solute removal at the freezing interface (13, 14, 15, 16). These latter two forms are still important, however, as they both help to form part of the interconnecting channel network needed for gravity drainage to be effective. Pressure expulsion forms small drainage channels parallel to the crystal faces while the diffusion of liquid inclusion forms short vertical channels in the direction of the thermal gradients.

These two, more localized permeability networks join with a third more extensive form of channeling, formed by interconnecting voids and gas bubble tubes. The interconnecting ice voids and irregularities in structure make up the major part of the ice permeability. As discussed earlier, the rate of freezing is a very important factor in terms of the continuity of the crystal structure. Rapid freezing being more conducive to the formation of voids or slender ice crystals (dendrites) than slow freezing which facilitates orderly crystal growth, as is discussed in a later section (2.7.2.). Measurements of the porosity of fast frozen ice have indicated values as



high as 15%. This porosity approaches that of some of our more permeable geologic materials.

Gas bubbles can also facilitate this permeable structure by breaking through or out of freezing ice crystals. The solubility of gases in the ice structure is very low such that dissolved gases are eventually trapped in voids. These gas bubbles can push their way through newly-formed crystals forming the vertical tubercles or "ice worms" that can often be seen in ice cubes (17). In this way, the different methods of channeling can form an extensive and inter-connecting drainage pattern facilitating the gravity removal of entrapped brine, (see Figure 5).

#### 2.2.4.2. Pressure Expulsion

Pressure expulsion has been found to be an important method of brine removal from ice crystal boundaries and to be particularly effective at the ice-brine interface (18). Pressure expulsion is caused by the ice volume increase that occurs during crystallization. This increase in volume results in a more tightly packed crystal structure that produces intercrystalline pressures much higher than the capillary forces that are tending to cause the solute to rise. As a consequence, fluids along the boundary area are forced downward into the concentrated brine.

This process is especially important at the freezing front where expulsion distances are small. Over longer distances, the permeability along the crystal faces is too low to be of any consequence when compared to gravity drainage.

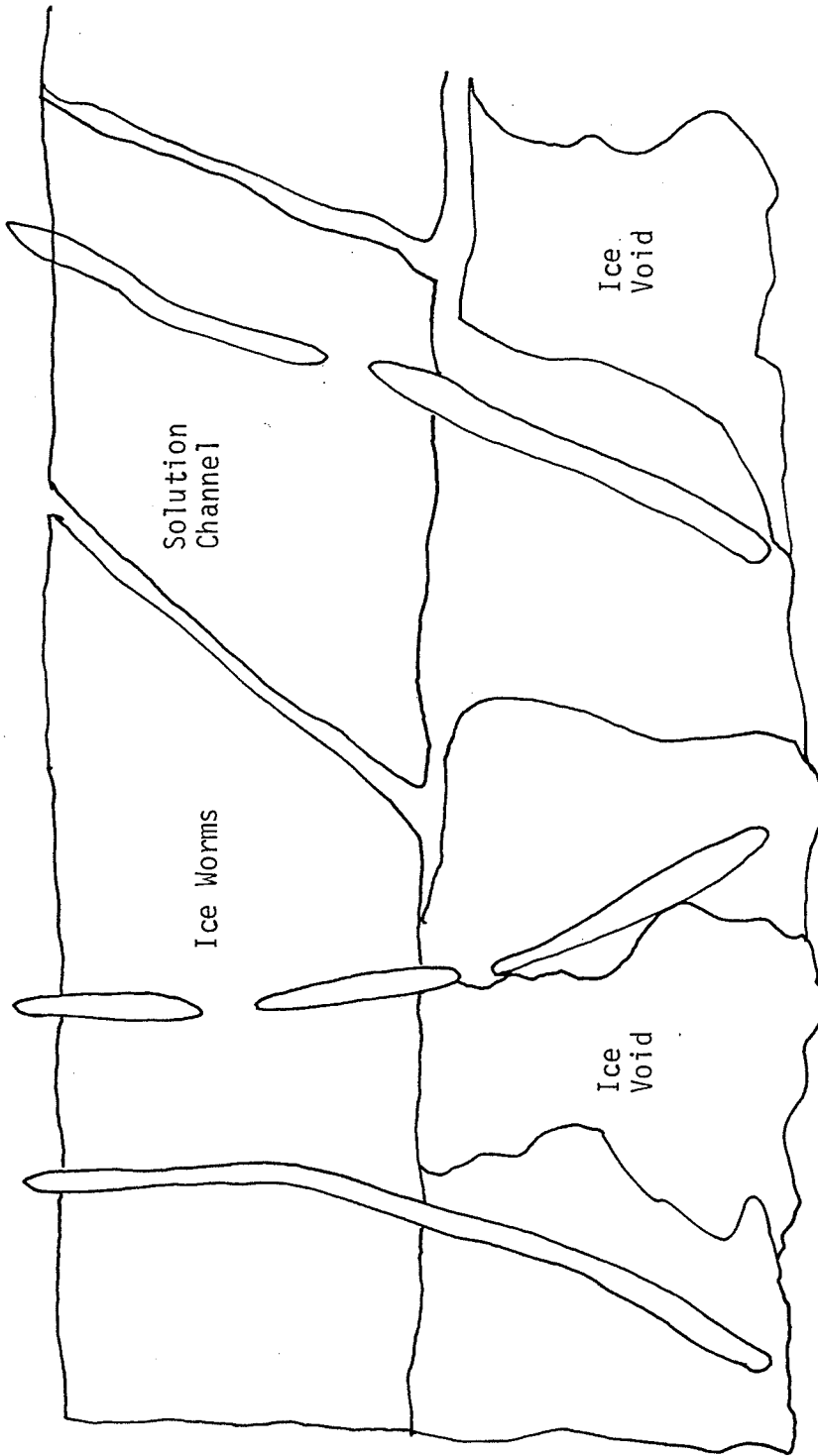


FIGURE 5. Idealized drawing of permeability network in ice.

#### 2.2.4.3. Diffusion

In terms of actual solute removal from ice, diffusion is a rather ineffective process. As mentioned previously, it increases the effectiveness of gravity drainage by interconnecting with other channels, but by itself, it is a slow process (17).

The work of Hockstra et al (17) has shown that the rate of migration can be predicted by classic diffusion theory and is a function of the chemical and thermal gradients set-up between the ice and the fluid. Their results as shown in Figure 6 indicate that the rate of brine pocket diffusion to be between 10 and 15  $\mu$ /hr for a NaCl solution with a  $1^{\circ}\text{C}/\text{cm}$  gradient. As natural gradients are normally only a fraction of  $1^{\circ}\text{C}/\text{cm}$ ; the diffusion distance over a complete winter could be expected to be only a few centimetres. Kingery, also found that the diffusion process reduced the salt content of ice only to a very small extent (13).

#### 2.2.5. Freeze-Purification of Aqueous Dispersions and Suspensions

Most wastewaters have a complete particle size distribution ranging from ionic right up to sand size and often larger. In the previous section, the most finely divided particles, namely the ions, were discussed in terms of the factors influencing their rejection from ice and ice crystals. In this section, the rejection phenomenon for the particles larger than anions and cations (i.e. larger than  $10\text{\AA}$ ) is discussed. This includes the colloidal to grit-sized particles.

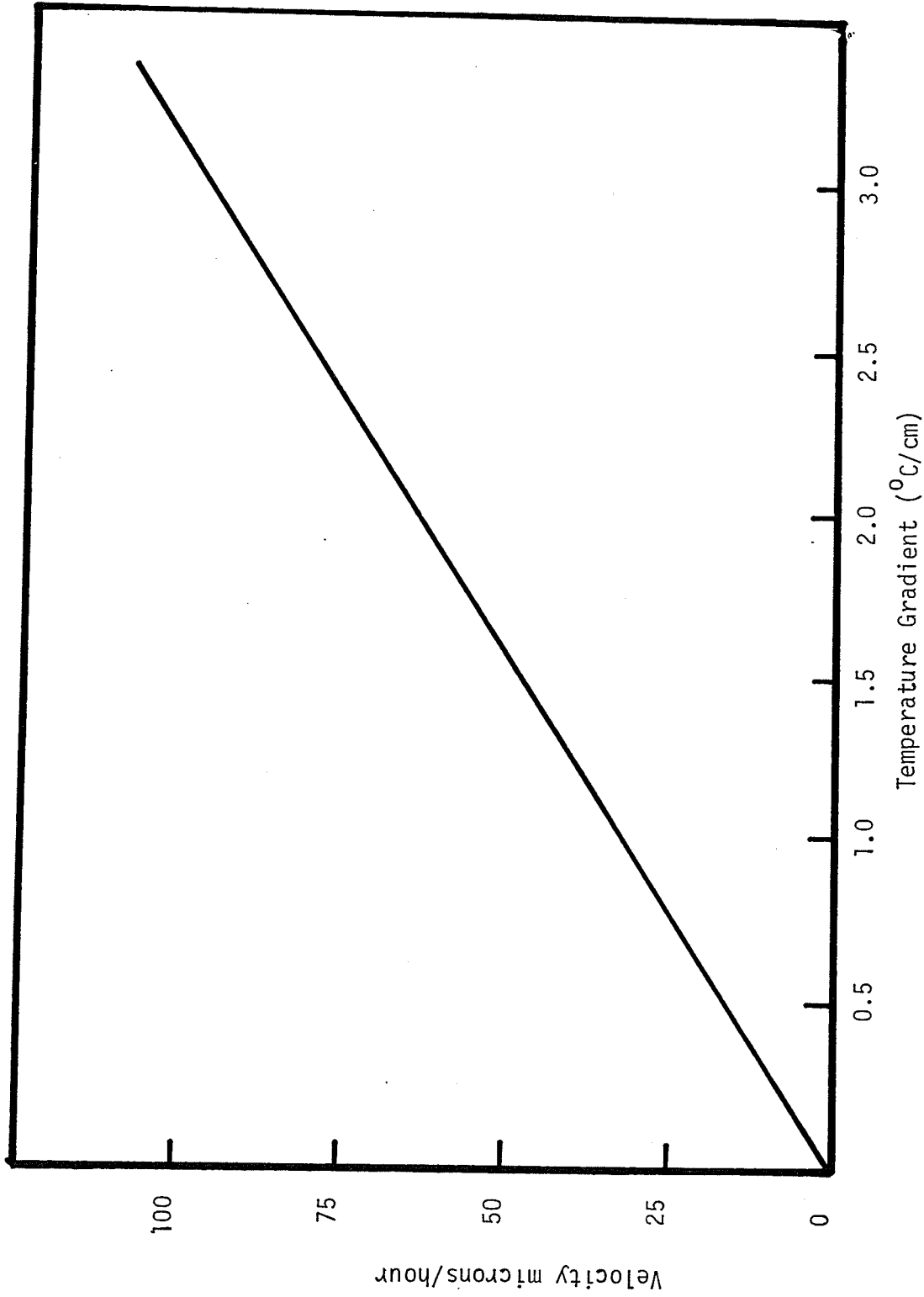


FIGURE 6. The diffusion velocity of brine pockets in ice relative to the temperature gradient (after Hoekstra, et al, 16).

### 2.2.5.1. Structure of Aqueous Dispersions and Suspensions

Most particles above the ionic size range are not truly soluble. They do not decompose or break down into components totally unlike their normal molecular structure as do electrolytes. They may have some mobile radicals but generally the size and number are small in comparison to the complete structure. Many of the more important organic substances in sanitary engineering have often been regarded as soluble while they should more correctly be called colloids. Proteins, cellulose and carbohydrates are some important examples.

It should be noted at this time, however, that the change from truly soluble to truly colloidal is gradual with no real hard and fast boundaries. Colloids are generally  $10\text{\AA}$  to  $1\mu$  in size and are distinguished from ordinary ions and molecules only by the fact that they cannot pass through membranes which allow these ionic forms to pass freely (14).

These larger, non-soluble particles can generally be subdivided into two main groups, dispersions and suspensions. Dispersions are differentiated from suspensions mainly by size. Dispersions include finer sized particles such that the surface forces play an important role in determining their interaction with the liquid and more importantly, with other particles (21). In dispersions, the size factor is of definite importance in terms of their removal potential. The colloidal sized particles which form part of the dispersion range, are often small enough that collisions with water molecules will cause them to move in a random, chaotic pattern called Brownian motion. This motion precludes any significant settling tendency by gravitational forces. The formation of an

active surface charge can, however, result in much more effective gravitational forces.

The suspensions include the largest of the particle sizes in a fluid. They have a negligible surface charge and are basically under the influence of gravity and the motion of the fluid. The exclusion of these larger particles from ice is one of the simpler phenomenon as it is based mainly on size. This and the previously mentioned factors influencing particulate removal from ice are discussed below.

#### 2.2.5.2. Fundamental Processes in the Freeze-Purification of Aqueous Dispersions and Suspensions

The removal of dispersed and suspended particles, as with ionic size particles, requires rejection from the ice crystal proper and then from the ice mass as a whole. The first step in this process as for the ionic size particles involves rejection from the ice crystal to the boundary. The second step in the rejection process, during which the particles are removed from the ice mass is based mainly on physical flushing. Generally, this process is much less efficient than the equivalent process for ionic solutions and this is due mainly to the physical blockage of the drainage pathways. These processes are discussed in the following section.

##### 2.2.5.2.1. Colloid and Suspensoid Size and Shape

Size and shape are the most important factors in the rejection of colloids ( $10 - 1,000\text{\AA}$ ) and suspensoids (greater than  $10,000\text{\AA}$ ) from water as it freezes. A single hexagonal ice crystal is only  $7.5\text{\AA}$  along the long axis and  $4.5\text{\AA}$  along the short axis (10). For colloidal particles with a minimum size of approximately  $10\text{\AA}$ , implies that

at least a couple and often many more ice crystals would have to be replaced. This is significantly more difficult than the replacement of one or two water molecules within a five molecule structure.

Shape is also an important factor influencing the rate of migration. Corte (25) found that the flat, plate-like minerals with large surface areas such as the micas and shales exhibited the greatest migration. The spherical minerals such as quartz with the lowest surface areas migrated the least.

#### 2.2.5.2.2. Surface Charge

The electrical charge of a colloidal particle is made up of two opposing forces, an attractive force or Van der Waals force and a repulsive zeta potential. The zeta potential is a result of the unequal charges balance that occurs at the surface of both organic and inorganic particles. In most situations, there is a general excess of negative charges such that these particles tend to attract positively charged ions and molecular radicals to their surface. The zeta potential is therefore a measure of the quantity. The stability, or tendency for this particle to remain as a single mass is a function of the magnitude of charge on the particle surface and the number of particles per unit volume. As long as the zeta potential is greater than the Van der Waals force, there is no net tendency to coalesce or coagulate and form a conglomeration of larger particles. A reduction in the zeta potential can result in the coalescence of the colloid particles and this can be accomplished in several processes such as coagulant (chemical) addition, boiling, as well as by freezing (17).

During freezing, the concentration of the colloids is increased

by ice crystal formation. The net result is this concentration increase is a reduction in the zeta potential (22).

Riddick (22) demonstrated the significance of this freezing process on colloids and their settling potential by a series of experiments. In the first of these experiments, colloidal samples were centrifuged at 37,000G for 3 hours with "no significant separation of the bulk and solid phases". In the second set of tests the identical samples were placed in centrifuge cells and frozen at  $-20^{\circ}\text{C}$  for 4 hours. The samples were again centrifuged at 37,000G but this time for only 10 minutes. The sample thawed during this period with the colloids settling and producing a very clear supernatant. Similar results have been obtained in field studies of the freeze-settleability of water treatment plant sludges (23, 24).

#### 2.2.5.2.3. Rate of Freezing

The rate of freezing, as with ionic solutions is very important in terms of the effectiveness of freeze-purification efficiency. Corte found that the slower the freezing rate the more effective was the removal of particulates (25). He showed that each particle size required a certain rate of freezing in order to migrate continuously without being "swallowed" by the ice. Also, he found that at a freezing rate of less than 1 mm/hr all particles migrate regardless of their shape or size.

In Manitoba, the freezing rate for lagoons is well below even this minimum value. For example, 1.4 m of ice is generally the maximum thickness produced in lagoon systems over a winter while 1.0 to 1.2 m are more typical averages. Using a freezing period of approxi-



mately 120 freezing days or 2,880 hours, this equivalent to an average freezing rate of 0.5 mm/hr. This indicates that on-ice processes should be quite effective for the removal of dispersed and suspended particles in a lagoon environment.

Estimates of the rate of freezing in a lagoon using average Manitoba weather data indicates that the rate of freezing does not go above 1 mm/hr all winter (see Figure 7). This is based on a gradual variation of temperature from 0°C to 20°C in 60 days and a warming to 0°C for an equal time period. Temperature variations do occur and Figure 6 shows that the early part of the freezing cycle when the ice is thin, would be most susceptible to higher freezing rates.

