PRINCIPLES AND TECHNIQUES FOR CONDITIONING OF WASTE-ACTIVATED SLUDGE BY DIRECT SLURRY FREEZING

by

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TABLE OF CONTENTS

Chapter Page

I. INTRODUCTION 1

Objectives of Investigation. 5

II. LITERATURE REVIEW. 7

Freezing Mechanisms and Applications 10
  Desalination by Freezing 10
  Freezing Processes Comparison. 18
  Application to Industrial Wastes 21
  Economics of the Freezing Process. 22
Description and Requirements of Direct Butane Freezing Process. 22
Freezing as a Conditioning Aid for Chemical Sludges 32
Freezing as a Conditioning Aid for Biological Sludges 48
Measurement of Conditioning Effects. 84
  Settleability. 85
  Filterability. 85
  Drainability 91
Summary. 94

III. EXPERIMENTAL METHODS AND MATERIALS 95

Sources of Sludge 95
Sludge Characterization Studies. 96
Freezing Processes and Experimental Design . 97
Tests and Procedures Employed for Sludge Conditioning Evaluations 103
Butane Recovery and Stripping. 107
Evaluation of Freon as an Alternate Refrigerant to Butane 108
Application of Direct Freezing to Waste Sludges from Other Sources 109

IV. EXPERIMENTAL RESULTS 111

Sludge Characterization. 111
  Sludge "A". 112
  Sludge "B" 112
  Sludge "C" 113
General Observations of the Direct Freezing Continuous Flow Process. 114

Chapter Page

Effect of Direct Slurry Freezing on Sludge, Supernatant, and Filtrate Properties. . 116
Effect of Butane Flow Rates 124
Comparison with Other Processes 124
Effect of Operational Procedures on Subsequent Dewaterability of Freeze Conditioned Sludge. 128
Free Solids Concentration 128
Variation of Applied Filtration Vacuum. . 143
Effect of Solids Loading and Alum Addition (gravo-vacuum system) 147
Effects of Storage Time on Subsequent Dewatering. 153
Dewatering Characteristics on Sand Beds . . 153
Physical Changes in Directly Frozen Sludge. 160
Wet Sieve Analysis. 162
Feasibility of Substituting Freon-114 for Butane 162
Effect of Sludge Origin on Applicability of Direct Freezing. 162
Pulp and Paper Waste Sludge Results . . . 164
Aerobically Digested Sludge Results . . . 164
Direct Freezing Process Economics 165

V. DISCUSSION OF RESULTS 169
Sludge Characterization 169
Direct Freeze Conditioning. 170
Specific Resistance, Coefficient of Compressibility and Filter Cake Quality . 177
Dewatering Characteristics on Sand Beds . 180
Butane Stripping from Supernatant 182
Application to Waste Sludges from Other Sources 182

VI. CONCLUSIONS 184

BIBLIOGRAPHY 186

APPENDIX I - DESCRIPTION OF SOURCES OF SEWAGE SLUDGES 203

APPENDIX II- C.O.D. AND SOLIDS MASS BALANCE . 206

APPENDIX III-GRAVITY DRAINAGE AND AIR DRYING ON SAND BEDS 213

APPENDIX IV-BUTANE PROCESS ECONOMICS AND COMPARISON TO OTHER PROCESSES 226

APPENDIX V - APPLICATION OF DIRECT FREEZING TO WASTE SLUDGES FROM OTHER ACTIVATED SLUDGE PROCESSES 236

VITA 242

LIST OF FIGURES

Figure Page

1. Schematic representation of waste sludge handling and disposal techniques 8

2. Schematic representation of possible methods for the physical conditioning of waste sludges. 9

3. Vacuum freezing vapor compression process. . . 12

4. Vacuum-freezing ejector or absorption process. 13

5. Secondary refrigerant process. 15

6. Hydrocarbon freezing process flow diagram for sea water conversion 24

7. Energy penalty for driving force (Wiegandt, 142) 29

8. Equilibrium concentration of butane in water (Total P = 1 atmosphere) 31

9. Mechanism of solids migration. 44

10. Influence of electrolyte concentration on freezing pattern (117) 46

11. Simplified bacterial structure 68

12. Diagrammatic representation of growth of extra-cellular ice (continuous black area) during freezing of muscle tissue, showing the progressive dehydration of cell. 71

13. Approximate survival of E. coli as function of temperature.. 73

14. Hypothetical model of cause of damage from intracellular freezing 74

15. Proposed mechanism of freezing injury by Levitt and Dear 76

16. Typical freezing curves for the rate at which the temperature of the food falls when the food is subjected to different rates of freezing 77

Figure Page

17. Survival of bacteria as a function of length of storage at immediate temperatures 82

18. Sludge freezing by batch process 98

19. Butane recovery and continuous flow apparatus. 100

20. Effect of butane contact time on specific resistance (Sludge "C") 117

21. Variation of moisture content with time of dewatering by gravity drainage (Sludge "C"). 118

22. Effect of butane flow rate and contact time on specific resistance (Sludge "B") 120

23. Effect of butane flow rate and contact time on the quality of cake (Sludge "B") 121

24. Effect of butane contact time on sludge settleability (Sludge "B") 122

25. Variation of interfacial settling velocity and S.V.I. with butane contact time (Sludge "B") 123

26. Effect of butane flow rate on sludge settleability (Sludge "B") 125

27. Variation of interfacial settling velocity and S.V.I. with different butane flow rates (Sludge "B") 126

28. Comparison of direct freezing method to others-sludge settleability as criteria (Sludge "B") 127

29. Effect of feed sludge solids concentration on sludge settleability (Sludge "B" 130

30. Effect of solids concentration on settling characteristics (Sludge "A") 131

31. Effect of solids concentration on the settling characteristics (Sludge "C") 132

32. Effect of solids concentration in feed sludge on the S.V.I. and interfacial velocity (Sludge "B") 134

Figure Page

33. Variation of settling velocity with solids concentration (Sludge "A" and "C"). 135

34. Effect of feed sludge solids concentration on the specific resistance (Sludge "B"). . . . 137

35. Effect of feed solids concentration on the specific resistance (Sludge "A") 138

36. Effect of feed solids concentration on specific resistance and moisture content (Sludge "C"). 140

37. Effect of feed sludge solids concentration on the filter cake quality (Sludge "B") . . 141

38. Effect of feed sludge solids concentration on the quality of cake (Sludge "A") 142

39. Effect of applied vacuum on specific resistance and coefficient of compressibility (Sludge "B"). 144

40. Effect of applied vacuum on specific resistance and coefficient of compressibility (Sludge "A"). 145

41. Effect of applied vacuum on specific resistance and coefficient of compressibility (Sludge "C"). 146

42. Effect of vacuum on the quality of filter cake (Sludge "B") 148

43. Effect of applied vacuum on the quality of filter cake (Sludge "A"). 149

44. Effect of applied vacuum on the quality of filter cake (Sludge "C"). 150

45. Effect of solids loading on dewatering time, after gravo-vacuuming (Sludge "A"). 151

46. Effect of solids loading on the rate of production of solids and cake quality (Sludge "A"). 152

47. Bench scale sand bed studies--dewatering due to gravity drainage (Sludge "B"). 154

Figure Page

48. Bench scale sand bed studies--dewatering due to air drying (Sludge "B") 156

49. Effect of feed sludge solids concentration on the cake quality (Sludge "B"). 157

50. Effect of feed sludge solids concentration on the cake quality (Sludge "A"). 158

51. Effect of feed sludge solids concentration on the cake quality (Sludge "C"). 159

52. Effect of solids loading on the cake quality (Sludge "B") 161

53. Effect of butane contact time on the flocculation (Sludge "C"). 163

54. Effect of applied vacuum on butane stripping from supernatant (Sludge "C"). 166

55. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "B") 214

56. Bench scale sand bed studies, dewatering due to air-drying (Corning Glassworks Sludge). . 215

57. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "B") 216

58. Bench scale sand bed studies, dewatering due to air-drying (Sludge "B") 217

59. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "A") 218

60. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "A") 219

61. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "A") 220

62. Bench scale sand bed studies, dewatering due to air drying (Sludge "A") 221

63. Bench scale sand bed studies, dewatering due to air drying (Sludge "A"). 222

Figure Page

64. Bench scale sand bed studies, dewatering due to air drying (Sludge "A") 223

65. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "C") 224

66. Bench scale sand bed studies, dewatering due to air drying (Sludge "C") 225

67. Effect of coagulant dosage on the specific resistance (Pulp and Paper waste sludge) . . 237

68. Effect of coagulant dosage on the filter cake quality (Pulp and Paper waste sludge) . 238

69. Settleability of pulp and paper waste sludge after direct freezing. 239

70. Variation of rate of solids production with 1000 p.p.m. Al+++ coagulant dosage using gravo-vacuum system (Pulp and Paper waste sludge) 240