Under layer freezing conditions, it would be almost certain that the freezing rate would exceed 1 mm/h. For example, at -20°C, a 15 cm layer would freeze in 24 hours. The freezing velocity would range from a high of about 90 mm/h to a low of about 3 mm/h with an average of 8 mm/h. It is quite likely that under these higher freezing velocities, the slow settling suspended solids would have relatively poor removal efficiencies. In terms of overall freezing potential in the Prairie environment, it would be possible to freeze 8 to 10 m of ice over an average winter.

#### 2.2.5.2.4. Particulate Migration Within Ice

The migration of particulate impurities in ice are subject to the same forces causing the migration of the ionic sized impurities, namely pressure expulsion, gravity drainage and diffusion. The major difference is, however, that the overall effectiveness is much less. Pressure expulsion and gravity drainage, to be effective, are depen-

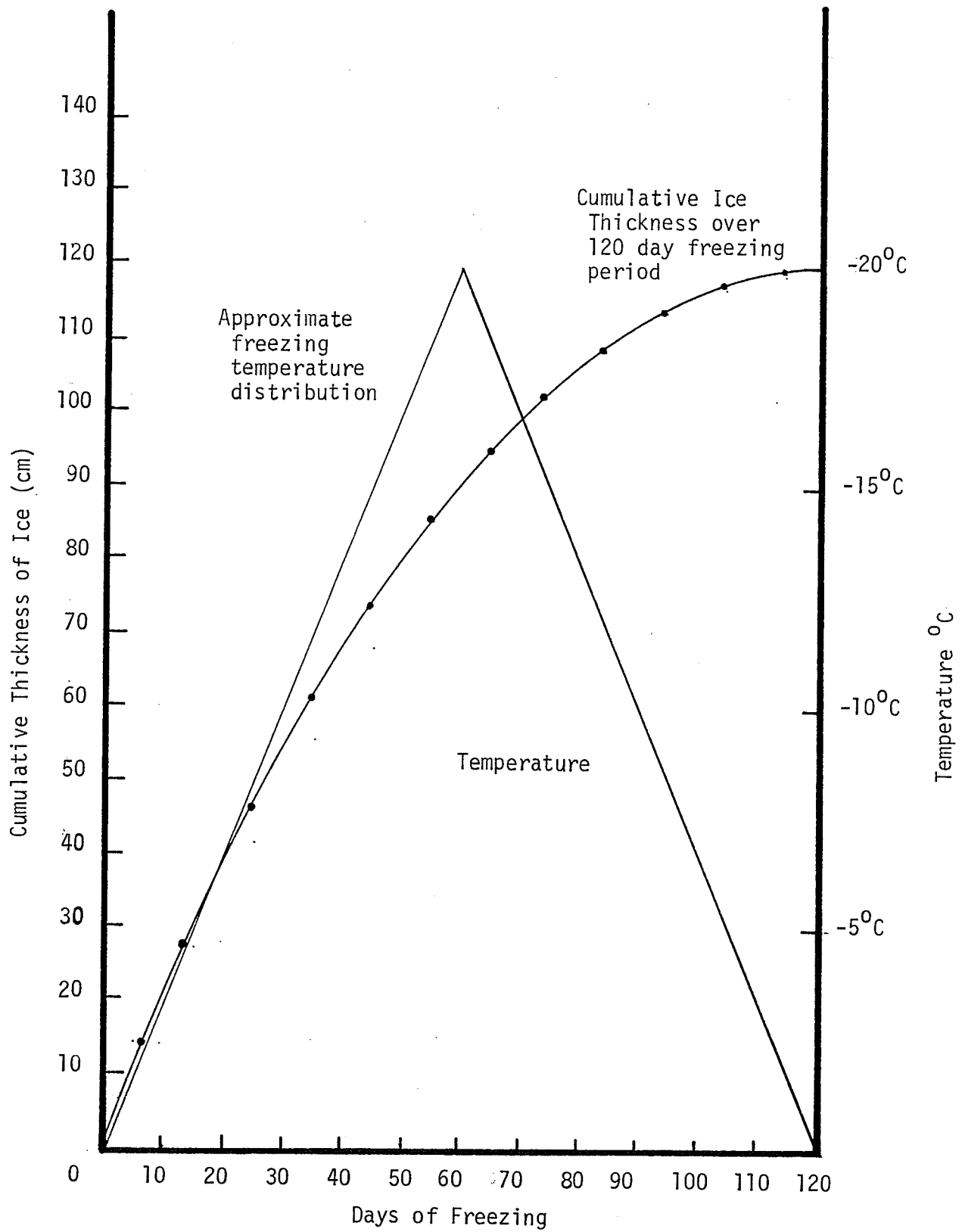


FIGURE 7. Theoretical ice formation rates for Prairie Winter conditions excluding influence of snow cover.

dent on brine migration through an irregular and interwoven channel system. Although well documented information on this particular aspect is lacking, it would seem logical that the larger particles and coagulated colloids would have a more difficult passage down a channel of irregular size and orientation than would a much smaller particle, of say ionic size. Some limited studies of micro-organism movement in ice show this result (26). Glen's work on particulate impurity migration by diffusion demonstrated much the same result as that of ionic impurity diffusion, namely, that the particles move due to thermal gradients and that the migration rate is very slow (12).

## 2.6. Consequences of Subzero ( $^{\circ}\text{C}$ ) Temperature on Micro-Organism Viability

Since all biological organisms contain water and nearly all exhibit normal biological functions above  $0^{\circ}\text{C}$ , it is not surprising, therefore, that temperatures below  $0^{\circ}\text{C}$  often have a profound effect on microorganism viability. In this section, the physical and chemical consequences of subzero temperatures on microorganism survival are discussed. Some of the more important factors in terms of cell viability are temperature and durations of freezing intracellular and extracellular ice formation, and the freeze-concentration of intracellular or extracellular solutes (27).

### 2.6.1. Temperature and Duration of Freezing

Low temperature alone, through supercooling (no ice crystal formation) is not generally lethal to a relatively wide variety of microorganisms including bacteria, yeasts, viruses, protozoa and even some higher forms. The common factor in these microorganisms is the

fact that they are all poikilotherms; organisms whose temperature adjusts to suit the environment. Homiotherms, the group to which humans belong maintain a more or less constant temperature by controlling energy flows. The poikilotherms can withstand a lowering of cell temperature of 10 to 20<sup>0</sup>C and to well below 0<sup>0</sup>C with almost complete metabolic reversibility. Homiotherms on the other hand, would find such a change lethal (28). It should be noted, however, that the metabolic activity of poikilotherms is often profoundly affected and normally ceases during this cooler period.

In general, the lower forms can withstand much lower temperatures than the higher microbial forms. For example, viruses and bacterial spores have been supercooled to -100<sup>0</sup>C, bacteria to -78<sup>0</sup>C and protozoa to -5<sup>0</sup>C with a 90% or greater survival rate (29, 30). These results were for only short durations but do show that the microorganisms commonly found in wastewater are rather hardy as far as temperature alone is concerned.

Over extended storage times, the survival of nearly all micro-organism species stored at between 0 and -60<sup>0</sup>C decreases with time. The parameters of consequence in the long-term survival of these organisms are temperature, storage medium and cell concentration. Generally, the survival rate is highest at the lower temperatures near -60<sup>0</sup>C and lowest near 0<sup>0</sup>C. The main reason for this difference is the fact that little or no chemical activity can occur at the low temperature and as a consequence, very little denaturation of proteins and enzymes occurs. This ensures that all metabolic functions will be possible after thawing (29).

The suspending medium is very important in maintaining cell viability during long term freezing. For example, organisms stored only in distilled water are almost always damaged by freezing. However, investigations of other substances, such as glycerol, sugars, amino acids and polymers have demonstrated protective properties during cell freezing (29). These substances appear to provide regions where the deleterious influence of solute diffusion gradients and ice crystals are much less severe.

The concentration of the cells being stored has also been found to be a factor influencing their long-term viability. The storage death is normally the lowest in the most concentrated suspensions. One theory for this phenomenon states that the most concentrated suspensions are more able to maintain their solutes within the cell as the fluids from damaged cells provide a more concentrated buffer, reducing the diffusional gradients into the suspending media.

#### 2.6.2. Intracellular and Extracellular Ice Formation

The formation of intra and extracellular ice is dependent on both the freezing temperature and freezing rate. Many investigations have observed that the interior of biological cells can remain in an unfrozen condition down to  $-5^{\circ}\text{C}$  and sometimes to  $-10^{\circ}\text{C}$ , even when totally surrounded by ice. However, in other cases, the cells are almost totally filled with ice crystals. These observations have been found to be related directly to the rates of freezing. At low freezing rates (less than  $100^{\circ}\text{C}/\text{min}$ ), the cell remains unfrozen while at high freezing rates ( $100$  to  $1,000^{\circ}\text{C}/\text{min}$ ), internal water crystallization occurs (27).

The reason for this difference has been attributed to natural defence mechanisms developed to combat internal ice formation. The lower freezing point of the cell fluids allows ice formation to occur around the cell. Once this ice has formed, there is a significant vapour pressure difference between the ice and cell fluids across the cell wall. This gradient causes intracellular water to flow from the cell and freeze outside the cell. This dehydrates the cell and can cause some biochemical disruptions as is discussed in the following section. In general, however, this is less of a problem than the consequences of intracellular ice formation.

Intracellular ice forms at high rates of freezing because the diffusional processes moving water out of the cell are unable to maintain equilibrium against the high energy gradients out of the cell. This non-equilibrated condition starts the formation of ice crystals which in themselves, tend to reduce vapour pressure difference across the cell wall.

The formation of internal ice crystals can severely damage both the physical and biochemical structure of nearly all biological cells. Rupturing of the cell walls or breakdown of macromolecular structures such as RNA or DNA ensures non-viability on thawing. Chemical damage can also occur to a wide variety of internal constituents by the reactions that take place during the freeze-concentration of internal fluids. These reactions are of major consequence in cell survival and are the subject of the following section.

### 2.6.3. Freeze Concentration of Intracellular and Extracellular Solutes

The progressive formation of ice whether inside or outside the cell proper, necessitates that the concentration of the solutes increase. The increased concentration of solutes can lead to some very damaging chemical reactions. For example, the structure of biological macromolecules such as DNA and RNA contain charged groups that are affected by the ionic strength of their environment. Modification of that chemical environment has been found to produce irreversible denaturation.

Of all the ionic species, the alkalic halides appear to be the most toxic of denaturing agents. The order of decreasing toxicity was found to be  $\text{Li}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$  and  $\text{Na}^+$ , and  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$  for the anions and cations respectively (27). These tests were conducted using E coli, bacteria very common in most domestic wastewaters. The severity of these toxic agents has been said to be comparable in terms of lethal capability, to the freezing of the E coli cells in a solution that totally freezes (27). This indicates, therefore, that those denaturing processes can be very destructive.

Chemical precipitation during freeze-concentration is another factor which has been found to be a causative agent of cell damage. The formation of precipitates within the cell can apparently trigger the coagulation of many molecules necessary for metabolic function. This phenomenon is not reversible and appears to be similar to the coagulation induced in colloid systems by freezing.

## 2.7. Engineering Applications of the Freeze-Purification Process

To date, there have been a significant number of field studies and a wide variety of different applications using the freeze-purification process. The two main areas involve natural and mechanical freezing. Due to the nature of this study, only those applications involving natural freezing processes have been discussed. The mechanical processes involved the desalination of sea water, wastewater treatment and sludge conditioning by means of refrigeration systems, typical of those used in freezers, refrigerators and air conditioners. These processes have had a number of investigators and appear to be cost-effective in terms of many other processes but as yet has not been applied on a large scale for extended periods (31, 32, 33, 34, 35).

Natural freeze-purification has been tested over a wide variety of conditions (reservoir freezing, layer freezing, spray freezing) as well as for many varied applications (water treatment and desalination, sludge conditioning, wastewater treatment). These topics are the subject of the following sections.

### 2.7.1. Reservoir Freezing

Reservoir freezing is the most natural of the freezing processes as it is typical of ice accumulations on lakes and ponds. It is probably for this reason, that it was the first method of freeze-purification to be investigated. The first documented research on this subject was in 1939 by Geller in the U.S.S.R. (36). This early work used small basins in the deserts of the Karakum Region. There, groundwaters with total dissolved solids (TDS) between 15,000 and 30,000 mg/L were freeze-purified to yield meltwaters containing only



3,000 to 6,000 mg/L TDS. These early experiments held promise to provide relatively good quality water for many arid regions of the U.S.S.R. and as a consequence this research was continued and expanded upon.

In the 1950's and 60's, Geller investigated the natural freeze-purification potential of small ponds with groundwaters with up to 40,000 mg/L TDS. These basins produced freshwater with a TDS of between 200 and 1,000 mg/L as well as yielding a water volume equal to 70% of the ice produced (37).

Other experiments conducted during this time involved the flooding of wide tracts of unproductive desert land with this high TDS groundwater during the winter. This produced several inches of ice over the sandy soil. It was theorized that by freezing this saline water, it would be possible to produce relatively fresh water suitable for crops. The dissolved solids would be freeze-purified out of the ice and then allowed to migrate downward into the soil. The first meltwater in the spring would then be able to flush these salts below the root zone of the crops and saturate the soil zone with relatively fresh water. Quantitative results for this study were not given, but it was indicated that this process was successful as these once a year irrigation systems were producing good harvests of grains and melons in the Turkemenia region of the U.S.S.R. (38).

From the U.S.S.R., the research moved to Canada in Saskatchewan. There, the objective was to produce fresh water from saline groundwaters for farm use using the freeze-purification technique. Their concept was to pump saline groundwater into a specially designed basin or lagoon in late fall and let it freeze during the winter. The

concentrated brines could then be drawn off through a sump system and discharged into the spring run-off or possibly into a deeper, more saline groundwater zone. The spring thaw could then be stored to provide potable water on a yearly basis (39, 40). The results of field test evaluations of the natural freeze-purification concept are presented in Table 2. In this study, 6 dugouts were tested using variable strengths of saline solution.

	Dug-out					
	1	2	3	4	5	6
Maximum Ice thickness (m)	0.90	0.74	0.85	0.81	0.90	0.91
Yield, (L/m <sup>2</sup> )	7.2	5.9	6.7	6.4	7.2	7.3
Initial TDS (mg/L)	4051	28391	21700	10610	4498	21700
Final TDS of ice, average (mg/L)	1031	14055	7040	3797	823	8223
TDS of brine drawn off (mg/L)	16594	43657	48000	--	11110	39257
Salinity reduction %	74.5	50.4	64.4	64.3	83.5	62.1

TABLE 2. Results of field studies of natural freeze-purification, winter of 1963-1964, Saskatoon, Saskatchewan.

The results of this work demonstrated purification efficiencies that ranged from 50.4 to 83.5%. These studies also showed that the best removal efficiencies were obtained for the brines with the lowest initial salinity. For human consumption, these tests indicated that the raw water quality should be no more than about 5,000 mg/L TDS in order that the treated quality be 1,000 mg/L, the generally accepted

upper limit for drinking purposes (38). For livestock which are more salt tolerant, the upper limit is closer to 15,000 mg/L TDS.

### 2.7.2. Layer Freezing

The layer freezing technique involves much the same basic equipment as the reservoir freezing technique except that the basin is deeper and the ice is frozen in successive layers. The advantage of this method over reservoir freezing is the fact that much more fresh water can be produced per unit of land area. The main disadvantage stems from the fact that more supervision and labour is required to manage this system.

The concept of layer freezing had its origin in some early observations of sea water ice made during the Arctic expeditions (42, 43, 44). The most significant observations made by these early investigators was the fact that the sea ice that was a few feet above the water surface was almost invariably fresh. It was theorized that this phenomenon was due to downward gravity flow of saline fluids trapped in pockets and voids. The concept behind layer freezing was therefore, that downward migration of fluids through thick ice would be possible as long as the ice temperature was above the fluid eutectic point and a reasonable period of "curing" could be maintained.

The first research on layer freezing was conducted, as with reservoir freezing, in the U.S.S.R. and somewhat later in Saskatchewan. The first experiments were conducted in the late 1920's by Krysllov who demonstrated that great thicknesses (greater than 10 m) were possible using the layer freezing technique. Experiments conducted in the Altay Kaay region demonstrated that ice 5 m in thickness

could be produced and that 90% of this ice could be turned to use-able freshwater from groundwater containing up to 8,000 mg/L TDS (37).

Research conducted by Mitlin (45), another Russian, in the early 1960's, concentrated on some specific aspects of layer freezing. Tables 3 and 4, shown below show the results of some of Mitlin's work. He found that the thick ice took only a little longer to reach a final salinity or TDS of 1,000 mg/L yet produced significantly more water per unit area. He also showed that the thicker layers were somewhat more effective in total salinity reduction. As well, he also found, as did the researcher using reservoir freezing that the more saline solutions were more difficult to freeze-purify. Efficiencies ranged from approximately 90% to 40% for initial salinities of 5,000 and 6,000 mg/L respectively.