71. Effect of direct freezing on specific resistance and moisture content of aerobically digested sludge at different temperatures 241

LIST OF TABLES

Table Page

A-1. Solids Mass Balance (Sludge "A"). 207

A-2. C.O.D. Mass Balance (Sludge "A"). 208

A-3. Effects of Solids Concentration on the Supernatant and Filtrate Quality (Sludge "A"). 209

A-4. Solids Mass Balance (Sludge "B"). 210

A-5. C.O.D. Mass Balance (Sludge "B"). 211

A-6. Solids Analysis Sludge "C" (Batch Process). . . 212

A-7. Comparison of Butane-Freezing Process for Waste Activated Sludge Dewatering with the Other Processes (Part 1). 232

Comparison of Butane-Freezing Process for Waste Activated Sludge Dewatering with the Other Processes (Part 2) 234

CHAPTER I

INTRODUCTION

During the past decade, waste generation, an inevitable consequence of life, has accelerated because of rapid growth in population, the rising standard of living and extensive industrial and commercial development. These wastes, if discharged without removal of pollutants to streams, rivers and estuaries, will deplete their assimilative capacities, thus resulting in deterioration of the water quality.

Because of increasing public concern over water pollution and more rigorous water pollution control requirements by legislation, there has been a considerable increase in the use of secondary or biological wastewater treatment facilities for the removal of pollutants from the wastes generated. Such treatment results in a by-product which contains most of the objectionable pollutants, pathogens, and heavy metals. This by-product, called "sludge," has become perhaps the most important consideration to be faced in cleaning up the nation's waters because of its potential effect on the environment. The most common practice, so far, has been ocean dumping or land disposal. It is expected that within the next 10 to 15 years, the sludge volumes produced will increase by 60 to 70 percent (3). Yet, suitable land disposal sites are becoming expensive and less accessible and ocean dumping is being prohibited by legislation. Furthermore, incineration, with its heavy capital investment and operating costs increased by the necessity of installing expensive air pollution control devices, has become nearly prohibitive in most areas. It is apparent that new sludge handling technologies are needed to meet the challenge (3).

The handling and disposal of sludge consists mainly of four steps:

1. concentration or thickening,
2. conditioning,
3. dewatering, and
4. disposal.

Of the four, Steps 2 and 3 are the most important because they contribute most to the success of the disposal process. The purpose of conditioning and dewatering is the removal of the large quantities of water associated with the sludges. For example, a thin waste activated sludge from biological treatment may contain well over 100 tons of water per ton of dry solids (1).

Economic studies have repeatedly shown that although the waste sludge quantity at the sewage treatment plant represents only 1 to 3 percent of the total wastewater flow, the sludge disposal costs are typically 30 to 50 percent of the total costs associated with complete treatments; i.e., both capital and operating costs (2, 6, 7, 12). It has been frequently noted by experts in the waste disposal field that "sludge handling is by far the most difficult problem in sewage treatment" (4, 5).

Of all the sludges produced during the processing of municipal wastewater, biological sludges are the most difficult to handle and dewater, and waste activated sludge, because of its flocculant, voluminous and hygroscopic nature, is the most difficult of all the biological sludges to handle. In spite of this drawback, more sewage is treated by activated sludge than by any other biological process and, because of its potential efficiency, its use is increasing as the treatment requirements become more stringent. It is expected that by 1980, 140 m.g.d. of secondary sludges (2% solids) will be produced in the U.S.A., whereas only 10 m.g.d. of primary sludges (6% solids) are expected in that year (3). The growth of the problem and concern about it is evidenced by the number of related publications (2, 8, 9, 10, 11).

Clearly the processing of sludge for ultimate disposal by progressive reduction in sludge volume through removal of associated water is a very significant part of pollution abatement from an economic standpoint, and should be seriously considered in design. In spite of its obvious importance, there is no one sludge treatment system that meets the needs of an expanding metropolitan area, and selection and design of a sludge handling system is a very difficult and confusing task. Yet very little basic research has been devoted to the development of new sludge handling procedures in recent years. Some of the existing sludge conditioning processes are either very costly, e.g., chemical conditioning (2) and indirect freezing (2), or the supernatants produced are so poor that the return of flow to the treatment system can cause efficiency failures of the entire system, e.g., anaerobic digestion (2) and heat treatment (13, 14, 15, 16, 17). Although indirect freezing is very efficient in sludge conditioning for improved dewatering (18, 19, 27, 28, 29, 32, 33, 36, 37), it is very uneconomical and restricted to batch processes. Burd (2) speculated that "undoubtedly artificial freezing (indirect freezing) can aid sludge-dewatering; however, it probably will never be practical unless the economics are improved greatly." The main reason this process is uneconomical is because of its inability to make use of the latent heat of fusion of previously frozen sludge to cool the refrigerant used. This would conserve about 75 to 80 percent of the energy (27) and it is one of the most important single factors in the economics of the freezing process.

Most of the sludge treatment processes have their difficulties and drawbacks, particularly in regard to certain types of sludges. Hence it would seem that any new sludge conditioning process which could overcome or reduce conditioning difficulties and be operated in a reasonably economical manner would be worthy of investigation and that the results of such an investigation would be of interest. Since freezing difficulties are primarily economical, developmental work on a sludge conditioning process by freezing would appear to be a promising area.

Objectives of Investigation

The principal objectives of this research were to: (1) develop a direct freezing process--one where the refrigerant is directly in contact with the aqueous solution--using normal butane as the refrigerant, that can overcome the shortcomings of indirect freezing, (2) study the conditioning effects of this type of freezing on waste activated sludge from different sources, and (3) determine the economic feasibility of the process from continuous flow studies.

Specific questions to be answered were as follows:

1. Is direct freezing applicable to waste activated sludge conditioning? If so, is solid or slurry freezing more desirable?
2. What are the butane requirements and contact times needed per unit of mixed liquor? How beneficial are prolonged contact times after freezing?
3. What are the relative effects of different rates of freezing, i.e., slow or fast; different feed sludge solids concentrations; and different

influent sludge temperatures on subsequent sludge dewatering? What quality of filter cake, filtrate, and supernatant can be obtained?

4. How does the direct freezing process compare to other sludge conditioning processes economically?
5. Can Freon be substituted for butane?
6. Can the process be applied without modifications or operational changes to waste sludges other than activated sludge?

CHAPTER II

LITERATURE REVIEW

While the problem of sludge handling and disposal is growing every day, it is not new. In fact, in 1869 the British Association Committee on the treatment and utilization of sludge seriously looked into this problem. A book entitled, A Digest of the Facts Relating to the Treatment and Disposal (utilization) of Sewage, (21) was published and, at a later date, a symposium (22) on the methods of sludge handling and disposal was conducted.

There is no "one" single method of sludge conditioning for disposal for all types of sludges and localities. The most suitable method varies from place to place, depending upon the economic situation, the land available, etc. A review of the literature reveals that for ultimate disposal of sludge there are many possible combinations of concentration (thickening), conditioning, and dewatering methods. These have been summarized in Figure 1. Possible methods of physical conditioning have been summarized in Figure 2.

It appears from the literature that processes like anaerobic digestion (44, 45, 49), aerobic digestion (2, 9, 11, 46, 47, 48), heat treatment (13, 14, 15, 16, 17), and polymer conditioning (40), are well defined and understood,