Ice Salinity mg/L	Purification Times, Days, for Ice Thicknesses of			
	25 cm	60 cm	100 cm	180 cm
4,963	-	9	10	12
10,000	7	9	10	13
14,956	-	9	11	14
20,026	8	10	12	15
28,893	8	10	12	19
39,893	9	11	14	21
49,903	9	12	15	22
59,903	10	13	16	23

TABLE 3. Time required to purify ice blocks of various ice thicknesses and initial salinities.



Ice Salinity mg/L	Purification Efficiencies, Per cent for Ice Thicknesses of			
	25 cm	60 cm	100 cm	180 cm
4,963	-	88	89	91
10,000	70	84	86	87
14,956	-	79	81	82
20,026	65	77	79	80
28,893	55	69	70	71
39,893	41	59	61	63
49,903	35	51	52	53
59,903	30	42	43	44

TABLE 4. Purification efficiencies for ice blocks of variable thicknesses and initial salinities.

In Saskatchewan, both laboratory and field studies were conducted using the layer freezing technique (47, 48). The results of both of these tests demonstrated efficiencies lower than those observed by Mitlin. The efficiencies were also less than those using the reservoir freezing method, but still in the order of 60 to 70% for saline waters at 5,000 mg/L TDS. Table 5 and Figure 8 below outline the results of the laboratory and field tests (after Spyker, 47, and Fertuck, 48). The results of both the laboratory and field studies indicate that layer freezing can be effective for desalination over a range of ice thicknesses. It is interesting to note that the field results are noticeably better than the laboratory studies and Fertuck concludes that at an initial TDS of 5,000 mg/L, 70% of the water could be treated to a final TDS of 1,000 (80% removal efficiency).

Layer Thickness cm	Initial Salinity ppm		Removal Efficiency %	Purification Time/Days	Purification Level of Ice Efficiency %	Purification Time/Days
	NaCl	Na <sub>2</sub> SO <sub>4</sub>				
1	5,000	-	62.3	13	-	-
3	5,000	-	61.9	13	-	-
6	5,000	-	71.5	14	-	-
1	10,000	-	49.5	14	-	-
3	10,000	-	61.7	12	-	-
6	10,000	-	55.0	15	-	-
1	-	5,000	-	-	51.5	19
3	-	5,000	-	-	53.8	19
6	-	5,000	-	-	57.4	19
1	-	10,000	-	-	46.8	18
3	-	10,000	-	-	43.3	18
6	-	10,000	-	-	42.9	19
1	10,000	-	47.0	9	-	-

TABLE 5. Influence of layer thickness and salinity on purification times and percentage of initial volume collected at a TDS of 500 mg/L (after Spyker, 47).

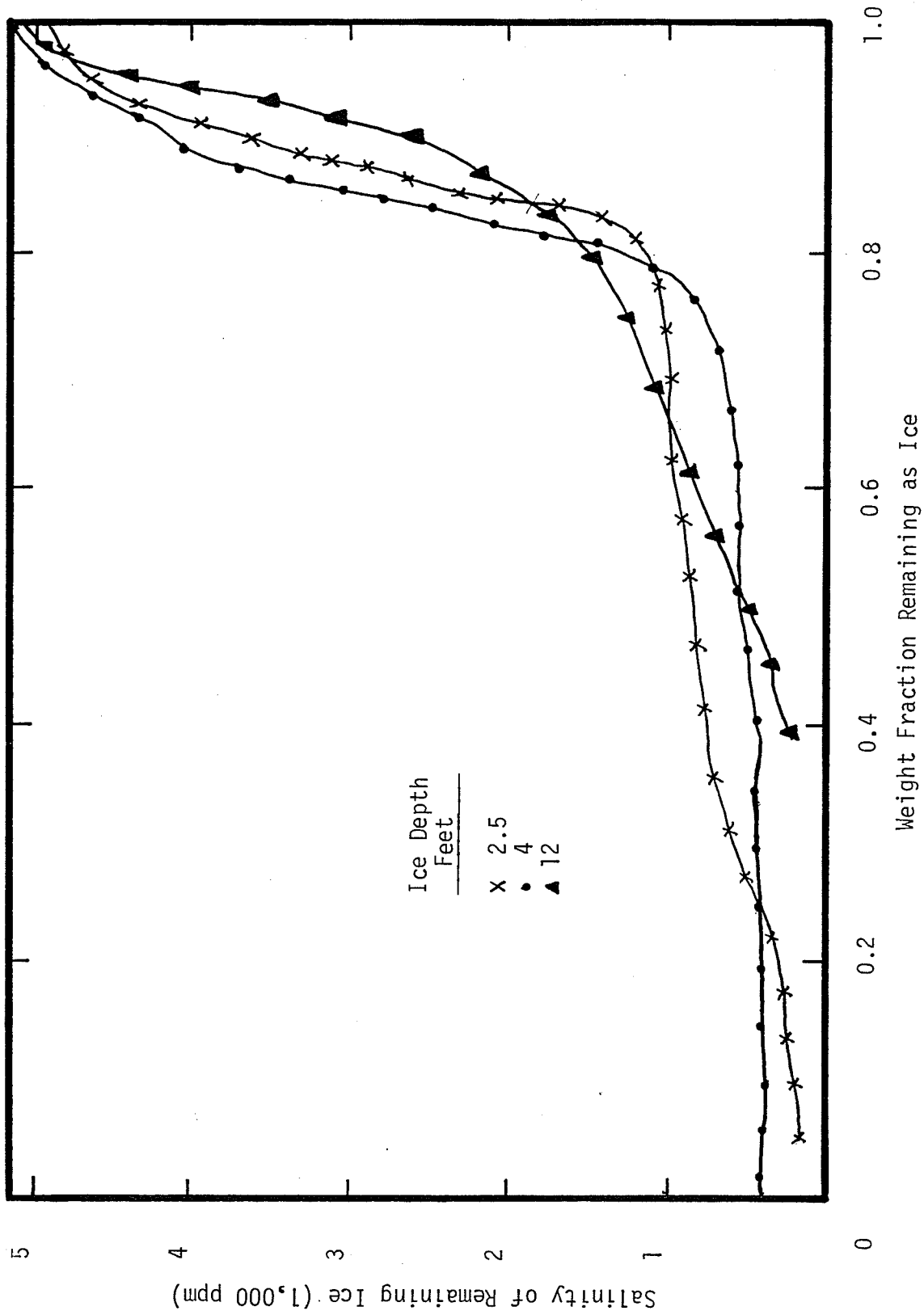


FIGURE 8. Desalination efficiency for layer freezing method (after Fertuck, 48).

The conditioning of water treatment plant sludge is a second application of layer-freezing that has been verified by field studies (24, 49). This work has shown that the colloidal and hydrated nature of alum sludges prevents the solid concentration from being efficiently increased. Freezing has been found to effectively coagulate these colloidal particles so that they settle much more rapidly after thawing. For example, the dry solids content of an alum sludge increased to approximately 94,000 mg/L from 4,300 mg/L after the freezing and settling had been completed (24). In the Canadian Prairie environment, sludge of this type could be lagooned and concentrated thereby enabling reclamation or landfill disposal instead of the common practice of discharging the process wastes back into the water source.

### 2.7.3. Spray Freezing

The bulk of the research on the freeze-purification potential of spray-freezing, as with the other techniques, has been directed towards desalination (50, 51, 52) although some limited work has been directed towards domestic wastewaters (53). The work on desalination has been conducted in the United States (50, Alaska) and in Saskatchewan (50, 52). The theory behind spray freezing is that spraying produces the maximum surface area exposed to the cold air and therefore, maximizes the rate of freezing and the volume of ice produced per unit time. Once on the ground, the frozen sea water in the form of ice and snow forms a porous and permeable structure allowing the brines to move downward, by gravity to an underdrain system. The concentrated fluid can be discharged back into the ocean, a highly mineralized aquifer system or, if necessary, into a surface water system. The ice and snow are



impounded in a suitable holding system until the spring thaw produces a potable water supply.

In Alaska, the desalination efficiency was found to be very strongly affected by the rate of freezing (50). At high spray rates ( $<9.8 \text{ L/m}^2/\text{min}$ ) the freeze-purification was essentially ineffective. At lower rates (0.1 to  $0.7 \text{ L/m}^2/\text{min}$ ) the efficiency ranged from 85% to 65%, respectively. On completion of this study, it was concluded that multiple freezing would be required for domestic water supplies from sea water.

In Saskatchewan, the results of field tests were much more promising than those in Alaska. Their results up to 1977, indicated that waters low in sulphate ( $\text{SO}_4^{=}$ ) could be reduced in TDS by greater than 75% while retaining 50 to 80% of the water. Sulphate bearing waters had lower efficiencies due to the difficulties in the freezing out of the  $\text{SO}_4^{=}$  ion. Tables 6 and 7 show the results from two such field evaluations indicated through the winter of 1976-1977 in Saskatchewan.

Cost evaluations of the spray freezing method were also encouraging. In 1973, the costs of spray-freeze desalination were less than all other viable methods for small water supplies (less than 454 million litres per year). At that time, the costs of spray freezing and its most competitive process, reverse-osmosis, were approximately \$1.20 and \$2.00 per 4,500 litres, respectively, for 4.54 million litres per year. Recent cost figures for a reverse-osmosis plant at Minnitonas, Manitoba, indicate the total cost (capital and operating) to be near \$8.00 per 4,500 litres for about 3,500,000 liters per year (57, personal communication, Jim Adams, Chemist, Rural Water Services Board). This certainly makes spray-freezing an attractive alternative as its costs have risen more modestly (52).

Sample	Analysis	Volume Imp. Gal.	Cumulative		Percent of Input Recovered
	ppm TDS		Analysis ppm TDS	Volume ppm TDS	
EL-16	108	8,810	108	8,810	2.9
15	88	22,830	94	31,640	10.5
14	262	16,710	152	48,350	16.0
13	261	26,900	191	75,250	24.9
12	182	25,710	189	100,960	33.3
11	145	17,610	182	118,570	39.2
10	110	1,840	181	120,410	39.8
9	218	3,740	182	124,150	41.0
8	285	23,730	199	147,880	48.8
7	161	13,540	195	161,420	53.3
6	657	14,130	233	175,550	58.0
5	3,577	6,830	358	182,380	60.2
4	2,446	16,860	535	199,240	65.8
3	2,252	19,160	685	218,400	72.0
2	2,232	22,040	827	240,440	79.4
1	3,421	17,260	1,001	257,700	85.1
Input	1,888	302,760			

TABLE 6. Product quality and quantity, for spray freezing field tests,  
Frontier Saskatchewan 1976-1977.

Sample	Analysis ppm TDS	Volume Imp. Gal.	Cumulative Analysis ppm TDS	Cumulative Volume ppm TDS	Percent of Input Recovered
DU-28	1,314	18,570	1,314	18,570	1.9
27	1,194	34,870	1,236	53,440	5.6
26	1,061	45,420	1,155	98,860	10.4
25	1,050	33,140	1,129	132,000	13.8
24	1,226	47,520	1,154	179,520	18.8
23	1,421	12,920	1,172	192,440	20.2
22	1,367	16,990	1,188	209,430	22.0
21	1,359	20,780	1,204	230,210	24.1
20	1,144	9,910	1,201	240,120	25.2
19	943	30,740	1,172	270,860	28.4
18	948	14,100	1,161	284,960	29.3
17	763	14,050	1,142	299,010	31.3
16	723	20,520	1,115	319,530	33.5
15	741	22,390	1,091	341,920	35.8
14	720	19,160	1,071	361,080	37.9
13	544	10,440	1,056	371,520	39.0
12	493	35,450	1,007	406,970	42.7
11	372	15,550	984	422,520	44.3
10	364	37,260	934	459,780	48.2
9	306	24,720	901	484,500	50.8
8	307	19,020	879	503,520	52.8
7	384	21,470	859	524,990	55.0
6	390	14,190	846	539,180	55.6
5	2,442 *	21,600	908	560,780	58.8
4	4,494	10,750	975	571,530	59.9
3	2,214	18,510	1,014	590,040	61.9
2	8,732	22,750	1,301	612,790	64.2
1	8,718	18,910	1,523	631,700	66.2
Input	4,169	953,790			

\* Sample lost; analysis assumed to be mean of analysis of DU-4 and DU-6.

TABLE 7. Product quality and quantity, for spray freezing field tests, Armley Saskatchewan, 1976-1977.

Spray freezing of domestic wastewater is the last, but possibly the most important in terms of relevance to the topic at hand. The objective of two spray disposal studies, outlined in the following paragraphs, was to evaluate the treatment capabilities for domestic wastewater using spray freezing technology (53, 54). The results were very positive and demonstrated that most of the nutrients in the domestic wastewater would form inclusions in the ice and snow. These inclusions would percolate through the ice and snow into the soil during thawing periods resulting in tertiary treated runoff in the spring. The following tables (Tables 8 and 9, after Flanders, 53, and Wright, 54, respectively) demonstrates the removal efficiencies obtained from samples taken from the meltwaters.

Constituent	Effluent Values (mg/L)	Average Ice Values (mg/L)	Average % Reduction
pH	6.9	-	-
TDS	425.0	31.0	93
PO <sub>4</sub> <sup>-P</sup>	8.0	0.65	92
NO <sub>3</sub> <sup>-N</sup>	17.0	2.8	84
Cl <sup>3-</sup>	180.0	14.8	92
SO <sub>4</sub> <sup>=</sup>	24.0	5.0	79

TABLE 8. Nutrient concentration in spring meltwater runoff in ice.

Constituent	Effluent Values (mg/L)	Average Snow Values (mg/L)	Average % Reduction
BOD	51.0	3.5	93
SS	67.0	32.0	52
NO <sub>3</sub> -N	1.0	0.4	60
NH <sub>3</sub> -N	12+	3.5	71+
TP	18.3	0.7	96
TDS	258.0	34.0	87
Fecal coliform	-	45/100 ml	-

TABLE 9. Nutrient concentration in spring meltwater runoff in ice.

The results of these studies indicated that with the provision of sufficient storage, disposal land area, and proper soil conditions, freezing systems could provide very effective recycling of nutrients back into the food chain. Soils of low permeability were found to be best suited to the freeze purification as they did not allow the migration of nutrients past the root zone or much total infiltration during spring melt. With these soil conditions, the nutrients can be retained in the root zone for plant growth with the bulk of the runoff leaving in a tertiary treated form.

#### 2.8. Laboratory Applications of Freeze Purification

Freeze purification has been used in laboratory tests to concentrate trace constituents up to detectable levels. In many situations the concentration of a particular constituent is below the detectable level of the analytical equipment, yet relatively accurate

estimate is desired. Other concentration techniques such as vacuum or heat vaporization often lose part of the sample or transform to convert part of it to another material, totally different from the start. The low temperature of freezing tends to minimize these problems yet still gives good concentration ability. The following tables demonstrate the results from several different authors work using freeze purification on dilute aqueous solutions. (See Tables 10 and 11).

These tables indicate that the freeze-purification process can be very effective with efficiencies as high as 99%. Also these tables include many organic compounds that theoretically should be quite difficult to remove by freeze purification. In fact, the results of Table 10 indicate the opposite to be true. These analyses indicate that the organic compounds are more easily removed by freeze concentration than the inorganic ions, at least at relatively low concentrations. The reason for these discrepancies is unclear but it may be related to molecular sizes greater than  $4.5\text{\AA}$  (the minimum dimension of an ice crystal) in which size and charge become less significant.

Constituent	Original (mg/L)	Concentrate (mg/L)	Ice (mg/L)	Removal Efficiency (%)
Conductivity ( $\mu$ mhos)	252.0	523.0	121.0	52
Calcium	6.6	15.0	3.0	55
Sodium	16.0	40.0	9.0	44
Potassium	1.4	3.5	0.8	43
Aluminum	0.2	0.5	-	-
Phenol	7.0	18.5	1.5	73
m-cresol	5.0	14.3	0.5	90
2,4-dichlorophenol	5.0	15.4	0.7	86

TABLE 10. Freeze concentration results for dilute aqueous solutions  
(after Baker, 55).

Compound	Initial Concentration mg/L	Strength of Concentration mg/L	Removal %	
Glucose	0.022	0.088	93	
	0.022	0.100	88	
	0.019	0.063	88	
	1.0	6.05	97	
	1.0	5.65	102	
	1.0	5.71	99	
	Glycine	0.023	0.143	103
		0.017	0.092	101
		0.019	0.089	99
1.0		4.91	102	
1.0		5.17	99	
1.0		4.35	99	
0.10		2.18	101	
Phenylalanine		0.013	0.081	98
		0.017	0.084	100
	0.013	0.059	106	
	1.0	5.75	90	
	1.0	4.0	96	
	1.0	3.14	98	
	Citric acid	0.015	0.081	97
		0.020	0.095	113
		0.016	0.065	102
1.0		6.02	93	
1.0		6.04	104	
1.0		4.65	99	

TABLE 11. Recovery of  $^{14}\text{C}$ -labelled compounds from distilled water using freeze concentration (after Kammerer and Lee, 56).