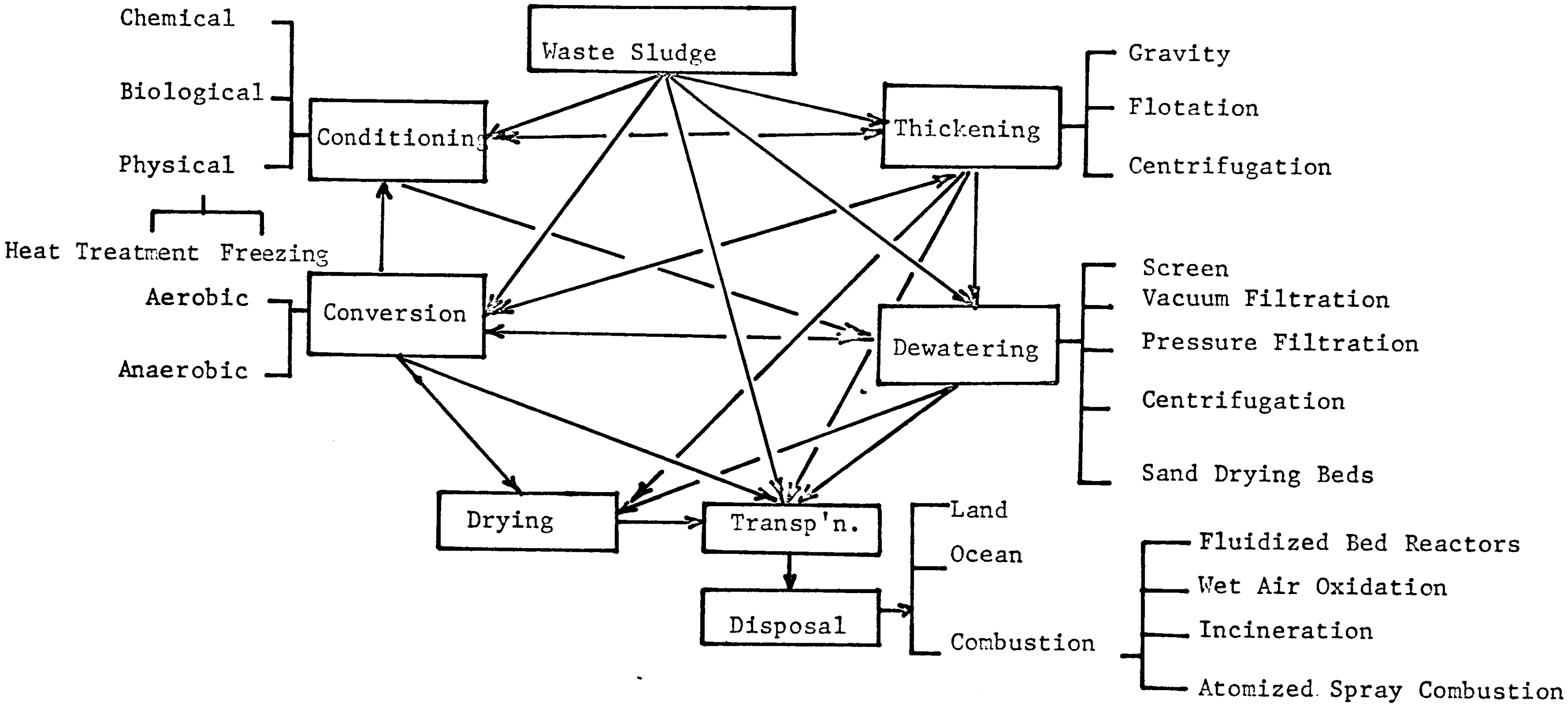

Chemical
Biological
Physical
Heat Treatment
Freezing
Aerobic
Anaerobic
Conditioning
Conversion
Waste Sludge
Drying
Transp'n.
Disposal
Thickening
Dewatering
Gravity
Flotation
Centrifugation
Screen
Vacuum Filtration
Pressure Filtration
Centrifugation
Sand Drying Beds
Land
Ocean
Combustion
Fluidized Bed Reactors
Wet Air Oxidation
Incineration
Atomized Spray Combustion

Figure 1. Schematic representation of waste sludge handling and disposal techniques.

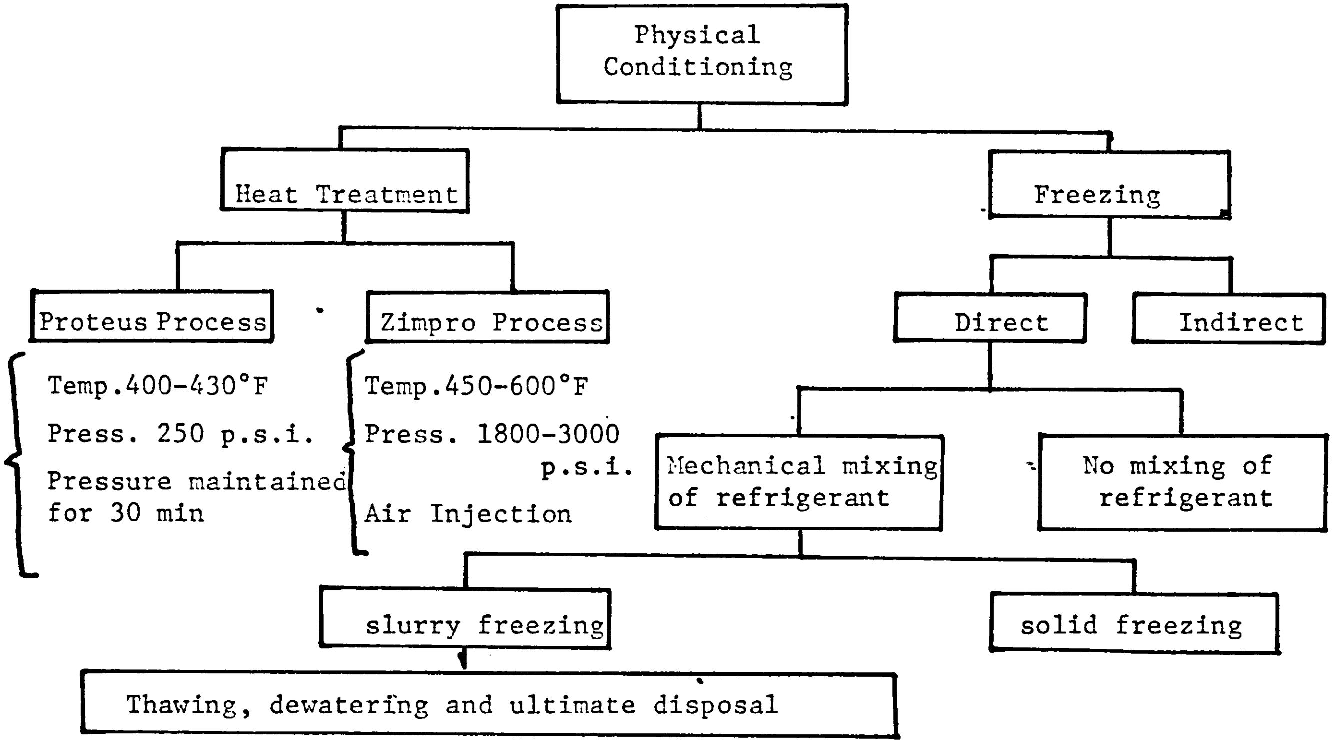

Physical Conditioning
Heat Treatment
Freezing
Proteus Process
Zimpro Process
Direct
Indirect
Temp.400-430°F
Press. 250 p.s.i.
Pressure maintained for 30 min
Temp.450-600°F
Press. 1800-3000 p.s.i.
Air Injection
Mechanical mixing of refrigerant
No mixing of refrigerant
slurry freezing
solid freezing
Thawing, dewatering and ultimate disposal

Figure 2 . Schematic representation of possible methods for the physical conditioning of waste sludges.

but the process of freezing, while known to be quite efficient for sludge conditioning, is still not very well understood and the need for additional research is recognized.

The first part of this chapter has been devoted to reviewing the literature pertaining to the utilization of the freeze-conditioning process for applications such as desalination, chemical sludge conditioning and biological sludge conditioning with emphasis on mechanism and economics. The second part of the chapter discusses theories and practice of sludge gravity settling and sludge dewatering by vacuum filtration and gravity drainage on sand beds.

Freezing Mechanisms and Applications

Desalination by Freezing

The primary role of freezing in desalination is to provide a means to concentrate and, at the same time, recover water from wastes containing dissolved solids. For the last 20 years, the concept of extracting pure water from saline solutions by freezing has been under active investigation and consideration. Several forms of freezing processes are as follows:

1. Natural freezing: Freezing occurs due to natural climatic temperature changes. No freezing cost is involved. It is very useful in the northern parts of the U.S.A. and other

parts of the world where temperatures are low enough to cause natural freezing; hence "natural" conversion of saline water to fresh water. Inhabitants of western Siberia and central Asia have, for generations, used the concept of desalination of saline water by freezing, using ditches where the ice is allowed to melt in sunlight and is then used for watering cattle, etc.

2. Vacuum-Freezing: (Figure 3). In this case ice is formed using the water itself as the refrigerant by vaporizing it under 3 mm absolute pressure. The water vapor may be compressed and condensed into washed ice, which is recovered as fresh water.
3. Vacuum-Freezing Ejector Absorption Process: (Figure 4). In this freezing concept, the same process is used as in simple vacuum freezing, but it includes a system consisting of an ejector and absorption. An ejector powered by a portion of the steam in the regenerator replaces the main (mechanical) compressor used in the vacuum freezing system (3). This is a much more complex system, but it is less mechanical in that both the primary and heat removal compressors have been eliminated.