## Chapter 3

### Experimental Equipment, Procedure, and Analyses

#### 3.1. Introduction

The objective of this study was to evaluate the effectiveness of freeze-purification as a treatment technique for domestic wastewaters by means of controlled laboratory simulations. In this study, primary and secondary treated wastewaters from treatment facilities in Winnipeg were used in tests of both the reservoir and the layer freezing techniques. The equipment, procedure and analyses used for the two different techniques are outlined in the following sections.

#### 3.2. Reservoir Freezing Method

The reservoir freezing method, as indicated earlier, is typified by the natural freezing of water in lakes, ponds and dugouts in which freezing occurs from top to bottom. The apparatus used to simulate the reservoir freezing process is shown in Figure 9. Photograph 1 shows the freezing cylinders in place in the environmental chamber.

The environmental chamber was constructed by Enconair Ltd. of Winnipeg. The chamber is an insulated aluminum frame with dimensions that are approximately 3m by 2.4m and 2m high. The chamber is cooled or heated by a refrigerant cycle using a water-cooled compressor. The interior of the chamber is cooled or heated using a fan coil. The practical temperature range for the unit is approximately  $-20^{\circ}\text{C}$  to  $+30^{\circ}\text{C}$  with an accuracy of about  $\pm 1^{\circ}\text{C}$ .

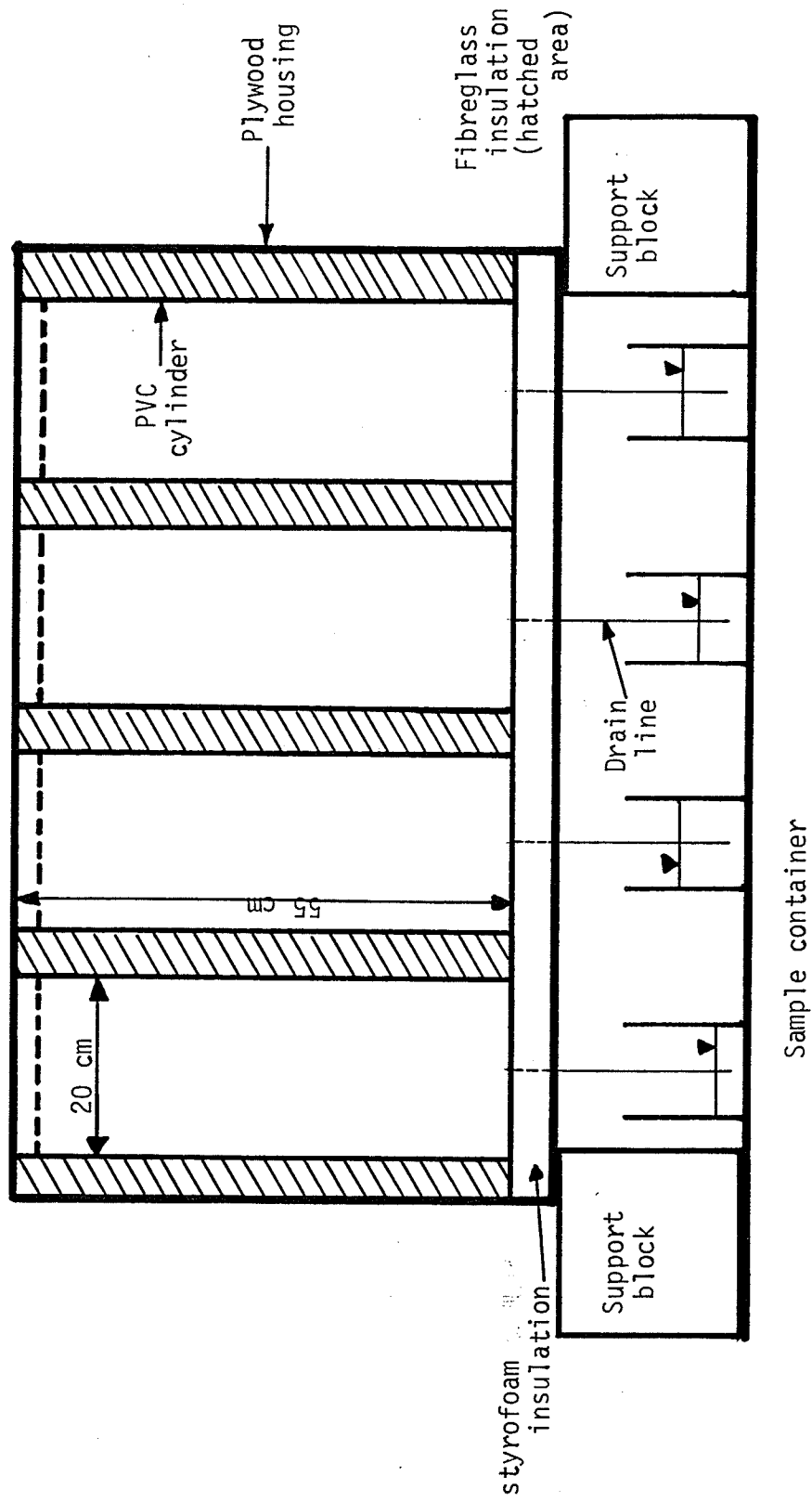
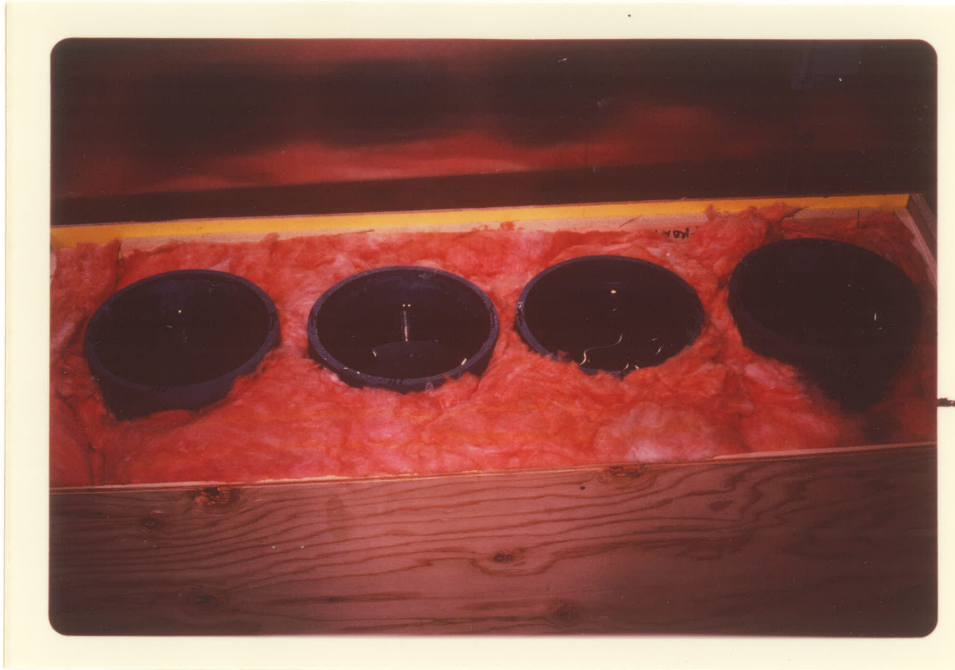


FIGURE 9. Diagrammatic representation of reservoir freezing apparatus.



Photograph 1: Reservoir freezing apparatus.

Prior to the start of testing, the apparatus shown in Figure 9, was placed in the environmental chamber against the wall and further insulated with fibreglass batts on all open sides to further reduce any horizontal heat flows. Also, two wastewater samples were collected from each of the South End and West End Water Pollution Control Centres in Winnipeg. At each location, a primary and secondary treated sample was collected. The secondary treated samples followed activated sludge treatment while the primary treated samples followed clarification in flow-through horizontal settling basins at the South End facility. At the West End facility, primary solids removal is managed by means of a physical screening apparatus (Trade name Hydra-sieve). The suspended solids loading for the secondary treated

effluents was similar at each facility, however, the primary effluent at the South End facility had a noticeably lower suspended solids level than the screened sewage from the West End facility.

From the outset, it had been decided that raw wastewater samples would not be used. In fact, there was some question on whether the primary treated effluents should be used as it was anticipated that a suspended solids content might interfere with the analyses of both the reservoir and layer freezing tests. It was decided to include the primary treated effluent so as to maintain some consistency between laboratory and field situations.

The four wastewater samples were placed in the environmental chamber with the testing apparatus and left overnight at 0°C. The next morning the four cylinders were filled to a depth of 50 cm, each with a different wastewater sample. The environmental chamber was then set at -20°C to start the freezing process. Calculations indicated that the wastewater would be frozen to within a few centimeters of the bottom in 9 days. After 7 days, daily visual checks were made through the clear bottom on one of the outside units to ensure that freezing did not occur right to the bottom. It was felt that freezing to the bottom might fracture the apparatus or possibly force some of the already concentrated liquid back up into the ice. Furthermore, lagoons in the Prairie environment rarely, if ever, freeze right to the bottom. The lower zone is most often a mixture of ice-crystals and fluid (slush).

The freezing process was completed in 10 days, indicating that the estimates of the freezing time were slightly inaccurate or that the temperature within the chamber was somewhat affected by the de-icing

cycle or possibly by incomplete air circulation at the air-ice interface. Simplifications in the equation used to estimate freezing time exclude the effect of the sensible heat in the fluid as well as the change in freezing point of the fluid as the concentration is increased. Both of these factors would tend to lengthen the freezing time. This may, have in part been compensated for by conduction losses through the insulated apparatus.

Temperatures were periodically measured inside the chamber and they were consistently  $-20^{\circ}\text{C} \pm 1^{\circ}\text{C}$ . Some slight temperature fluctuation could be expected during a de-icing cycle, however, it was not anticipated that the overall effect would be significant as they were of relatively short duration and the fans were automatically shut off. In reality, the opening and closing of the door to the chamber was probably as great an environmental influence. Overall, the apparatus and environmental chamber functioned quite satisfactorily.

On completion of the 10 day freezing period at  $-20^{\circ}\text{C}$ , the temperature of the environmental chamber was raised to  $0^{\circ}\text{C}$  for a 3-week purification period. During this period, the brines within the ice were allowed to drain through to the bottom by gravity flow. The gravity drainage was facilitated by a drain tapped into the acrylic base. Plastic tubing was connected to this drain through a pre-drilled hole and its end was inserted into a 1 L Erlenmeyer flask (see Figure 8). Also, cellophane was placed over the surface of the ice to minimize evaporation or sublimation losses.

Samples were collected at the start and at the end of each week of the 3-week purification period. On completion of the purification period, the acrylic base plate was removed and the ice sample was pushed from the PVC cylinders. This ice block was then cut into 4 - 10 cm thick slices with the bottom segment being approximately 5 cm thick. The samples were thawed at room temperature and then stored at 0°C. The analyses conducted on these samples are outlined in section 3.4 of this chapter.

### 3.3. Layer Freezing Method

The layer freezing method is a technique that utilizes much the same theory and concept as well as similar apparatus to the reservoir freezing method. The major difference is the fact that the wastewater is frozen in a series of thin layers. The advantage of the layer freezing method over the reservoir freezing method is the capability of producing much greater thicknesses of ice in the same time period. Previous estimates indicated 8 to 10 m of ice would be possible for an average Prairie winter using layer freezing while a little over 1 m is the average for reservoir freezing.

The apparatus used to simulate the layer freezing method is shown in Figure 10 and Photograph 2. Four identical units were used to freeze each of the individual samples. Additional insulation was packed around and under the units to further minimize any horizontal heat flow during the freezing period. Four 15 cm layers of wastewater (same sample source as reservoir freezing) were to be poured into each drum. Estimates of the freezing period indicated that a

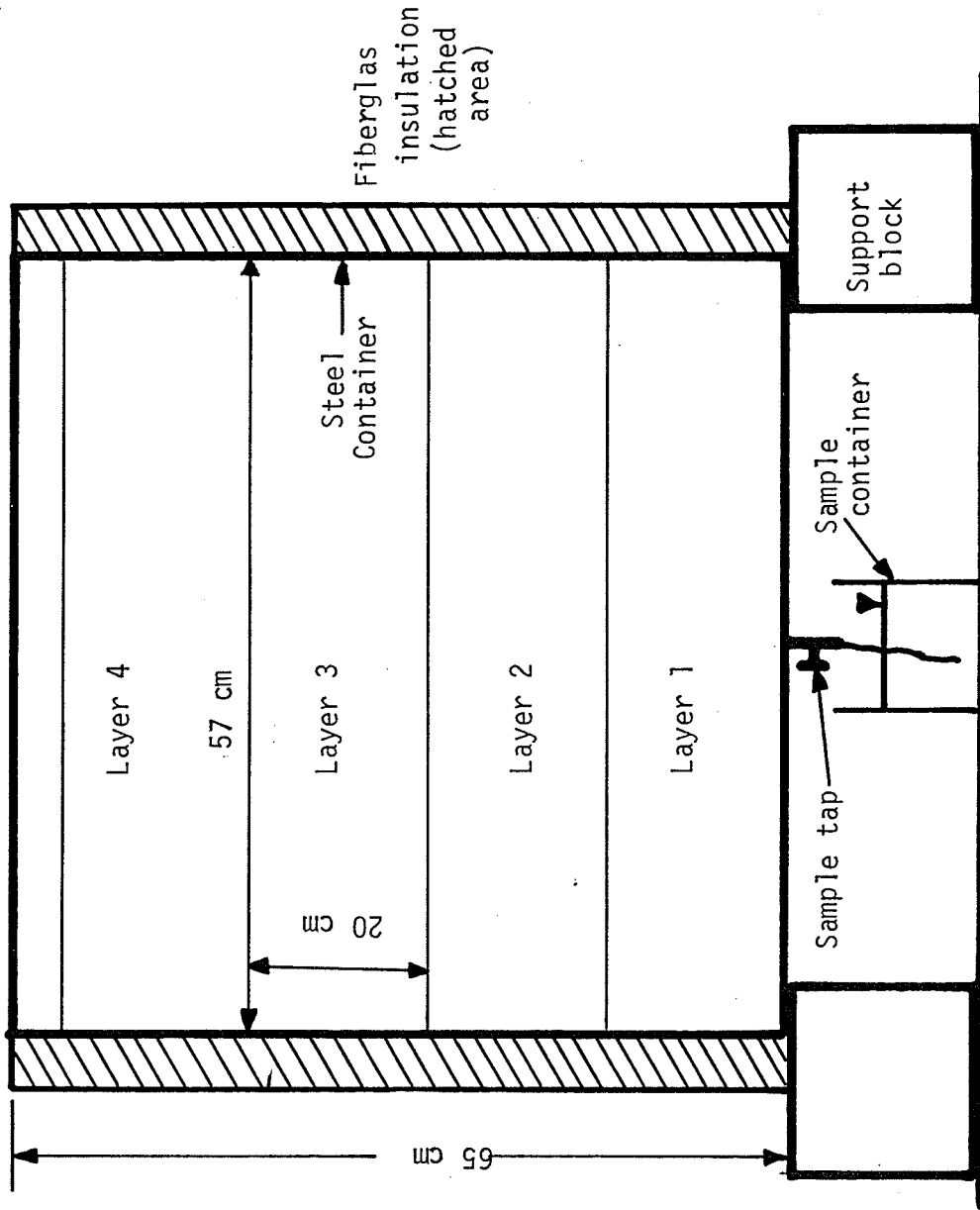
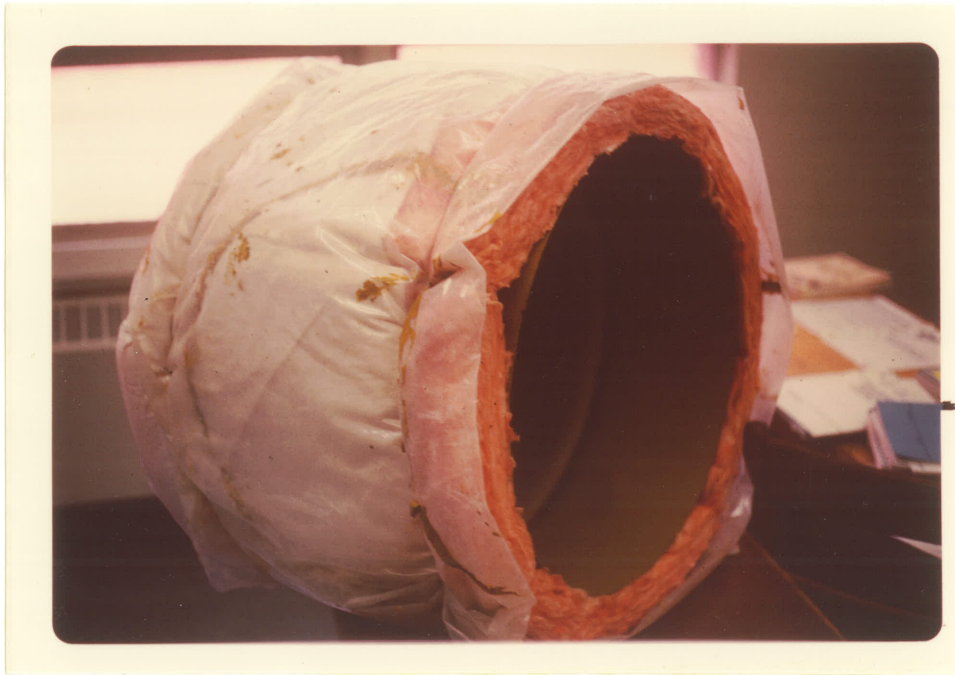


FIGURE 10. Diagrammatic representation of layer freezing apparatus.