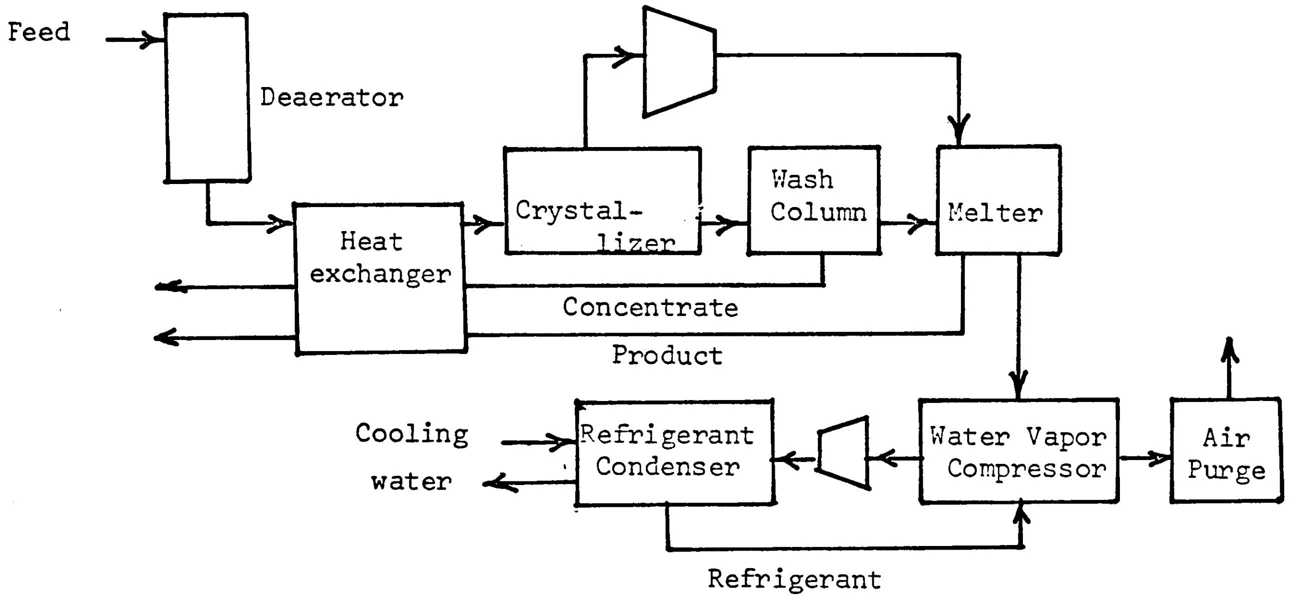

Feed
Deaerator
Heat exchanger
Crystal-lizer
Wash Column
Melter
Concentrate
Product
Cooling water
Refrigerant Condenser
Water Vapor Compressor
Air Purge
Refrigerant

Figure 3. Vacuum Freezing Vapor Compression Process. (Fraser, 163)

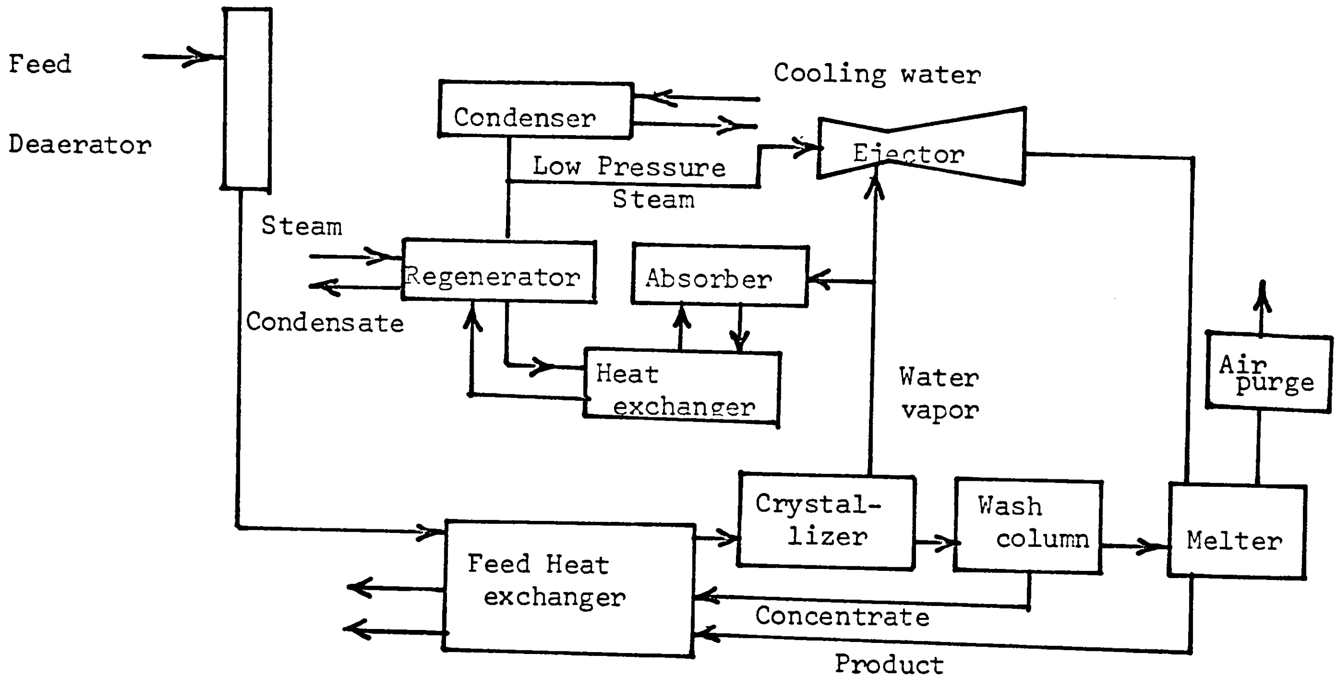

Feed
Deaerator
Steam
Condensate
Condenser
Cooling water
Low Pressure Steam
Ejector
Regenerator
Absorber
Heat exchanger
Water vapor
Air purge
Crystal-lizer
Wash column
Melter
Feed Heat exchanger
Concentrate
Product

Figure 4. Vacuum-Freezing Ejector or Absorption Process.(Fraser, 163)

4. Secondary Refrigerant Process: (Figure 5) In this process an immiscible refrigerant, which has a boiling point lower than the freezing point of aqueous solution, is introduced into the system. Heat exchange occurs between the refrigerant and the aqueous solution, refrigerant is vaporized and then compressed and condensed onto the ice crystals, which are recovered as fresh water. In turn, hot refrigerant vapors are liquified for reuse in the system.

The desalination mechanism of the freezing process can be explained using the following theories: 1) theory of crystallization, 2) theory of separation and wash, and 3) theory of melting.

1. Theory of Crystallization: Crystallization of ice from sea-water consists of two steps, the formation of nuclei and their growth to desired dimensions. The degree of undercooling of brine is the controlling factor in both steps. To obtain high quality crystals, the rate of cooling and the uniform distribution of undercooling of brine throughout the system are the most important factors. The cooling rate depends upon the rate and efficiency of heat transfer, which may be summarized as follows:

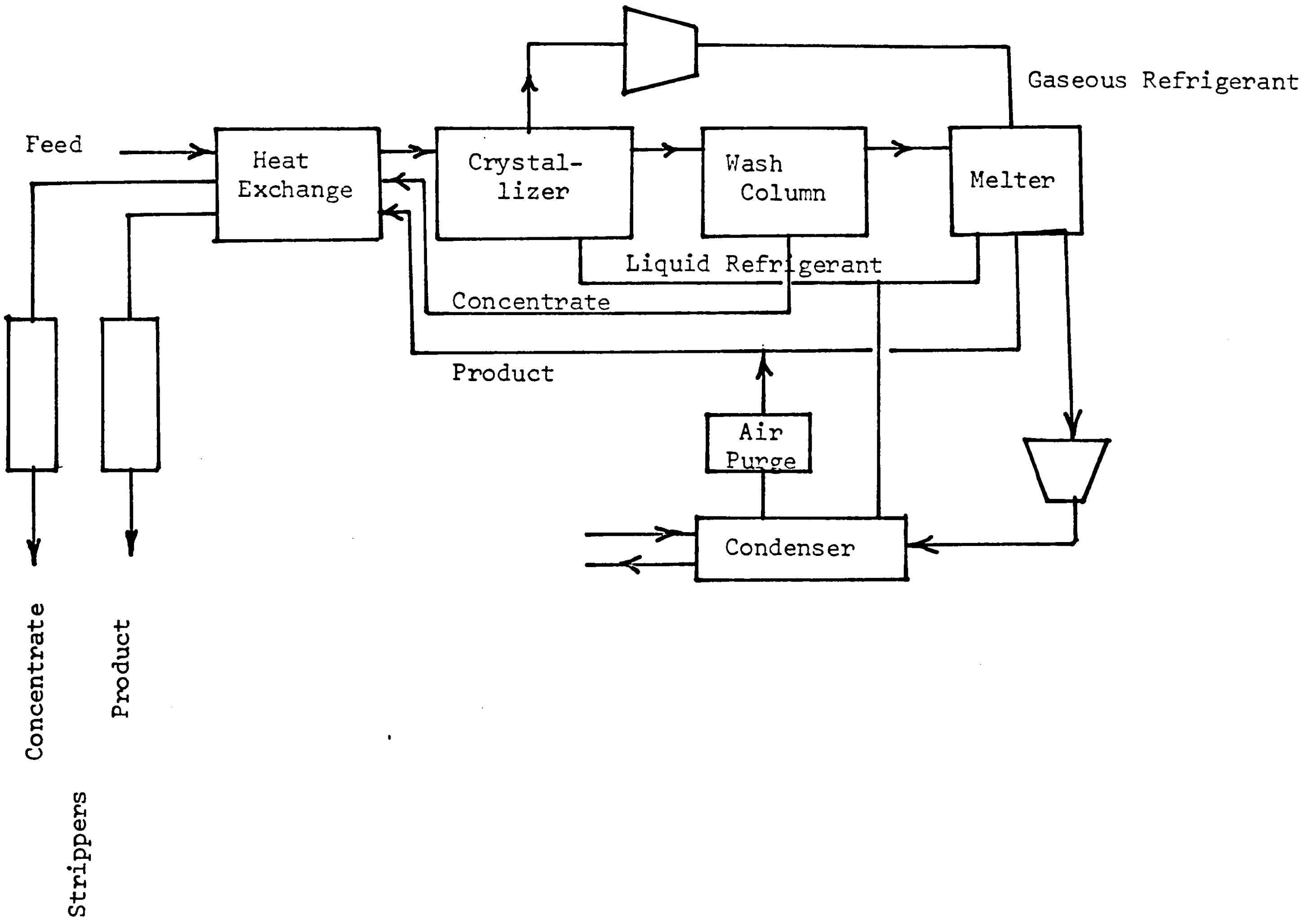

Gaseous Refrigerant
Feed
Heat Exchange
Crystal-lizer
Wash Column
Melter
Liquid Refrigerant
Concentrate
Product
Air Purge
Condenser
Concentrate
Product
Strippers

Figure 5. Secondary Refrigerant Process. (Fraser, 163)

Ice	Aqueous liquid	Refrigerant liquid	Refrigerant vapor	
→	→	→	→	Heat Transfer
	→			Salt Diffusion
	←			Salt Bulk Transport
	←			Water Transport

As the crystal grows, the heat generated is transferred to the aqueous phase, which in turn warms the refrigerant liquid and vaporizes it.

2. Theory of Separation and Wash: The separation of ice crystals from the ice-brine is carried out in especially designed equipment. Physical characteristics, i.e., the size and specific gravity, of the ice crystals affect their efficient separation from the brine. A description of the mass transfer taking place in the separation wash column was proposed by Bosworth et al. (31). In the wash column a consolidated porous bed of ice particles moves upward vertically. Brine adheres to the surface of the particles because of viscous forces and is held in the interstices by capillary forces. Washwater flows downward in a countercurrent direction. A velocity gradient exists between the fluid associated with the ice and the washwater, but mixing

of the two occurs by diffusion. Salt diffuses from the brine to the washwater, thus freeing the ice of its salt content and increasing the salt concentration in the wash liquor. Pure ice crystals are then pumped to the melter.

3. Theory of Melting: Hot refrigerant vapors from the freezer or crystallizer are condensed onto the ice crystals in the melter, where heat exchange occurs between the refrigerant vapors and the ice crystals. The ice crystals after melting become liquid water, which is drawn off at the bottom of the melter, while hot vapors of refrigerant become liquified and because of a lower specific gravity than water, float in the top section of the melter, from which they are recirculated for reuse in the freezer.

The potential economic attractiveness of the freezing processes for desalination is due to the following inherent advantages: 1) low energy consumption, 2) low capital cost, 3) no pre-treatment required, and 4) universal applicability to a wide variety of waters.

1. Low energy consumption is due to the direct contact heat transfer resulting in smaller temperature differences.
2. Low capital cost is due a) to direct contact

heat exchange in the freezer, thus eliminating the use of heat transfer surfaces and possible scaling and fouling thereof, b) to the absence of air (or oxygen) and the presence of low temperatures which prevent significant scaling or corrosion, thereby permitting the usage of low cost materials of construction such as mild steel, plastics and other inexpensive materials.

3. Pre-treatment of feed water is not required, because of direct contact heat transfer in the freezer. Due to the absence of transfer surfaces there are no concentration gradients near surfaces to cause scaling, and precipitates formed due to changes in solubility will leave the freezer with the brine.
4. Almost any liquid containing dissolved solids, organic and inorganic, can be treated, because of absence of scaling, fouling and no pretreatment. Thus the process can be used for the concentration of industrial wastes as well as for desalination.

Freezing Processes Comparison

Vacuum freezing, though comparatively simple, has many disadvantages, the main one being the handling of large volumes of low pressure vapors resulting in a larger overall size of plant but low efficiency. Due to low pressure operation in the freezer (3 mm absolute pressure) water pressure has a specific volume of 4,600 cubic feet per pound. Such processes have been used by Zarchin (Israeli government), Colt Industries (U.S.A.) and also by Carrier Corporation (U.S.A.). Colt (136) pointed out that such a plant at St. Croix, Virgin Islands with a capacity of 100,000 g.p.d. will produce water for $1.35/1000 U.S. gallons, assuming 45 Kw.hr/1000 gallon, 75°F sea water temperature, $0.01 per Kw.hr for power and labor cost for one-half man per day. The recent design includes all three major functions, freezing, washing and melting, in the same vessel.

The vacuum freezing ejector-absorption process, though comparatively simpler than the vacuum freezing process, still has the physical size disadvantage associated with the low pressure. Another disadvantage is due to the use of NaOH as an absorbant. NaOH is very corrosive and, hence, more expensive materials of construction must be used in the system. Also a factor which will limit application is that steam could be used as a source of pressure only at places where low cost steam is available. If steam generation equipment has to be installed, the additional equipment will make the process more complex.

The secondary refrigerant process overcomes most of the disadvantages of the low pressure in vacuum freezing caused by the introduction of an immiscible refrigerant. The volume needed to be handled in this case is 1/100th of the volume of the water vapor. It eliminates energy loss associated with condensing the excess water vapor on a refrigerated surface as in the vacuum freezing process.

Carrier (136), while comparing different freezing processes for desalination assuming a plant size of 600 m^3/day fresh water, reported that costs were \$0.51/m^3 and \$0.39/m^3 respectively for vacuum flash freezing (with absorption) and secondary refrigerant (C-318) respectively. Brian (140) reported that water costs by butane freezing were \$0.337/m^3 (for a plant size of 4000 m^3/day) and \$0.188/m^3 (for a plant size of 20,000 m^3/day (5 million U.S. gallon/day).

Fraser (163) reported that direct freezing costs, in addition to the process cost, could increase due to the following influent effects:

1. Influent Temperature Effects: Temperature affects the size of feed heat exchangers and the size and approach temperature of heat condensers. In case of desalination, sea water is used in both of the above cases, but for industrial wastes freezing where separate heat removal arrangements have to be made, the increase in cost could be 2¢ to 3¢ per 1000 gallons of feed per 10°F temperature rise.

2. Increase in Freezing Point Depression: The combined effect of increased energy consumption and increased capital cost caused by lowering the freezing point amounts to about 2¢/°F per 1000 gallons of product water.
3. Viscosity: Heat transfer in the feed heat exchanger varies inversely as the square root of the viscosity, and the pressure drop varies as the two-thirds power of the viscosity. To compensate for a reduced heat transfer coefficient, agitator power has to be increased. The viscosity effects could cost a few cents per 1000 gallons of water.

Application to Industrial Wastes

Fraser (163) showed that freezing of industrial wastes could be grouped into three main categories: 1) concentration for by-product recovery, 2) concentration for reuse in a process, and 3) concentration for disposal. He showed that freezing could be used to concentrate different streams from the following industrial wastes at reasonable costs: 1) metal finishing, 2) paper mills, 3) acid mine water (162), and 4) tanneries and textiles. The costs of recovery were comparable to or better than other potential processes.

Economics of the Freezing Process

Power consumption for the process can vary from 30 to 60 Kw.hr per 1000 gallons of water extracted, so with power costs varying from .005 to 2¢ per Kw.hr, the treatment cost could range from $0.15 to $1.20 per 1000 gallons. Capital cost could contribute $0.21 to $1.27 per 1000 gallons to the treatment cost. Labor costs, using one-half man per year for a 100,000 g.p.d. plant and a man year for a one m.g.d. plant, would be 61¢/1000 gallon and 8¢/1000 gallon respectively for the above plants. Other costs, such as maintenance, materials, and make up refrigerant would add about 4¢ to 8¢/1000 gallons. Hence, the total cost of the freezing process would vary over a wide range, but the secondary refrigerant process would still be cheaper.

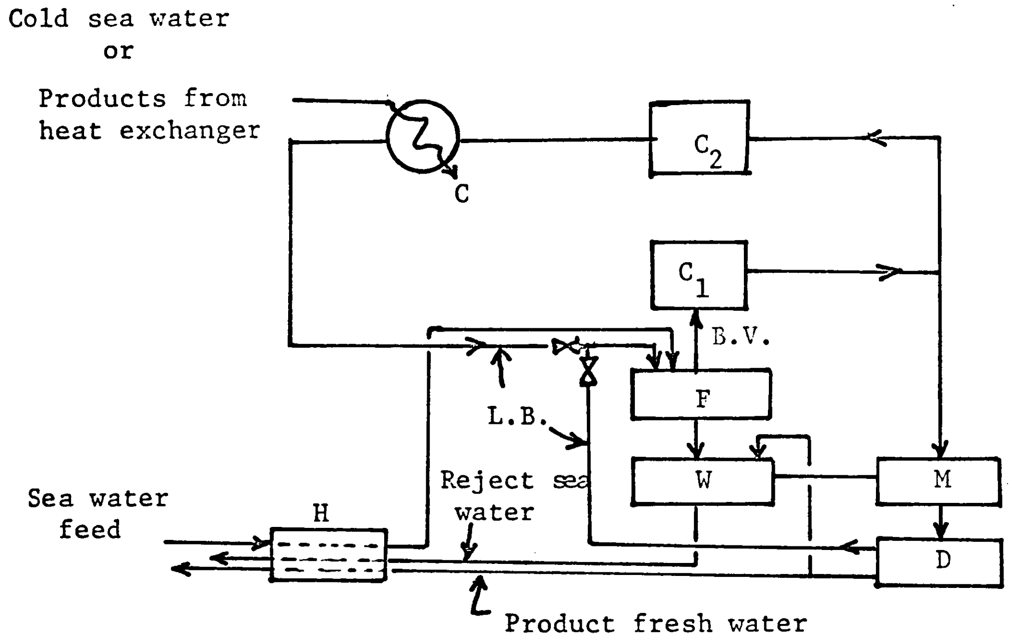
Description and Requirements of Direct Butane Freezing Process

Of the numerous processes which have been proposed for desalination of sea water, direct freezing and melting with normal butane (or isobutane) in a closed cycle offers the most immediate promise of achieving a thermodynamic efficiency in practical equipment. The process was briefly described by Gilliland (141) and was proposed to the Office of Saline Water by Wiegnadt (142) and analysed by Henrickson *et al*. (143). Zarchin patented a process of freezing with a secondary refrigerant (144). In Japan, sea water is concentrated in a pilot plant capable of producing 8000 kg/

hr of ice, based on a patent (145) to Umano. Wiegnadt (142) and the Blawknox Company have done some work on this process.

The process is shown schematically in Figure 6. Sea water is partially frozen to a slush in the freezer (F) by direct contact with boiling butane at a pressure slightly below atmospheric. Since butane (boiling point is 31°F at 14.7 p.s.i.) will boil below the freezing point of salt water, the heat of vaporization (165 BTU/lb) is supplied by the heat of freezing of water (144 BTU/lb). It is necessary that butane and water be brought into intimate contact by mechanical mixing. The ice-brine slurry is pumped to the ice-washer (W) by counter-washing with a clear stream of water. Brine, being heavier, remains in the lower chamber from where it is pumped to the heat exchanger (H), while the ice crystals are taken into the melter (M) where the butane vapors from the freezer are compressed. The mixture flows from the melter into the decanter (D) where liquid butane from the top is recycled back in the freezer and the melted fresh water is recovered.

Freezing occurs when the temperature of the sea water to be purified is reduced in temperature to a point where ice crystals are formed. This is a thermodynamic system, in which inflow and outflow of heat must be carefully controlled. The cost of energy is one of the largest items of expense in any desalination process. Regardless


Cold sea water
or
Products from
heat exchanger
C
C_2
C_1
B.V.
F
L.B.
W
M
D
H
Sea water
feed
Reject sea
water
Product fresh water

M -- Melter
D -- Decanter
F -- Freezer
W -- Ice Washer
C_1-- Compressor I
C_2-- Compressor II
C -- Condenser
H -- Heat Exchanger
B.V. -- Butane Vapor
L.B. -- Liquid Butane

Figure 6. Hydrocarbon freezing process flow diagram for sea water conversion.

of what form of energy is utilized in a particular system, thermodynamic theory dictates that there is a minimum value for the energy required in any process to separate salt and water.

The theoretical energy requirement of the freezing process has been defined (142, 152) as the minimum work required for pumping latent heat of freezing from the freezing temperature of brine to that of pure water.

Reversible work in BTU per pound of product is:

$$W = \Delta H \frac{(\Delta T_{f.p.d.})}{T}$$

ΔH = change in enthalpy of process water (latent heat of freezing).

$\Delta T_{f.p.d.}$ = freezing point depression, for conditions of process.

T = temperature of process.

Assuming freezing point depression at approximately 50 percent conversion and taking standard values for the sea water temperature of 25°C and a salinity of 3.5%, theoretical energy is 6.3 Kw.hr/1000 gallon of product water (1 BTU/lb = 2.42 Kw.hr/1000 gallon). But, from a practical point of view, this value is 40 Kw.hr/1000 gallon.

Normally, the practical values are 10-15 times greater than the minimum theoretical value (148).

Sea water contains normally 3.5 percent salt by weight and has an initial freezing point of -1.9°C, and this decreases approximately 0.56°C for each one percent increase in salt content. Most of the freezers used in the process are well stirred and usually single stage. The equilibrium temperatures of freezing are those of the brine leaving the freezer. For a 50 percent water recovery, as ice, the brine contains 7 percent salt and freezes at -4°C. To provide a reasonable driving force for heat transfer the refrigerant must evaporate below this temperature and an additional 1° to 1.5°C would be adequate for ice or hydrate production. Thus, the refrigerant evaporating temperature in the freezer for 50 percent conversion of saline water is -5.5°C.

The heat abstracted at low temperature is upgraded by the primary compressor to a level where it may be rejected onto ice, thus simultaneously condensing the refrigerant (water or butane) and melting the ice. A ΔT of about 1.1°C is needed to provide the melting driving force and the condensing temperatures are thus +1.1°C, since the salt content of the washed ice is only 500 p.p.m. and it melts substantially at 0°C.

For a 50% yield of fresh water, the primary compressor must raise the refrigerant condensing temperature by 6.6°C, which gives a compression ratio for butane or butane mixture of 1.3. For 35% conversion or yield of fresh water, the temperature lift is 5.6°C and compression ratio is 1.6. The excess refrigerant vapor, because of heat sources from pumps, compressor, and leakage from atmosphere, cannot be condensed onto the ice and must be compressed to higher pressures for condensing. Typically this vapor amounts to 15 percent of the total, but the pressure ratio through which it must be compressed is rather high so that 40 percent of the compression energy used in freezing is for this secondary cycle.

The overall driving force for all the processes taking place is the difference between T_1, the equilibrium freezing temperature at the bulk salt concentration, and T_3, the equilibrium vaporizing temperature of the refrigerant at the presence in the vapor space. Both can be determined in practice and both are independent variables, because they can be set by the designer or operator. An intermediate temperature T_2 between T_1 and T_3 can be determined as the temperature of the brine slurry leaving the freezing. T_1-T_2 measures the potential across the processes taking place between the crystal and the aqueous liquid. T_2-T_3 measures the potential for evaporating refrigerant. T_2 can be set or changed, by changing T_1 or T_3 which are really independent temperatures.

There are several other intermediate temperatures which can be defined such as that of a) the crystal itself, b) the crystal interface, c) the aqueous-organic liquid interface, or d) the organic gas-liquid interface, but these cannot be measured. The temperature levels are further complicated by the fact that a hydrostatic head effect changes the local vaporizing temperatures and there are usually some gradients in salt concentration from inlet to outlet. Since agitation does not produce complete mixing (154), most people report the ΔT driving force as T_1-T_2, but they call them ΔT, hence care must be taken in interpreting and comparing data from different experiments.