Photograph 2. Layer freezing apparatus.

15 cm thick ice layer would freeze in about 24 hours at  $-20^{\circ}\text{C}$  in the environmental chamber.

On completion of the 4-day freeze period, the temperature of the chamber was raised to  $0^{\circ}\text{C}$  for a 3-week purification period during which samples were drawn off the bottom of the drums. Samples were collected at the start of the 3-week period and at the end of each week for a total of 4 samples per drum. On completion of the 3-week purification period, ice samples were taken for analyses.



The ice samples were taken using a 6 inch diameter ice auger. Samples were taken from the approximate centre of the drum at 15 cm intervals (4 samples). The ice samples were placed in 2000 mL beakers, thawed at room temperature and then placed in the environmental chamber which was still set at 0°C.

#### 3.4. Analyses and Analytical Procedure

The purpose of this study was to evaluate the effectiveness of natural freeze purification for the renovation of domestic wastewater. For this reason, the analyses conducted were directed toward the major contaminants in wastewater, namely carbon (including biochemical and chemical oxygen demand), nitrogen, phosphorous and micro-organisms. Samples of the initial wastewater, the underdrain concentrate and the ice were taken and analysed.

The analyses were conducted in accordance with the procedures outlined in Standard Methods for the Examination of Water and Wastewater (52), hereafter referred to as Standard Methods. The ice samples could not be handled in any prescribed manner as Standard Methods does not include the procedure for the handling and thawing of ice samples.

Of major concern for the ice samples was that they not change chemically or more importantly, microbiologically during the thawing process. It was felt that a rapid thaw over a few minutes could cause more serious alterations than a slow thaw at room temperature. A longer thaw period, in the order of 3 to 4 weeks, typical of lagoon conditions was not practical for laboratory simulations. On completion of the thawing period, the analyses were prioritized in terms

of sample stability. Aliquots of the samples were taken for those analyses prescribing preservatives. All samples were stored at 0°C until analysed. All analyses were conducted in the Environmental Engineering laboratory at the University of Manitoba with exception of the microbiological analyses, which were conducted by the Bacterial Division of the Cadham Provincial Laboratory.

The specific analyses conducted including the pertinent sections of Standard Methods in which they are found are outlined below:

<u>Analysis</u>	<u>Section of Standard Methods</u>
Biochemical Oxygen Demand (BOD)	219
Chemical Oxygen Demand (COD)	220
Total Organic Carbon (TOC)	138
Nitrate-Nitrogen (NO <sub>3</sub> -N)	213C
Ammonia-Nitrogen (NH <sub>3</sub> -N)	132A & B
Organic-Nitrogen (Org-N)	215
Total Phosphorus (TP)	223C, 223E
Organic Phosphorus (Org-P)	223B, 223C, 223E
Most Probable Number (MPN)	407A
Standard Plate Count (SPC)	406

### 3.5. Initial Wastewater Characteristics

The following Tables (12 and 13) outline the characteristics of the wastewaters used during the freeze-purification simulations. As outlined in section 3.2, these samples were taken after primary and secondary treatment at both the South End and West End plants. The

samples were collected using a pail and 5 gallon (23 L) carboys. For the layer freezing tests, the carbon samples were completely mixed on the testing apparatus so as to ensure a relatively uniform wastewater for each layer. This was not required for the reservoir freezing tests as the total volume required was somewhat less than 1 (23 L) carboy.

Constituent	South End Plant		West End Plant	
	Primary	Secondary	Primary	Secondary
Total Organic Carbon (TOC) (mg/L)	90.0	18.0	165.0	31
Biochemical Oxygen Demand (BOD) (mg/L)	140.0	27.0	178.0	49
Chemical Oxygen Demand (COD) (mg/L)	135.0	47.0	230.0	59
Nitrate-Nitrogen (NO <sub>3</sub> -N) (mg/L)	0.16	0.68	0.14	0.43
Ammonia-Nitrogen (NH <sub>3</sub> -N) (mg/L)	29.0	18.0	23.0	24.5
Organic-Nitrogen (Org-N) (mg/L)	7.3	1.9	4.9	1.6
Organic Phosphate (Org-P) (mg/L)	2.2	0.92	1.6	0.53
Total phosphate (TP) (mg/L)	5.6	3.8	5.7	2.7
Most Probable Number (MPN)	-	150,000+	-	150,000+
Standard Plate Count (SPC)	-	10,000+	-	10,000+

TABLE 12. Initial wastewater characteristics for reservoir freezing analyses.

Constituent	South End Plant		West End Plant	
	Primary	Secondary	Primary	Secondary
Total Organic Carbon (TOC) (mg/L)	110.0	18.0	110.0	19.0
Biochemical Oxygen Demand (BOD) (mg/L)	170.0	36.0	122.0	26.0
Chemical Oxygen Demand (COD) (mg/L)	215.0	49.0	240.0	43.0
Nitrate-Nitrogen (NO <sub>3</sub> -N) (mg/L)	0.85	1.5	0.23	0.81
Ammonia-Nitrogen (NH <sub>3</sub> -N) (mg/L)	33.0	24.0	24.0	27.5
Organic-Nitrogen (Org-N) (mg/L)	4.2	2.3	8.3	2.4
Organic-Phosphate (Org-P) (mg/L)	2.05	0.86	1.6	1.2
Total Phosphate (TP) (mg/L)	3.8	2.9	5.75	4.8

TABLE 13. Initial wastewater characteristics for layer freezing analyses.

## Chapter 4

### Experimental Results

#### 4.1. Introduction

The results of this study are in the form of chemical and microbiological analyses conducted on wastewater samples modified by freeze-purification using both the reservoir and layer freezing methods. The underdrain samples are the sink into which the contaminants are concentrated while the ice is the source out of which the contaminants are removed. The variation between the underdrain and ice samples is therefore a measure of the overall freeze-purification process.

The results of the analyses have all been presented in tabular form. The analyses of both the underdrain and ice samples have been placed together in order that the differences in quality be more easily determined.

Also samples noted as N.A. (not available) are nearly in all cases samples that were lost. In one case, a complete sample had a small fraction remaining. The spilled liquid could not be sponged up as it had mixed with condensate that had accumulated from drippings from the walls and ceiling. In cases noted as > (greater than) or < (less than), the analysis was outside the range applicable for the particular analysis. The value noted is closest determination with acceptable reliability.

The individual groups of analyses for the reservoir and layer freezing tests have been presented together. This was done to facilitate a comparison of results (from one method to the other and also due to the fact that the theoretical considerations discussed in the following chapter are quite similar). The data has been grouped into separate tables for BOD, COD and TOC, nitrogen, phosphorus, and MPN and SPC. The individual tables were arranged to demonstrate the variation and changes in chemical constituent from the start to the finish of the 3 week purification period as well as from the top to the bottom of the ice.

The testing of the microbiologic samples (MPN and SPC) were carried out by the Bacterial Division of the Cadham Provincial Laboratory due to the fact that MPN and SPC tests are carried out on a very infrequent basis in the University of Manitoba Environmental Laboratory. This aspect of the study was limited to an evaluation of the influence of freezing on bacterial numbers for the reservoir freezing simulation using secondary treated effluent only. The Bacterial Division was operating with a limited summer staff and it was indicated that the number of samples would have to be limited to a reasonable level. The reservoir freezing samples using secondary effluent were used as they minimized the potential problems associated with solids. The SPC and MPN samples were siphoned from below the surface of the thawed ice samples into "bacti bottles" supplied by the Cadham Laboratory.

4.2. Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)

	Underdrain Samples			Ice Sample Interval (cm)					Bottom 40-50
	Initial 0	1	Final 3	0-10	10-20	20-30	30-40		
<b>SOUTH END PLANT</b>									
<b>Primary Effluent</b>									
BOD (mg/L as O <sub>2</sub> )	970	>415	105	21.0	16	20	27	>42.5	
COD (mg/L as O <sub>2</sub> )	1760	845	180	61.0	24	29	28	41.0	
TOC (mg/L as O <sub>2</sub> )	745	175	31	12.5	11	11	14	17.5	
<b>Secondary Effluent</b>									
BOD	245	62	18.0	29	7.0	8	6.5	21.0	
COD	433	225	51.0	54	20.0	22	12.0	31.0	
TOC	205	71	7.5	55	14.5	21	23.0	-	
<b>WEST END PLANT</b>									
<b>Primary Effluent</b>									
BOD	1560	420	-	31	21	29	26	14.0	
COD	2440	1260	188	67	32	20	30	24.0	
TOC	1230	695	131	22	15	15	16	10.5	
<b>Secondary Effluent</b>									
BOD	335	-	47	18.0	24	27	14	>45.0	
COD	469	210	94	28.0	26	24	27	21.0	
TOC	273	105	57	11.5	16	15	18	13.5	

< - Less than  
 > - Greater than  
 - - Not available

TABLE 14. Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD) concentrations for reservoir freezing simulations.



	Underdrain Samples			Ice Sample Interval (cm)			
	Initial 0	(weeks) 1	Final 3	Top 0-15	15-30	30-45	Bottom 45-60
<b>SOUTH END PLANT</b>							
Primary Effluent							
BOD (mg/L)	1150	270	24	13.5	17	12	28
COD (mg/L)	1850	900	80	24.0	34	32	88
TOC (mg/L)	710	230	16	17.0	14	19	21
Secondary Effluent							
BOD	280	>120	4.5	3.5	3.6	4.7	18.5
COD	495	190	9.0	9.0	1.4	-	14.0
TOC	204	43	2.5	3.0	4.0	2.5	6.6
<b>WEST END PLANT</b>							
Primary Effluent							
BOD	1500	122	86	19	6.8	3.2	>40
COD	3650	325	265	12	40.0	53.0	102
TOC	2450	224	106	16	12.5	25.0	22
Secondary Effluent							
BOD	131	86	11	12.0	5.0	8.5	15.5
COD	360	125	27	16.5	12.0	20.0	33.0
TOC	123	73	13	6.5	10.0	5.0	8.0

< - Less than  
> - Greater than  
- - Not available

TABLE 15. Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) concentrations for layer freezing simulations.

## 4.3. Nitrogen

	Underdrain Samples			Ice Sample Interval (cm)					
	Initial 0	1	2	Final 3	Top 0-10	10-20	20-30	30-40	Bottom 40-50
SOUTH END PLANT									
Primary Effluent									
NO <sub>3</sub> -N (mg/L)	2.5	1.3	0.25	0.16	<0.1	<0.1	<0.1	<0.1	0.14
NH <sub>3</sub> -N (mg/L)	370.0	88.0	17.5	1.3	0.82	1.5	1.7	4.6	2.0
Org-N (mg/L)	94.0	5.8	0.44	0.40	0.37	0.40	0.53	1.4	0.94
Secondary Effluent									
NO <sub>3</sub> -N	10.2	5.0	0.25	0.22	<0.1	<0.1	<0.1	<0.1	0.14
NH <sub>3</sub> -N	170.0	56.0	1.7	1.3	<0.1	<0.1	<0.1	0.51	2.7
Org-N	24.0	22.0	0.53	0.65	<0.1	<0.1	<0.1	<0.1	0.93
WEST END PLANT									
Primary Effluent									
NO <sub>3</sub> -N	2.2	1.0	1.1	2.0	<0.1	<0.1	<0.1	<0.1	0.1
NH <sub>3</sub> -N	270.0	95.0	9.6	8.7	1.6	2.7	2.9	5.4	5.2
Org-N	47.0	37.0	31.0	1.9	0.45	0.44	0.57	0.86	1.35
Secondary Effluent									
NO <sub>3</sub> -N	4.1	2.6	0.22	0.12	<0.1	<0.1	<0.1	<0.1	<0.1
NH <sub>3</sub> -N	235.0	27.0	1.9	0.65	1.1	0.85	0.75	1.7	2.2
Org-N	17.6	5.5	2.3	0.35	<0.1	<0.1	0.25	0.45	1.1

< - Less than  
> - Greater than  
- - Not available

TABLE 16. Nitrogen concentrations for reservoir freezing simulations.

	Underdrain Samples			Ice Sample Interval (cm)				
	Initial 0	1	2	Final 3	Top 0-15	15-30	30-45	Bottom 45-60
SOUTH END PLANT								
Primary Effluent								
NO <sub>3</sub> -N (mg/L)	13.0	2.7	0.22	0.24	<0.1	<0.1	0.18	0.22
NH <sub>3</sub> -N (mg/L)	31.5	68.0	43.0	6.5	3.3	3.8	3.7	9.5
Org-N	68.0	1.1	0.86	0.98	0.53	0.57	0.43	0.96
Secondary Effluent								
NO <sub>3</sub> -N	11.8	1.75	0.28	0.25	0.14	0.13	0.33	0.28
NH <sub>3</sub> -N	160.0	9.6	1.3	1.1	2.3	1.35	2.7	4.3
Org-N	33.0	1.3	0.32	0.37	0.14	0.13	0.33	0.28
WEST END PLANT								
Primary Effluent								
NO <sub>3</sub> -N	23.3	2.2	2.4	-	<0.1	<0.1	<0.1	0.14
NH <sub>3</sub> -N	1250.0	79.0	68.0	-	5.3	6.2	8.6	10.3
Org-N	75.0	4.4	2.8	-	1.7	1.5	1.7	2.4
Secondary Effluent								
NO <sub>3</sub> -N	5.5	4.3	0.38	0.28	<0.1	<0.1	<0.1	<0.1
NH <sub>3</sub> -N	440.0	51.0	29.0	9.6	3.0	4.4	4.9	6.4
Org-N	22.0	5.3	4.7	1.9	0.77	0.58	1.25	1.55
<	Less than							
>	Greater than							
-	Sample unavailable							

TABLE 17. Nitrogen concentration for layer freezing simulations.

#### 4.4. Phosphorus

	Underdrain Samples			Ice Sample Interval (cm)					
	Initial 0	1	2	Final 3	Top 0-10	10-20	20-30	30-40	Bottom 40-50
SOUTH END PLANT									
Primary Effluent									
TP (mg/L)	33.5	6.4	2.9	0.54	0.22	0.43	0.32	1.05	3.3
Org-P (mg/L)	13.5	0.47	0.32	0.26	<0.1	<0.1	<0.1	<0.1	<0.1
Secondary Effluent									
TP	16.5	3.4	3.6	0.96	<0.1	0.19	<0.37	0.85	0.56
Org-P	7.6	0.26	0.18	0.17	<0.1	<0.1	<0.1	0.15	0.27
WEST END PLANT									
Primary Effluent									
TP	26.0	13.2	3.7	0.85	0.52	1.6	1.8	1.7	0.62
Org-P	13.5	.63	0.18	0.14	0.11	0.11	0.13	0.13	0.145
Secondary Effluent									
TP	34.0	8.8	5.7	0.86	<0.1	0.33	0.66	1.05	0.93
Org-P	5.6	0.76	0.33	0.135	<0.1	<0.1	<0.1	<0.1	0.12

< - Less than  
> - Greater than  
- - Not available

TABLE 18. Phosphorus concentrations for reservoir freezing simulations.

	Underdrain Samples			Ice Sample Interval (cm)				
	Initial 0	1	2	Final 3	Top 0-15	15-30	30-45	Bottom 45-60
SOUTH END PLANT								
Primary Effluent								
TP	26.0	16.0	1.7	-	1.0	1.22	1.35	1.30
Org-P	12.0	1.25	0.84	-	0.72	0.87	0.68	0.53
Secondary Effluent								
TP	21.0	1.85	1.20	0.44	0.37	0.39	0.72	0.89
Org-P	5.6	0.25	0.22	0.20	0.13	0.16	0.16	0.27
WEST END PLANT								
Primary Effluent								
TP (mg/L)	34.5	18.5	16.0	1.04	0.59	1.03	1.85	3.2
Org-P (mg/L)	18.0	0.47	0.38	0.32	0.19	0.17	0.21	0.37
Secondary Effluent								
TP	47.5	16.0	14.5	2.3	0.75	1.05	0.8	1.75
Org-P	8.5	1.03	0.45	0.25	0.37	0.36	0.52	0.63

< - Less than  
 > - Greater than  
 - - Sample unavailable

TABLE 19. Phosphorus concentration for layer freezing simulations.

## 4.5. Most Probable Number (MPN) and Standard Plate Count (SPC)

Ice Concentration Interval (cm)	South End		West End	
	MPN	SPC	MPN	SPC
Initial Concentration	150,000 <sup>+</sup>	10,000 <sup>+</sup>	150,000 <sup>+</sup>	10,000 <sup>+</sup>
0-10	240	6,000	240	400
10-20	240	3,000	460	1,100
20-30	240	10,000 <sup>+</sup>	240	9,000
30-40	NA	NA	240	1,100
40-50	1,500	10,000 <sup>+</sup>	240	1,100

NA - Not available

TABLE 20. Microbiological concentrations evaluated during reservoir freezing analyses using secondary effluent.

## Chapter 5

### Discussion of Results

#### 5.1. Introduction

The first research on the subject of freeze-purification was conducted using the reservoir freezing technique. This was a logical first step as it most closely simulated natural freezing in ponds, lakes and rivers. At the time of the first research, some 40 years ago, there was little or no theory to justify such research, only the observations of many different people, mainly Arctic travellers.

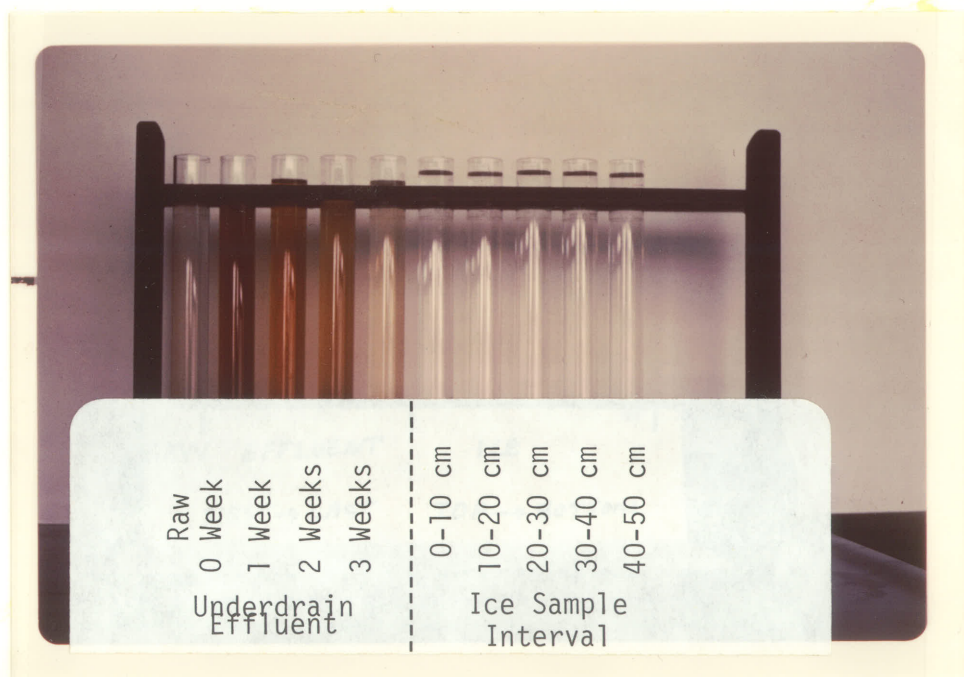
These early Arctic explorers, out of necessity, observed that frozen seawater was invariably less salty than seawater and further, that ice above the ocean surface was most often significantly fresher than the ice below the seawater surface. In many instances, this upper ice could be melted and used for all potable water uses.

To date, almost the total focus of research on natural freeze-purification has been directed to the desalination of high TDS waters, for agricultural and domestic use. This research initially involved only reservoir freezing but with the advancement of the science, new concepts brought about investigations on layer freezing and even more recently on spray freezing studies.

The research conducted in this study, is another redirection of the freeze-purification phenomenon to another type of water quality problem namely wastewater renovation. At the present time, the available literature, pertinent to wastewater renovation by freeze-purification is very limited to the point of almost non-existence. As a consequence,

the evaluation of the results is somewhat hampered when compared to other, more researched areas of environmental engineering. The result is that only qualitative and semi-quantitative comparisons with other studies, whether theoretical or field orientated, are possible.

Photograph 3 below is an example of the qualitative data that was collected. The individual test tubes contain actual samples taken from the reservoir freezing simulations. The underdrain samples had been stored for several weeks at 0°C prior to the photograph, however, there was little or no significant change in their colouration. The raw sample was obtained just prior to the time of photograph such that it was not the same sewage as was used in the experiment, again the difference is unlikely to be noticeable. The ice samples had just been thawed.



Photograph 3: Colour variation among samples of initial wastewater, underdrain effluent and thawed ice.



This photograph shows the definite change and difference in colour among the raw, underdrain and ice samples. The underdrain samples demonstrate a definite change in colour from the first to last samples. The initial underdrain sample also had a strong odour associated with it, at the time of sampling and for several weeks later. It is possible that odour was associated with low levels of anaerobic activity near  $0^{\circ}\text{C}$ , similar to that in lagoons during spring thaw.

The ice samples are quite different from the underdrain samples in both degree and variation. They are quite clear in the photograph and in some instances looked almost crystal clear. They do not show any noticeable change in colour from top to bottom as might be expected. This is likely due to the much smaller range in overall quality that was generally found between the ice samples as compared to the underdrain samples.

## 5.2. Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC)

### 5.2.1. Biochemical Oxygen Demand (BOD)

The BOD test is used as a quantitative measure of the biologically oxidizable organic content in a particular wastewater. These organic materials are normally composed mainly of carbon, nitrogen and phosphorus, the major constituents typically found in biologically formed organics. To be biologically oxidizable, these organics must be capable of being degraded or broken down by a range of microorganisms, but mainly by bacteria. These bacteria must be able to break down the molecular bonding, mainly the form of carbon bonds, using their intra or extra cellular enzymes. The breakdown of these bonds releases or

provides the energy necessary for the bacteria to maintain its metabolic functions. The amount of energy released is related to the energy difference (entropy) between the organic substrate and the by-products, usually  $\text{CO}_2$ , the lowest oxidative level, and possibly lower entropy organic molecules. The general consequence of this degradation process is the potential for a range of organic molecular sizes even when the starting concentration is quite homogeneous.

In terms of the effect of freeze-purification on the removal of these organic molecules, molecular or ionic size and charge have been theorized to be the principal, operative factors in the overall process. Podolsky (3) found in his work on the fluidity of water, that singly charged ions with radii between 1.5 and  $3\text{\AA}$  were the least able to be held within the water structure by any type of bonding force. These ions could readily move in and out of the water structure and actually reduce the viscosity of the water. With increasing radial size and higher charge and to a more limited degree, decreasing radial size, the ions and molecules become increasingly more tightly bound in the water structure. The organic molecules included in Figure 3 have the largest radii of the lot and for singly charged ions, they have lowest fluidity. This means that these larger organics will bond more tightly into the water's molecular structure than will the smaller ions. The result is that at the moment of freezing, these larger molecules are more likely to be retained in the ice structure and as a consequence, should theoretically have a lower freeze-purification effectiveness or efficiency.

The efficiency of BOD removal for both the reservoir and layer freezing results of Tables 9 and 10 have been summarized in Table 21.

If we compare these results with those of the Saskatchewan Research Council (SRC) (Tables 2, 5, 6) and Mitlin (Table 4), one finds that the reservoir freezing results compare more closely than do those of the layer freezing tests. For the reservoir freezing tests, the SRC data indicated removal efficiencies ranging from 50.4 to 83.5% while the BOD data ranged from 46 to 86%. For the layer freezing tests, Mitlin's data ranged from 30 to 70% for 25 cm thick layers and from 44 to 91% for 180 cm thick layers; Spyker's (SRC) laboratory data ranged from 49.5 to 71.5% for NaCl solutions and 42.9 to 57.4% for Na<sub>2</sub>SO<sub>4</sub> solutions and Fertuck's field data ranged from 61 to 90%. For comparative purposes, the spray freezing data of Table 10 demonstrated BOD reductions from 51 mg/L in the effluent to 3.5 mg/L in the snow for an overall removal rate of 93%.

For the reservoir freezing tests, the removal efficiencies for the BOD and desalination data are quite similar. In fact, considering the disparity in test conditions, one would not generally expect such close correlations. The results from the desalination tests indicated that the overall efficiency improved as the initial or input salinity decreased, 50.4% at 28,000 mg/L to 83.5% at 5,000 mg/L (TDS). These figures imply some form of saturation limit beyond which freeze-purification become less effective. Considering that the wastewater TDS would be in the order of 200 to 400 mg/L, efficiencies of 90 to 95% could be anticipated. For spray freezing, a 93% efficiency has been reported. This rather simplistic trend is further complicated however, by the fact that the larger, organic molecules react differently than do simple ionic solutions.

	Reservoir Initial (mg/L)	Freezing Ice Removal (Ave)	Freezing %	Layer Initial	Freezing Ice Removal %
South End Plant					
Primary Effluent BOD (mg/L)	140	28.9	79	170	17.6
Secondary Effluent BOD (mg/L)	27	13.5	50	36	7.6
West End Plant					
Primary Effluent BOD (mg/L)	178	25	86	122	17
Secondary Effluent BOD (mg/L)	49	26	47	26	10

TABLE 21 . Effectiveness of BOD removal for both reservoir and layer freezing simulations.

These molecules are theoretically more difficult to remove from the ice crystal as well as from the ice mass as a whole. They tend to bond into the ice crystal more tightly than do Na or Cl, the principal seawater constituents, and have a much higher tendency to coagulate into a larger solid mass at the ice crystal boundary or in a crystal void than do most inorganic ions which must reach some solubility limit. For example, the solubility limit for NaCl is in the order of 300,000 mg/ such that NaCl precipitation is a relatively infrequent occurrence in nature.

In summary, this data in conjunction with rather limited corroborating data indicates that BOD removal by freeze-purification can be effective. However, the inter-acting and counter-acting forces indicate that the overall phenomenon is probably quite complex and will require significantly more work before even a few of the theoretical problems are solved.

As for the layer freezing results, the rather significant differences in testing conditions makes meaningful comparisons difficult. The Russian, Mitlin (see Table 4) worked with thicknesses ranging from 25 cm to 180 cm. It is questionable if thickness even as high as 25 cm are worth investigating for reasons other than pure research. Certainly, in terms of field evaluations of layer freezing, thickness of greater than 100 cm are essentially reservoir freezing evaluations. In fact, it would be a very rare winter that would produce even a single layer of ice 180 cm thick.

This is probably a significant part of the reason that the SRC directed its work to ice thickness between 2.5 and 15 cm. At the

closest extremities of these ranges, the work of Mitlin, Spyker and Fertuck (45,47,48) are much the same. At 25 cm thicknesses and initial TDS values of 10,000 mg/L, Mitlin indicated removal efficiencies of 70%, at 15 cm thickness and initial TDS values of 10,000 mg/L (as NaCl), Spyker reported removal efficiencies of 55% while Fertuck, using 15 cm thickness had 80% removal efficiencies for initial TDS values of 5,000 mg/L.

The results of Table 21, indicate that the BOD removal efficiencies for 15 cm layers range from 61 to 90%. These results are overall, significantly better than those for desalination alone. Again, however, as with the reservoir freezing tests, the disparity in test conditions make comparisons difficult. The difference in overall initial salinity from 10,000 mg/L during the desalination tests to about 200 to 400 mg/L, for a 50 to 25 fold decrease should increase the removal efficiency. This potential increase is again, countered by the theoretical factors which indicate a more difficult removal from the ice as well as by practical factors such as the settling of suspended solids. Suspended solids often comprise a significant portion of total BOD strength but influence desalination minimally. The fact that the BOD data shows a definite increase in overall removal efficiency when compared to the desalination data, indicates that the salinity factor may be an overall term, more important than the theoretical negative influences that have been attributed to the organic ions. This is reinforced by the results of laboratory freeze-concentration studies (Section 2.8) in which the organic molecules were more effectively removed than the inorganic ions. Also, the evidence for dilute solutions indicates the overall efficiency can approach 100%.

Probably of more significance than the differences between the results of other tests and those of this study are the differences among the various samples and testing methods. Firstly, in both the reservoir and layer freezing simulations, the primary effluent had higher BOD removal efficiencies than did the secondary effluent. The difference between the BOD of the initial wastewater samples is made up of both colloidal and suspended solids particles. It would appear that the higher solids concentration in the primary effluent was preferentially or more easily removed than the more soluble, colloidal sized organic particles. Also, the result is most noticeable in the reservoir freezing samples where there was a 10 day period of rather quiescent settling. Even the layer freezing tests, with only 24 hours of settling time demonstrated a significant settling tendency with a noticeable black layer of solids at each layer interface. It was anticipated from the outset, that the settling of solids would tend to mask the effectiveness of the freeze-purification simulations and it was for that reason the raw wastewater was not used.

Another interesting result of the BOD data was the fact that it showed the layer freezing tests to be more efficient in overall terms, than the reservoir freezing tests. The results of the SRC (Table 2 and Figure 7) also indicate that layer freezing can be more effective than reservoir freezing for initial solutions without solids. For wastewaters containing appreciable amounts of solids, there is reason to believe that the solids might interfere and reverse this general trend. Certainly this difference could not be attributed to the settling of solids as that factor was in favour of the reservoir method. The

The freezing rate or velocity was one factor that was of major

difference between the two freezing methods tested. The average freezing velocity was more than three times higher for the layer freezing tested than for the reservoir freezing tests. The freezing velocity influences both the structured continuity of the ice mass as well as the removal efficiency of the solids, and to a lesser degree the dissolved particles at the ice-water interface. The net result appears to be that slow forming ice is quite effective in removing impurities while freezing and tends to form a well ordered and fairly continuous ice structure. The fast forming ice is however, less able to remove impurities during freezing and forms an unordered crystal structure full of voids and crystal faults. These voids have been observed to reduce the overall porosity of ice.

During rapid freezing, Mitlin (45) found that the porosity of ice can be as high as 15% while Glen (12) found that slow freezing could produce ice with almost negligible porosity. The net consequence of these differences is a greater permeability for fast frozen ice when compared to slow frozen ice. It is possible therefore, that this potentially greater permeability in the layer frozen ice produced better removals during the purification period than did the reservoir frozen ice and resulted in better overall treatment efficiencies. The results of the SRC (Table 2 and Figure 7) also tend to substantiate this general result.

#### 5.2.2. Chemical Oxygen Demand (COD)

The COD test is a second commonly used method to estimate the oxygen demand or requirement of wastewaters. Normally, the COD test is operative over a wider range of organic materials than the BOD test.



There are many organic molecules that have bonding sufficiently strong that bacterial enzymes are incapable of breaking them down. The COD test uses a strong commercial oxidant as an oxidizing agent such that it can facilitate the breakdown of both biodegradeable and many non-biodegradeable organic substances. In terms of size or molecular charge, there is nothing in the literature to suggest that the organic molecular oxidized by the COD test are any different than those evaluated by the BOD test.

The results of the removal efficiencies for COD for both the reservoir and layer freezing tests are outlined below:

	Reservoir Freezing Initial Ice Removal % (Average)			Layer Freezing Initial Ice Removal % (Average)		
South End Plant						
Primary Effluent (mg/L)	135	37	72	215	44.5	79
Secondary Effluent (mg/L)	47	21	54	49	8	84
West End Plant						
Primary Effluent	230	30	87	240	52	78
Secondary Effluent	59	27	54	43	20	53

TABLE 22. Effectiveness of COD removal for both reservoir and layer freezing simulations.

A comparison of this figure with the equivalent for the BOD data (Figure 21) shows, as would be generally expected, a reasonable close comparison. It would appear that the factors influencing the removal of BOD measured organic compounds are quite similar to those affecting COD removal in both degree and quality. Considering the overall similarity of the organic test species, this is not an unexpected result.

### 5.2.3. Total Organic Carbon (TOC)

The TOC test is a more recent testing procedure than either BOD or COD and is gaining significantly in popularity, mainly at the expense of the BOD test. The BOD test suffers from extended testing times (5 days) for test results and often poor reproducibility. The TOC test is an attempt to overcome some of these problems. The City of Winnipeg Wastewater Division, for example, now relies almost exclusively on TOC data for determining process effectiveness for organic removal.

The TOC test measures the organic carbon content (as carbon in mg/L) by combusting the carbon in a heated pure oxygen environment in which  $\text{CO}_2$ , with very little CO, is the combustion product. The  $\text{CO}_2$  concentration content within the combustion chamber is determined by an infrared analysis which totals the  $\text{CO}_2$  content exiting the chamber.

The following table (18) outlines the removal efficiencies obtained for TOC for both the reservoir and layer freezing tests.

	Reservoir Freezing Initial Ice Removal % (Average)			Layer Freezing Initial Ice Removal % (Average)		
South End Plant						
Primary Effluent	90	14.9	83	110	18	84
Secondary Effluent	18	18.4	0	18	4	78
West End Plant						
Primary Effluent	165	17.3	89	110	19	83
Secondary Effluent	31	16.8	46	19	7.4	62

TABLE 23. Effectiveness of TOC removal for both reservoir and layer freezing simulations.