The disadvantage of having greater ΔT is that it results in greater power requirements, as shown in Figure 7.

The advantages of using normal butane as a refrigerant in the freezing process have been summarized as follows (151):

1. Normal butane is the cheapest and probably the best refrigerant. It does not form hydrates (150).
2. It does not react chemically with water.
3. Butane loss is low in the freezing process.
4. Butane and water are readily separated by decantation, because, theoretically, there is no tendency to form emulsions and there is a considerable density difference for gravity separation.
5. Ice crystals formed are free of salt.

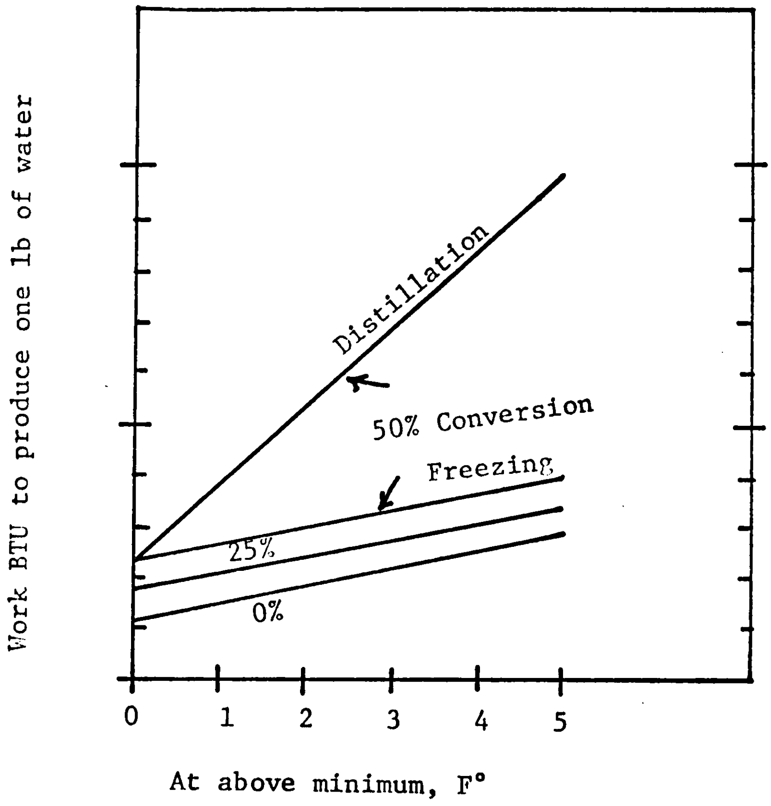


Figure 7. Energy penalty for driving force (Wiegandt, 142).

6. Salt water can form a slush with a minimum loss of product water.
7. Freezing and melting can be accomplished by direct mixing with small temperature differences between the butane and water (or ice) phases.

Butane is one of the most commonly used refrigerants for the secondary refrigerant freezing process for the desalination of sea water. However, the fresh water produced and the brine residue from the process both contain 50-150 p.p.m. of dissolved or trapped butane. This must be recovered down to about 1 to 10 p.p.m. to recover their economic value and/or to prevent explosion hazards, and probably down to the 0.1 p.p.m. range to meet public health standards for drinking water. Solubility of butane at a temperature range of 10°C to 75°C at a total pressure of 1 atmosphere was investigated by Winkler (155), and Morrison and Billet (156). Further studies confirmed the Morrison and Billet result. The results are presented in Figure 8.

Solubility increases at lower temperatures but can be stripped at smaller vacuums when the temperature of the solution, which is to be stripped, is around room temperature. Naimpally (161) stripped butane from 40-70 p.p.m. in aqueous solution to as low as 5 p.p.m. in vacuum spray chambers. He concluded that the butane could be stripped to 0.2 p.p.m. by improving the geometry of spray nozzles in the vacuum chamber.

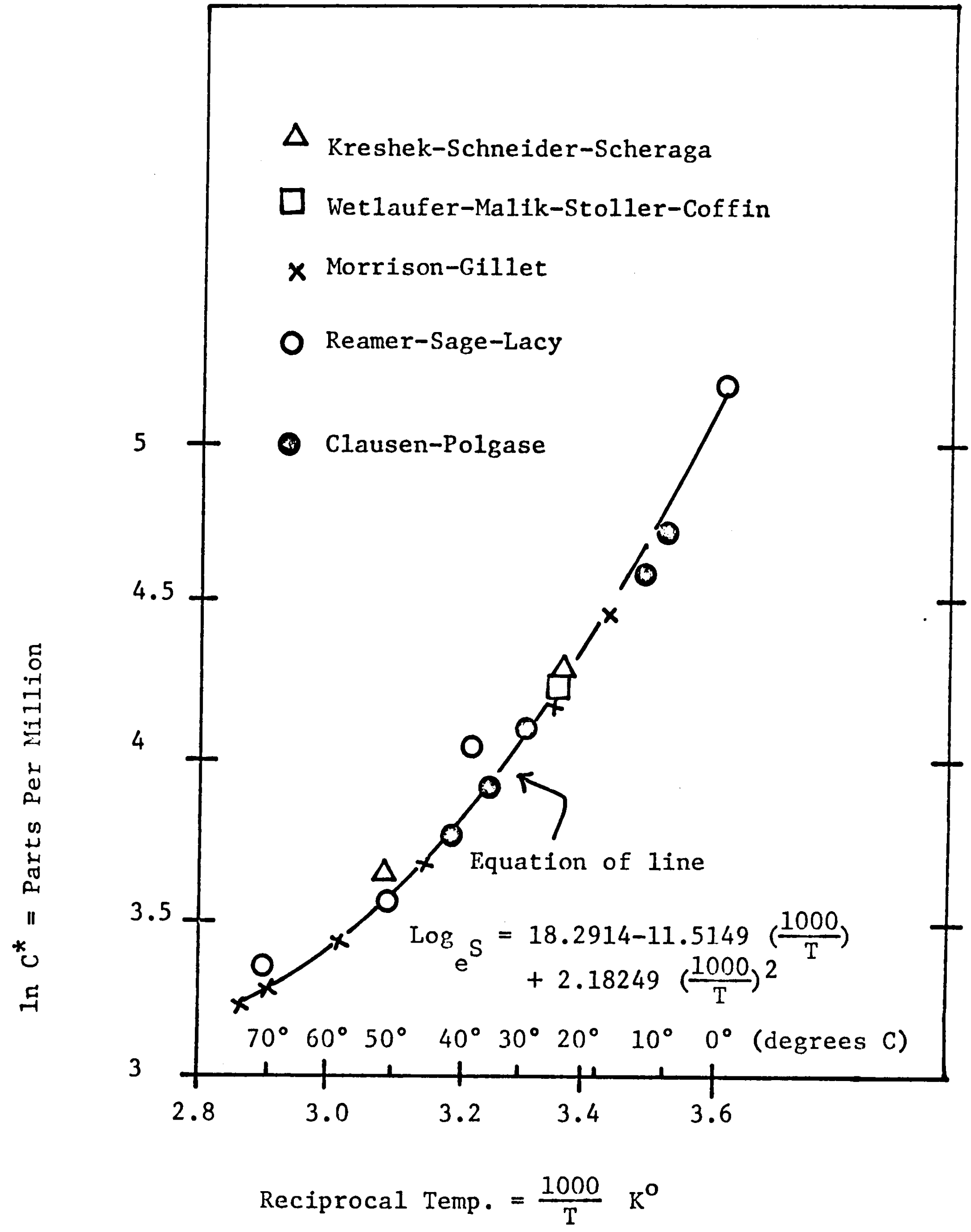


Figure 8 . Equilibrium concentration of Butane in water (Total P = 1 atmosphere).

Freezing as a Conditioning Aid for Chemical Sludges

The generation of waste sludges in advanced wastewater treatment and water treatment plants results from the chemical separation of the solids and nutrients through coagulation, sedimentation and filtration processes. The sludges may contain suspended loam or clay particles; colloids, both organic and inorganic in nature; microorganisms; and chemical precipitates resulting from the use of coagulants. The type and amount of sludges generated vary considerably from plant to plant due to the amount and type of chemicals added, plant operating practices, and efficiency of the process.