The removal efficiencies for TOC as demonstrated by Table 23 are similar in nearly all respects to those determined by BOD and COD data. Again, the layer freezing results show better overall removals than the reservoir freezing tests, possibly indicating a higher ice permeability associated with a higher freezing rate.

The results of Table 23 also indicate that the removal efficiencies for the primary effluents are significantly better than the secondary effluents, especially for the reservoir freezing simulations. This can be at least partly explained on the effect of gravity settling on the suspended solids load. The extended settling times of the reservoir freezing technique, and to a lesser degree the layer freezing technique, has a definite effect on overall TOC removals.

Also, the results from the secondary treated effluent indicate that removal to very low levels, as has been observed in dilute aqueous organic solutions, does not in fact occur. It appears that either the organic molecules reach some lower saturation level or a low level of solids interferes with the results. The latter is the more likely, in that, the results presented in Table 11 indicate no such saturation phenomenon. In addition, it would seem quite likely that slow settling solids or colloids could be entrapped in the ice.

### 5.3. Nitrogen

#### 5.3.1. Introduction

Nitrogen in its different forms is the second-most abundant nutrient found in wastewater. The analyses conducted in Tables 16 and 17 normally constitute greater than 95% of the total nitrogen content. The nitrate ( $\text{NO}_3^-$ -N) and ammonia ( $\text{NH}_3$ -N) ions are both inorganic nitrogen forms while organic nitrogen, as its name indicates, is a measure of organically bound nitrogen generally as amino acids, polypeptides and proteins.

#### 5.3.2. Nitrate ( $\text{NO}_3^-$ -N)

The  $\text{NO}_3^-$ -N concentration in raw wastewater is normally low (less than 1 mg/L) although sufficient concentrations can be found in secondary treated effluents where nitrification is occurring. Nitrification is the oxidation of  $\text{NH}_3^+$ -N to  $\text{NO}_3^-$ -N by bacteria. The data for the South and West End Plants indicates that nitrification is not occurring, a factor most often associated with low solids retention time (SRT). As a consequence, the  $\text{NO}_3^-$ -N concentrations are relatively low through the complete treatment process.

The overall removal efficiencies for the two freeze purification processes are outlined below in Table 24.

	Reservoir Freezing Initial Ice Removal % (mg/L)(Ave )			Layer Freezing Initial Ice Removal % (mg/L) (Ave)		
South End Plant						
Primary Effluent	0.16	<0.1	>85	0.85	0.15	82
Secondary Effluent	0.68	<0.1	>85	1.5	0.22	85
West End Plant						
Primary Effluent	0.14	<0.1	>29	0.23	<0.1	>56
Secondary Effluent	0.32	<0.1	>69	0.81	<0.1	>87

TABLE 24. Effectiveness of  $\text{NO}_3^-$ -N removal for both reservoir and layer freezing simulations.

The results of Table 24 indicate that both forms of freeze purification can be quite effective for  $\text{NO}_3^-$ -N removal. The very low  $\text{NO}_3^-$ -N levels in both the initial samples and ice made many calculations inconclusive, however, those results that were within the analytical range demonstrated effective removals. In fact, the highest removal efficiencies were higher in both cases than those obtained from field studies in Saskatchewan. These values were, however, comparable to the removal efficiencies of 84 and 60%, obtained in nutrient removal testing by spray freezing (See Tables 8 and 9).

The theoretical considerations for ionic removal as demonstrated in Figure 2 indicate that the  $\text{NO}_3^-$ -N ion is particularly mobile within the water structure and as a consequence, it should be easily removed by the freeze-purification process. Also, the fact that  $\text{NO}_3^-$ -N is not

associated with suspended solids in the wastewater, there should be little tendency for  $\text{NO}_3\text{-N}$  to be removed by gravity settling or be entrapped in the ice along with solids.

On the basis of this test data it is not possible to determine the dominant forces at work during the freezing process. However, the fact that these results are much the same in terms of overall effectiveness when compared to the larger organic molecules as measured by BOD, COD and TOC indicates that the ionic forces are less important in overall terms than the effects of drainage. That is to say that the influence of brine drainage from the ice mass predominates and masks the effects of ionic radius and charge.

### 5.3.3. Ammonia ( $\text{NH}_3\text{-N}$ )

$\text{NH}_3\text{-N}$  is normally the most abundant form of nitrogen in raw or primary treated wastewater and can be the predominant nitrogen species in secondary treated wastewater whose biological nitrification is lacking. For both the South and West End Plants in Winnipeg, nitrification rates are relatively insignificant and as a consequence,  $\text{NH}_3\text{-N}$  is the predominant nitrogen concentration in all initial samples used during the simulations.

The results of the freeze-purification simulations for  $\text{NH}_3\text{-N}$  removal are presented in Table 25.

	Reservoir Freezing			Layer Freezing		
	Initial (mg/L)	Ice (Ave)	Removal %	Initial (mg/L)	Ice (Ave)	Removal %
South End Plant						
Primary Effluent	29.0	2.1	93	33.0	5.1	85
Secondary Effluent	18.0	0.7	96	24.0	2.7	89
West End Plant						
Primary Effluent	23.0	3.6	85	24.0	7.6	68
Secondary Effluent	24.5	1.3	95	27.5	4.7	83

TABLE 25. Effectiveness of  $\text{NH}_3\text{-N}$  removal for both reservoir and layer freezing simulations.

The results of Table 25 indicate overall, an excellent removal efficiency for  $\text{NH}_3^+\text{-N}$  from ice. If we compare these results with those of the Saskatchewan Research Council the Russian, Mitlin (Tables 2, 4, 5, 6), the removal efficiencies for  $\text{NH}_3\text{-N}$  are higher for both reservoir and layer freezing for every simulation except one. In terms of theory, the work of Podolsky (3) predicts that  $\text{NH}_3^+\text{-N}$ , along with  $\text{NO}_3^-\text{-N}$ , should be readily rejected from ice. The ionic radius and ionic charge are in the optimum range for freeze desalination (See Figures 2 and 3).

In the earlier discussion of BOD, COD and TOC, any influence of these ionic factors was not discernible. It may well be that the organic molecules are of a size that is well beyond the  $4\text{\AA}$  size limit of Figure 3 and as a consequence, no longer react as an ionic species.

The  $\text{NH}_3^+$ -N ion, unlike the organic molecules, has a definite ionic radius and charge. For this reason, there is a greater likelihood of the  $\text{NH}_3^+$ -N ion to be influenced by the radius and charge factors. There is a hint of this relationship in the data, by the fact that the reservoir freezing data has higher overall removal efficiencies than the layer freezing results. The BOD, COD and TOC data indicated the opposite to be true, that is, the layer freezing results were noticeably better in terms of removal efficiency than through the reservoir freezing tests. This was explained by the effect of freezing rate on the openness of the ice structure. It has been observed that fast frozen ice is much more porous than slow frozen ice and as a consequence, there exists the potential for an improved gravity drainage system. If this was the overriding factor in removal efficiency, one would anticipate that the layer freezing technique would demonstrate consistently better results than the reservoir tests. The fact that the  $\text{NH}_3^+$ -N data does not follow this trend, indicates the possibility of active forces, other than gravity drainage alone. The influence of ionic radii and charge would be to enhance the effectiveness of slow freezing, typical of the reservoir technique.

#### 5.3.4. Organic Nitrogen (Org-N)

Organic nitrogen is a measure of nitrogen mainly in the form of amino acids, polypeptides and proteins and are normally of colloidal size or larger. These forms of nitrogen are measured by converting the Org-N to  $\text{NH}_3^+$ -N using a digestion process.



The results of the removal efficiencies for the Org-N analyses is presented in Table 26.

	Reservoir Freezing Initial Ice Removal % (mg/L) (Ave)			Layer Freezing Initial Ice Removal % (Conc.)(Ave)		
South End Plant						
Primary Effluent	7.3	0.73	90	4.2	0.62	85
Secondary Effluent	1.9	<0.27	86	2.3	0.22	90
West End Plant						
Primary Effluent	4.9	0.73	85	8.3	1.8	78
Secondary Effluent	1.6	<0.2	>88	2.4	1.04	57

TABLE 26. Effectiveness of Org-N removal for both reservoir and layer freezing simulations.

The results of Table 26 indicates that both freeze purification techniques can be quite effective for Org-N removal. The overall efficiencies are somewhat better than those determined by the SRC for desalination alone and may reflect some influence of gravity settling, associated with the larger suspended solids. The fact that the reservoir freezing tests had somewhat better efficiencies than the layer freezing tests is another indication that the larger organic particles may be more greatly affected by gravity settling or the freezing rate at the ice-water interface.

## 5.4. Phosphorus

### 5.4.1. Introduction

Phosphorus is normally the thrice most abundant nutrient in wastewater, after carbon and nitrogen. In most instances, the bulk of the phosphorus is in the form of phosphates, primarily orthophosphate, the stable form, with generally smaller amounts of organically bound phosphorus.

### 5.4.2. Total Phosphorus (TP)

Total phosphorus is a commonly measured parameter in wastewater engineering. It is a measure of all phosphorus in both the soluble and particulate states, measured as orthophosphate ( $PO_4$ -P). The removal efficiencies for TP are outlined as follows in Table 27.

	Reservoir Freezing Initial Ice Removal % (mg/L) (Ave)			Layer Freezing Initial Ice Removal % (Ave)		
South End Plant						
Primary Effluent	5.6	1.06	81	3.8	1.22	68
Secondary Effluent	3.8	0.41	89	2.9	0.59	80
West End Plant						
Primary Effluent	5.7	1.25	78	5.75	1.67	71
Secondary Effluent	2.7	0.6	78	4.8	1.09	77

TABLE 27. Effectiveness of TP removal for both reservoir and layer freezing simulations.

The results of Table 27 indicate that TP removal does occur during freezing of wastewater and that the results are in general agreement with those of the SRC where the upper efficiency limits for reservoir and layer freezing were 83 and 80% respectively.

In general, both the desalination data and freeze-out tests on dilute aqueous (See Section 2.8.) indicate that removal efficiencies increase with decreasing TDS while the theoretical information predicts that TP, which is composed mainly of  $\text{PO}_4\text{-P}$ , should be relatively difficult to freeze-purify out of ice. Podolsky (3) has shown that sulphate ( $\text{SO}_4$ ), an ion similar in size to the  $\text{PO}_4\text{-P}$  ion is relatively difficult to remove from water and this has been verified by Vaslov and Chernychev in field tests (5). Based on curves of Figure 3, the  $\text{PO}_4\text{-P}$  ion, being triply charged should be even more difficult to freeze-purify out of water than the  $\text{SO}_4$  ion, a doubly charged particle. The net result is, however, that these counter-acting factors make an evaluation of the relative factors influencing the overall process difficult.

For comparative purposes, the only definitive phosphorus removal data using the freeze purification technique is that of Flanders (53) and Wright (54), who found overall removal efficiencies for  $\text{PO}_4\text{-P}$  and TP of 92 and 96% respectively, for spray freezing tests. These results further complicate any theoretical predictions by adding in what appears to be process related factors. For example, their results show that phosphorus is more effectively removed from the wastewater than either  $\text{NH}_3^+\text{-N}$  or  $\text{NO}_3^-\text{-N}$ , a result that is inconsistent with theoretical considerations.

### 5.4.3. Organic Phosphorus (Org-P)

Org-P measures organically bound phosphorus, associated with biologic cell mass, proteins, polypeptides, adenosine triphosphate (ATP), etc. The effectiveness of freeze-purification in removing Org-P is presented in Table 28.

	Reservoir Freezing			Layer Freezing		
	Initial (mg/L)	Ice (Ave)	Removal %	Initial (mg/L)	Ice (Ave)	Removal %
South End Plant						
Primary Effluent	2.2	<0.1	>95	2.05	0.70	66
Secondary Effluent	0.42	<0.14	>84	0.86	0.18	79
West End Plant						
Primary Effluent	1.6	0.13	92	1.6	0.24	85
Secondary Effluent	0.53	<0.1	>81	1.2	0.47	61

TABLE 28. Effectiveness of Org-P removal for both reservoir and layer freezing simulations.

The results of Table 28 indicate that the reservoir freezing method, and to a lesser degree, the layer freezing method can be effective in the removal of Org-P from wastewaters. The results demonstrate a definite similarity to those found for the Org-N tests in terms of both degree and kind and suggests similar operative or influencing factors. The fact that the reservoir freezing results are generally better than the layer freezing results indicates that gravity settling may well be playing an important role. Especially since

Org-P is usually a constituent of suspended solids particles as well as colloids.

The higher Org-P concentrations in the layer freezing ice may also be related to the suspended solids located at each ice-water interface. It is quite possible that this layer of solids may facilitate the downward migration of colloidal sized particles as the internal brines flow vertically downwards past and through the layers of solids

#### 5.5. Most Probable Number (MPN) and Standard Plate Count (SPC)

The MPN and SPC are analyses used to determine the microbiological quality of wastewater. The results of these tests indicated a definite decrease in microbial numbers in the ice for the MPN and to a lesser degree for the SPC results. The MPN results demonstrate reductions in the ice from 100 to 1,000 fold while the SPC varied from no decrease to a 10 fold decrease.

This difference between the MPN and SPC results indicate that the coliform bacteria, measured by the MPN test are more sensitive to low temperatures and freeze-thaw than the microorganisms measured by SPC tests (24). The SPC measures a much wider variety of microorganisms than does the MPN test with the result that there is a greater probability of having one or more microorganisms than can withstand freeze-thaw.

Also, the results of Wright's (54) work indicates that spray freezing can effectively reduce fecal coliform numbers from the wastewater to the snow. No data is presented for the fecal coliform concentration in the initial wastewater, however, if values in the literature are used as estimates of initial fecal coliform levels, the removal efficiency is in the order of 100 to 10,000 fold (60). This compares favourably with the results of the MPN coliform tests.

The results of the MPN test data also indicates that the thawed ice will require little or no disinfection to meet the 1,500 MPN discharge requirement for lagoons in Manitoba (61).

#### 5.6. Field Applicability of Freeze-Purification in Lagoon Environments

The applicability of freeze-purification for desalination or nutrient removal in the Prairie environment will ultimately be determined on the basis of economics and practical considerations. This is certainly a major reason for continuing research being carried out by the Saskatchewan Research Council on freeze-purification, especially spray freezing. Figure 11 below outlines the approximate total costs (both capital and operating) of several different desalination processes over a range of water requirement(s). The cost effectiveness of spray freezing is applicable for most small towns up to a population of approximately 5,000 people, based on a per capita consumption of 250 l.p.d. (55 I.G.P.D.).

In terms of nutrient removal in lagoons, there are both economical and practical factors to be considered. In terms of natural freeze-purification, layer freezing for example, the economics appears to be the least favourable in terms of economics and has

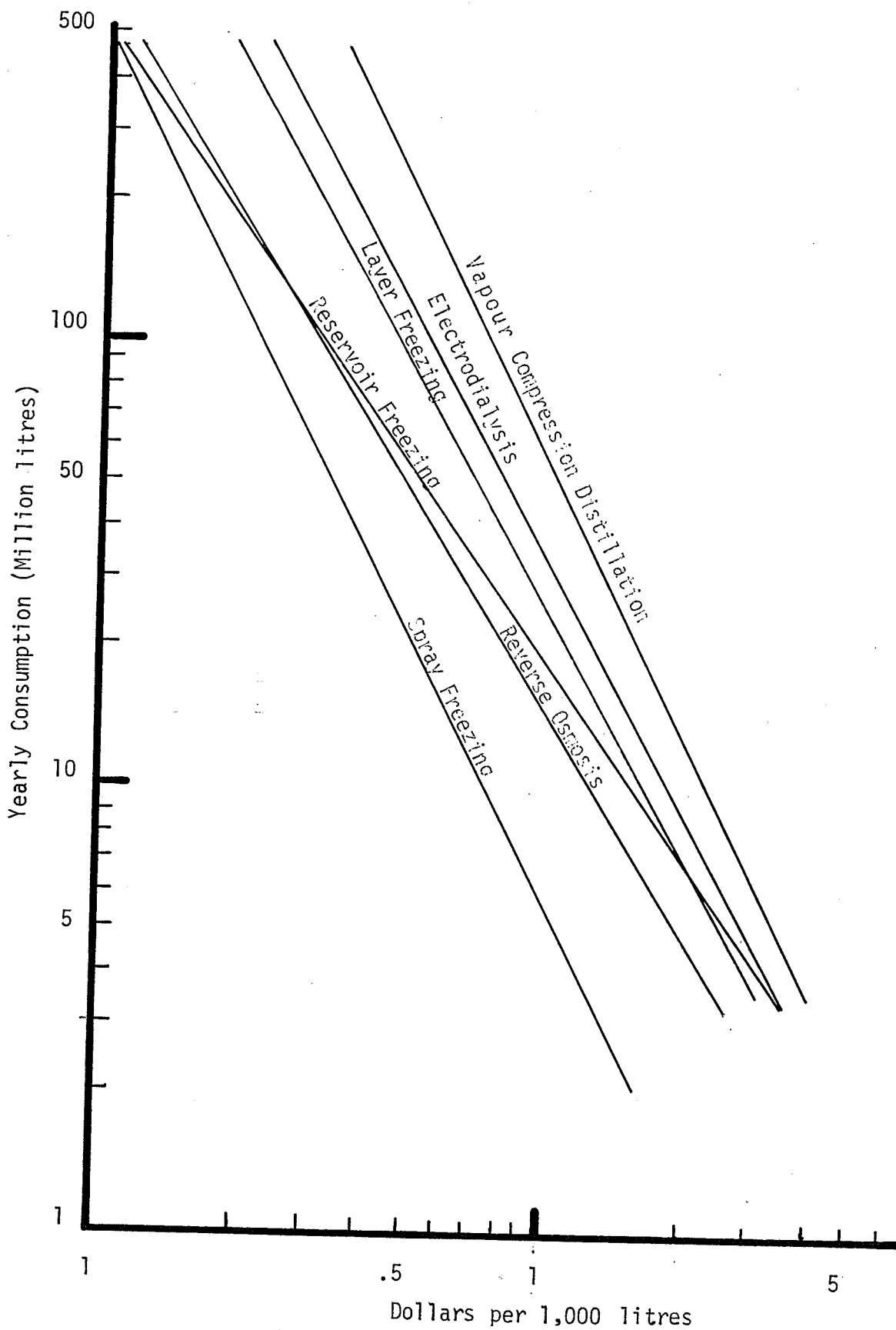


FIGURE 11. Cost comparison for several feasible desalination processes.

several practical problems to overcome as well. One serious problem would be the effect of wastewater solids and would likely necessitate a settling pond prior to freezing. The interlayers bond is also a potential problem in full scale lagoons. In small test situations, the ice has a high adhesive strength at the container's ice interface. In a large lagoon this adhesive strength will be much less and the interlayer ice bond will have to be sufficiently high to prevent the upper fluid from seeping through ice cracks and causing the lower layer to float. Also, some provision must be made to store about 30% of the ice volume, as the underdrain fluid containing approximately 80% of the nutrients must be removed.

Reservoir freezing is not without limitations either, even when the lagoons are already built. Firstly, the lagoons are designed to hold approximately 1.5 m (5 feet) of fluid before they are discharged. Since Prairie winters produce approximately 0.6 m (2 feet) to 0.9 m (3 feet) of ice, 40 to 60% of the fluid would have to be drawn off and stored in order to remove the nutrients. To make reservoir freezing practical, some modifications to present designs will be necessary.

Spray freezing also has potential for nutrient removal applications, especially since field studies (53, 54) have shown the process to be quite effective. As with layer freezing, primary solids removal will probably be necessary to minimize snow-jet plugging problems, however, in combination with some storage and summer irrigation, there is potential for year-round nutrient utilization.



## Chapter 6

### Conclusions

- (1) The results of this study indicates that both reservoir and layer freezing will effectively freeze concentrate the major organic and inorganic nutrients out of wastewater;
- (2) The removal efficiencies for both the reservoir and layer freezing tests ranged from 0% to 89% and 53% to 90% respectively for carbon-oxygen demand from >29% to 96% and >56% to 90% respectively for nitrogen and from 78% to >95% and 61% to 85% respectively for phosphorus;
- (3) The efficiency of nutrient removal for both reservoir and layer freezing compared favourably with results obtained by other investigators, primarily the Saskatchewan Research Council;
- (4) The results of the study demonstrate a significant variation in overall removal efficiency that indicates the removal mechanisms to be quite complex;
- (5) The results of this study do not demonstrate any strong relationship to theoretical considerations in which ionic or molecular radius and charge are influencing factors;
- (6) The influence of suspended solids and gravity settling, although not evaluated specifically, were visually noticeable and almost certainly influenced the results of both the layer and reservoir freezing simulations;

(7) The results of the freezing simulations do not show either of the freezing techniques, reservoir or layer to be superior in overall terms of nutrient removal;

(8) The microbiological results of both freezing techniques demonstrated a significant reduction in bacterial number measured by the Most Probable Number and Standard Plate Count. The Most Probable Number data demonstrated reductions from  $150,000^+$  to an average of about 500 for a 300 fold decrease, the Standard Plate Count data showed a reduction from  $10,000^+$  to an average of about 4,000, for a 60% overall reduction.

## Chapter 7

## Recommended Future Research

The results of this study indicate that the major nutrients in wastewater can be reduced in the ice by either reservoir or layer freezing. The results of spray freezing tests on wastewater corroborate this general conclusion. To practically utilize this technology however, there are a number of questions both theoretical and applied in nature that must be answered before freezing purification technologies can be used in any meaningful way. Much of the highly theoretical work is outside the field of environmental engineering and would fall into the research field of physical chemistry. At a more applied level, there are still some theoretical questions along with the many practical questions that require research. The research recommended to answer some of these engineering related questions is outlined below:

- (1) From a theoretical point of view, there is little laboratory data available to test the theories or mechanisms responsible for freeze-desalination. For example, very little is known of the make-up of the porosity or permeability network within ice or to what degree such factors as the rate of freezing affects the drainage network. A laboratory investigation of the physical make-up of permeability network would be very beneficial in leading to an understanding of the drainage process as related to ionic colloidal and larger sized matter;

(2) A theoretical evaluation of the influence of ionic and molecular radii and charge would also be of value in further understanding the process. This would necessarily include the freeze testing of a broad range of ionic and molecular species found in sanitary engineering. A range of solution strengths would demonstrate whether any saturation limit exists while mixtures of different species would indicate if and to what degree the results are interrelated;

(3) Of rather significant practical importance would be an evaluation of the conditions necessary to make any of the three freezing purification processes, whether reservoir, layer or spray freezing, economically viable. The concept behind this research was to reduce the organic loading on our rivers and streams. Irrigation is a promising application for the recycling of nutrients back into the food chain, however irrigation is possible without freeze purification. It is yet to be determined if freeze-purification would enhance the economics by reducing for example the acreage required. Without land application, some other forms of nutrient removal technique would be required. The viability of economically coupling freeze-concentration with other nutrient removal techniques should also be evaluated;

(4) From a more applied point of view, there are many questions that must be answered. For example, the influence of solids must be determined for both reservoir freezing but especially for layer freezing. The solids in raw wastewater could effectively reduce the permeability of the ice during the draining of layer freezing tests or it may be found that such solids settle quite rapidly on thawing of the ice;

(5) The Saskatchewan Research Council has demonstrated the feasibility of spray freezing for desalination using several full-scale applications. As well, at least two studies of spray freezing in the United States have verified the applicability of the process to wastewaters. The same is not however, true for reservoir but especially for layer freezing. There are questions as to whether layer freezing will work from a practical point of view. On the other hand, full scale reservoir freezing occurs each winter on the many lagoons on the Prairies.

It is recommended therefore, that periodic samples of the ice and supernatant quality be carried out for several lagoons in Manitoba. Lagoons with low, intermediate and high loading as well as lagoons that freeze almost to the bottom (leaky lagoons) would provide valuable information as to proof of concept for full scale applications.

References

- (1) Basset, L.G., et al, "Principles of Chemistry", Prentice Hall Inc., Englewood Cliffs, N.J., 1966.
- (2) Castellan, G.W., "Physical Chemistry", Addison Wesley Publishing Co., Toronto, Ontario, 1964.
- (3) Podolsky, R.J., "Transport Processes in Electrolyte Solutions", J. Amer. Chem. Soc., Sept. 1958, p. 4442-4451.
- (4) Luyet, B.J., "Anatomy of the Freezing Process in Physical Systems", Cryobiology, Academic Press, N.Y.C., 1966, pp. 115-138.
- (5) Vlasov, N.A., Chernyshev, L.A., "Hydrochemistry of the Ice and Dynamics of Distribution of Salt Between Ice and Brine in the Selenga Sulphate Lake", Dzvestia Fiz. Nauchno. Issled Inst., Vol. 5, No. 2, 1961.
- (6) Kervan, L., "Demineralization De L'Eau par Congelation", L'Eau, Nov. 1957, pp. 243-247.
- (7) Garrels, R.M. and Crist, C.L., "Solutions, Minerals and Equilibria", Harper and Row, New York, 1965.
- (8) Miller, C.E. and Turk, L.M., Fundamentals of Soil Science, John Wiley and Sons, New York, 1947.
- (9) Sawyer, C.N., McCarty, P.L., "Chemistry for Sanitary Engineers", McGraw-Hill Book Co., Toronto, Ontario, 1967.
- (10) Kreith, F., "Principles of Heat Transfer", International Textbook Co., N.Y.C., 1973.
- (11) Alter, A.J., "Sewerage and Sewerage Disposal in Cold Regions", Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, 1969.
- (12) Glen, J.W., "Physics of Ice", Cold Regions Research and Engineering Laboratory, Hanover, N.H., 1974.
- (13) Kingery, W.D., Goodnow, W.H., "Brine Migration in Ice", Ice and Snow, Properties, Processes and Applications, M.I.T. Press, Cambridge, Mass., 1963.
- (14) Handbook of Chemistry and Physics, Chemical Rubber Company, 46th Ed., 1967.

- (15) Harrison, J.D., "Solute Transpiration Pores in Ice", J. App. Physics, Vol. 36, 1965, pp. 326-327.
- (16) Lewis, E.L., and Lake, R.A., "Salt Rejection by Sea Ice During Growth", J. Geophys. Research, Vol. 75, No. 3, Jan. 1970, pp. 583-597.
- (17) Hoekstra, P., Osterkamp, T.E., and Weeks, W.F., The Migration of Liquid Inclusions in Single Ice Crystals, J. Geophys. Research, Vol. 70, No. 20, Oct. 1965, pp. 5035-5041.
- (18) Chalmers, B., "How Water Freezes", Scientific American, Vol. 200, No. 14, Feb. 1959.
- (19) Untersteiner, N., "Natural Desalination and Equilibrium Salinity Profile of Perennial Sea Ice", J. Geophys. Research, Vol. 73, No. 4, Feb. 15, 1968.
- (20) McKinney, R.E., "Microbiology for Sanitary Engineers", McGraw-Hill Book Co., N.Y.C., 1962.
- (21) Van Olphen, H., An Introduction to Clay Colloid Chemistry, Interscience Publishers, New York, 1963.
- (22) Reddick, T.M., "Control of Colloid Stability Through Zeta Potential", Levington Publishing Co., Wynnewood, Penn., 1968.
- (23) Wilhelm, and Gilverblatt, "Freeze Treatment of Alum Sludge", J.A.W.W.A., June, 1976.
- (24) Farrell, J.B., et al, "Natural Freezing for Dewatering of Aluminum Hydroxide Sludges", J.A.W.W.A., Vol. 62, Dec., 1970, pp. 787-791.
- (25) Corte, A.E., "Migration of Particles in Front of a Moving Freezing Plane", J. Geophys. Research, Vol. 67, No. 3, March, 1962, pp. 1085-1090.
- (26) Alter, A.J., "Treatment of Freezing", Purdue Water and Wastewater Conference, 1970, pp. 374-383.
- (27) Mazur, P., "Physical and Chemical Basis of Injury in Single-Celled Microorganisms Subjected to Freezing and Thawing", Chapter 6, Cryobiology, Academic Press, N.Y.C., 1966.
- (28) Hoar, W.S., General and Comparative Physiology, Prentice Hall Inc., Englewood Cliffs, New Jersey, 1966.
- (29) Nei, Tokio, Low Temperature Preservation of Microorganisms, Cryobiology, Federation Proceedings, Vol. 24, No. 2, Part 3, 1966, pp. 284-286.

- (30) Melnick, J.L., Preservation of Viruses by Freezing, Cryobiology Federation Proceedings, Vol. 24, No. 2, Part 3, 1966, pp. 284-286.
- (31) State-of-the-Art Survey and Economic Comparison of Freezing Processes, Office of Water Research and Technology, Dec., 1976, Pub. #PB-273-298.
- (32) Logsdon, G.S. and Edgerly, E., Sludge Dewatering by Freezing, J.A.W.W.A., #63, Vol. 11, 1971, pp. 734-740.
- (33) Cheng, C.Y., et al, Sludge Dewatering by High-Rate Freezing at Small Temperature Differences, Env. Sci. and Tech., Vol. 4, No. 12, December, 1970, pp. 1145-1147.
- (34) Fraser, J.H. and Johnson, W.E., The Role of Freezing Processes in Wastewater Treatment, Applications of New Concepts of Physical-Chemical Wastewater Treatment, Sept. 18-22, 1972, Vanderbilt University, Nashville, Tennessee.
- (35) Doe, P.W., et al, Sludge Concentration by Freezing, Water and Sewage Works Journal, Nov., 1965, pp. 401-406.
- (36) Geller, S.U., New Methods to Obtain Fresh Water in the Desert, Problemy fizichiskoy geografii, 1939, Vol. 7.
- (37) Geller, S.U., Desalting of Water by Natural Freezing for Farm Use, Izvestiya Akademii Nauk, U.S.S.R., seriya geograficheskaya, 1962, No. 5, pp. 71-77.
- (38) Geller, S.U., Desalting of Water by Freezing, Priroda, V.I., 1954, pp. 92-95.
- (39) Szekely, T., Water Purification by Freezing in Dugouts, Saskatchewan Research Council Report E-64-10, July, 1964, pp. 1-102.
- (40) Fertuck, L.J., et al, Desalination of Prairie Water Supplies by Natural Freezing in Reservoirs, Engineering Journal (C.S.C.E.), Jan., 1970, pp. 12-16.
- (41) Canadian Drinking Water Standards and Objectives, 1968.
- (42) Walker, D., Ice Observations, Philosophical Magazine and Journal of Science, Jan. - June, 1856, pp. 437-439.
- (43) Rae, J., On Some Physical Properties of Ice, Philosophical Magazine and Journal of Science, Vol. 47, Series 4, July - Dec., 1874, pp. 56-58.
- (44) Whitman, W.G., Elimination of Salt from Sea Water Ice, Amer. Jour. Sci., Series 5, Vol. 11, 12, 1926, pp. 126-132.
- (45) Mitlin, M.F., "Purification of Saline Water by Freezing", Vodosnabzh. i Sanit. Fekhn., 1963, No. 2, pp. 24-27.



- (46) Walton, W.C., Groundwater Resource Evaluation, McGraw-Hill Book Company, New York, 1970.
- (47) Spyker, J.W., "Laboratory Studies of Water Desalination by Layer Freezing", Saskatchewan Research Council Report E-67-8, 1967.
- (48) Fertuck, L.J., et al, "Desalination of Brackish Water Supplies by Layer Freezing", Engineering Institute of Canada, Chem. #1, 1971, pp. 29-33.
- (49) Bishop, S.L., et al, "Lagooning and Freezing for Disposal of Water Plant Sludge", Public Work Journal, 99(6): June, 1968.
- (50) Adams, C.M., et al, "Field Solidification and Desalination of Sea Ice", Ice and Snow, Properties, Processes and Applications, The M.I.T. Press, Cambridge, Mass., 1963, pp. 277-387.
- (51) Spyker, J.W., et al, "Desalination of Brackish Water by Spray Freezing", C.S.C.E., April, 1973, pp. 24-38.
- (52) Spyker, J.W., "Desalination of Brackish Water by Spray Freezing", Saskatchewan Research Council Report E-78-3, Feb., 1978, pp. 1-107.
- (53) Flander, P.H., "Spray Disposal of Treated Domestic Wastewater on Upland Fragepan Soils in Severe Winter Climate", Conference on "Water Pollution Control in Low Density Areas", University of Vermont, Hanover, New Hampshire, 1975.
- (54) Wright, K.R., Sewage Effluent Turned to Snow: Provides Storage Removal Pollutants, A.S.C.E., May, 1976.
- (55) Baker, R.A., "Microchemical Contaminants by Freeze Concentration and Gas Chromatography", W.P.C.F. Journal, Vol. 38, No. 8, August, 1965.
- (56) Kammerer, P.A. and Lee, G.F., "Freeze Concentration of Organic Compounds in Dilute Aqueous Solutions", Env. Sci. and Tech., Vol. 3, No. 3, March, 1969.
- (57) Personal Communication, Jim Adams, Senior Chemist, Rural Water Services Board, Dept. of Agriculture, Government of Manitoba.
- (58) Standard Methods for the Examination of Water and Wastewater, 14th Ed., 1975, A.P.H.A., A.W.W.A., 1015 - 18th Street N.W., Washington, D.C.
- (59) Dorfner, K., Ion Exchanges, Properties and Applications, Ann Arbor Science, 1972.

- (60) Gehm, H.W. and Brigman, J.I., Handbook of Water Resources and Pollution Control, Van Nostrand Reinhold Co., Toronto, 1976.
- (61) Design Objectives for Standard Sewage Lagoons, Manitoba  
Dept. of Mines, Resources and Environmental Management,  
Environmental Engineering, April, 1973..