1. Types of Sludges: Generally there are three types of sludges that may be generated from the combined processes of flocculation, sedimentation and filtration, and one additional type from filter back-wash.

   a. Lime Sludge--Lime sludges usually have good dewatering characteristics because of the dense, granular nature of the calcium carbonate floc and the resulting high specific gravity of lime sludge. The pH of lime sludges usually range from 9.5 to 11.5. Optimum phosphorus removal occurs between pH 11 and 11.5. The solids content can be as high as 50 percent for water softening sludges that are lagooned (107). The C.O.D., suspended solids, and volatile solids levels are comparable to aluminum and iron salts sludges.

b. Ferric Sulfate Sludge--The sludge has a reddish-brown color due to oxidized iron compounds. The total solids content of the sedimentation basin sludge is 0.2 to 5 percent, which is higher than the aluminum systems. The pH varies from 3 to 10, while optimum pH for phosphorus precipitation occurs between 4.5 and 5.0. The sludge is feathery and bulky at dilute concentrations, but tends to be heavy and resistant to shear at higher concentrations (108). Most of the solids are in the suspended form; C.O.D. values range from 500 mg/l to 15000 mg/l. Settling and dewatering characteristics are good.

c. Aluminum sludges--The sludge is light and bulky, containing high moisture content (98.5 to 99 percent), settles rapidly but its gelatinous consistency renders it very difficult to dewater without treatment (109, 110). The total solids content ranges from 300 mg/l to

15,000 mg/l with suspended solids amounting to 75 to 90 percent of the total solids. Albrecht (5) noted B.O.D.$_5$ values of 30 to 100 mg/l, but C.O.D. values were 500 to 10,000 mg/l. The pH of the sludge is usually 5 to 7. Because of its highly compressible nature, this type of sludge will clog the soil if disposed of on land.

d. Filter back-wash water--This usually contains total solids concentrations of about 400 mg/l, with suspended solids in the range of 40 to 100 mg/l (112). The B.O.D.$_5$ and C.O.D. values usually are less than 5 mg/l and 160 mg/l respectively.

2. Processes Utilized and Studied: Plain (114) was the first one to report the feasibility of freezing for the concentration and conditioning of wash-water sludge. Later on, Doe (34), while working at the Stocks Filtration plant of Fylde Water Board, Blackpool, London with a unique wash-water sludge which was a dark brown, viscous liquid, had an offensive odor, and changed color from brown to deep blue-green on storage, found filter presses and lagooning unsuitable as disposal processes. So he began a series of

batch experiments similar to those conducted by Plain (114), Clements et al. (27) and other researchers. Some of Doe's (34) conclusions were that:

a. The time taken to freeze a sample was critical; e.g., the instantaneous freezing of droplets on a cold surface produced little or no change in colloidal nature of the sludge.

b. After freezing the sludge cake contained 18.5 percent solids and had lost its cohesive properties.

c. The physical change which took place during freezing was irreversible.

Doe et al., (115) on the basis of batch results (34) set up a full scale pilot freezing plant to handle 4800 g.p.d. of wash-water sludge. The freezing and thawing was accomplished by ammonia flowing through 3/4" diameter pipes. The results in terms of improvement in the dewatering characteristics of wash-water sludge were encouraging, but the major problem encountered was that the pipes were subject to fatigue due to indeterminate stresses resulting from continual freezing and thawing cycles. Doe et al. (32) further extended the work (34) to concentrate 33,000 g.p.d. of sludge containing 0.5 percent to 2.4 percent solids by slow stirring and then freezing with the ammonia refrigeration system. He theoretically explained that the dramatic effect of freezing on solids dewatering was due to the formation of ice crystals as the freezing commenced. As temperature fell, the particles of sludge were dehydrated and enmeshed in ice. The resulting ice pressure caused coalescence of sludge particles into fine hard grains. The pressure was released upon thawing allowing the grains to settle quickly. Evidence for this theory could be found by experiments on two important aspects:

a. Visual inspection of slowly frozen sludge showed the fine grains embedded in clear ice.

b. "Flash" freezing resulted in a dark brown, opaque mass which, after thawing, reverted to the original gelatinous state.

Fulton and Bishop (36), while studying the effect of natural freezing on aluminum sludge at Monroe County Water Authority Plant near Rochester, New York, ran some laboratory freezing experiments, which showed that the total solids concentration could be increased from 3.5 to 17.5 percent. Later on, a lagoon was filled with alum sludge containing 0.3 percent solids to a depth of 30 inches. After natural freezing and thawing, the solids concentrations was 35 percent and evaporation increased it to 50 percent when high air temperatures were reached, i.e., 80°F. The final sludge with 50 percent solids concentration could be used for a sanitary landfill.

The concept of natural freezing as an aid in sludge dewatering was also utilized at Sonderson Filtration Plant in Copenhagen, Denmark (115, 116). After two years of operation of freezing, the alum sludge in the gravel bottomed lagoons settled to a four cm thick layer, leaving a clear supernatant.

Farrell *et al*. (37) attempted to provide basic information necessary for the design of facilities for dewatering aluminum hydroxide sludges by natural freezing, by subjecting the water-treatment sludges of Ely (Minnesota) and Cincinnati (Ohio) to climatic temperatures under controlled conditions. They concluded that:

a. The freezing of water and aluminum hydroxide took place at the same rates;

b. Snow cover was a serious obstacle to cold climate natural freezing because of its insulating effect;

c. Slow and complete freezing dramatically increased the dewaterability and solids content;

d. Repeated cycles of freeze-thaw increased dewaterability and solids content, but to a lesser degree than slow, complete freezing;

e. Natural freezing in a mild climate, such as Cincinnati's, required application of thin layers of sludge and could result in excessive management costs; and

f. Phosphorus content had only a slight effect on sludge filterability and solids content.

The specific resistance of unconditioned sludge was reduced from 10×10^8 sec^2/gm to 5×10^6 sec^2/gm after conditioning. Total organic carbon measurements on supernatant from freeze conditioned samples indicated that 99 percent of all carbon was in the solids (37).

King *et al*. (118), while studying the effect of freeze conditioning of water-treatment sludges, reported that freezing and thawing resulted in volume reductions of 86.2 percent and that the total solids content in sludge increased from 2.96 to 18.2 percent. Freezing also resulted in very rapid dewatering and filtration of sludge.

Simmons (119) observed the dramatic changes in the dewatering and filtration characteristics of a variety of water-treatment sludges; i.e., lime, ferric sulfate, and aluminum sulfate, after freezing and thawing. He reported that there was a direct relationship between solids content and the gravity sand filtration and refiltration rates for freeze conditioned sludges, while the relationship was inverse with respect to specific resistance. Increased storage times of frozen sludges resulted in greater improvements (119).

Logsdon and Edgerley (117) reported on extensive fundamental research on barium sulfate, iron and aluminum sludges. The results suggested that freezing could be made more effective by treatment with a polymer but that the effects were reversed by using electrolytes. Spraying of sludge into the atmosphere could make natural freezing of sludges in lagoons in cold areas more effective.

Dorr-Oliver (120) obtained a patent for a technique for freezing and concentration of water treatment sludges. The settled sludge, after thawing, was recycled to the feed sludge to be frozen. This resulted in solids concentrations in the range of 100-150 percent more than the unconditioned sludge. The process was somewhat similar to Doe *et al*. (115).

Messerschmidt (121), reported that ferric hydroxide sludge had a partly netlike and partly honeycomb structure, in which water was retained by capillarity. Temperatures below 0°C and slow freezing rates resulted in the formation of larger ice crystals which exerted tension in capillaries and thus broke the capillary walls, resulting in changes of the sludge structure. On thawing, water adsorbed only to those capillaries which were not destroyed. Freezing rates greater than 17 cm/hr had no change on the structure of the above sludge (121).

Albany Water Filtration (122), New York, disposed of its 280,500 lbs. of alum sludge every year into the Onesquethaw Creek, until 1965, when the State Department of Health required all municipalities to treat their liquid wastes before discharge into surface water. One of the two alternatives considered for sludge conditioning was natural freezing of lagooned sludge, and the conclusions were:

a. During a rather mild Albany winter, a frozen sludge depth of 4 feet was achieved by application of the sludge in layers of varying thicknesses.

b. The characteristics were completely changed after freezing and thawing.

c. There was a complete separation of solids and liquid and upon thawing the solids immediately settled out.

d. The water, which was substantially clear, seemed to drain freely through the solids and the gravel bed.

e. The process appeared to be suitable to a northern climate where land availability was not a problem.

Free thaw conditioning also was reported for iron oxide sludge (123), aluminum hydroxide sludge (124), mine dewatering sludge (125) and sludge from titanium dioxide production (126).

3. Mechanism of Chemical Sludge Conditioning: To understand the mechanism, sludge freezing and soil freezing literature were reviewed. The following theories were found:

a. Capillary Theory (32, 121)--According to this theory, water in the capillaries freezes, forming large ice crystals (slow freezing), which, due to increase in volume, exert compressive pressure on the sludge particles, thus resulting in dehydration and dewatering.

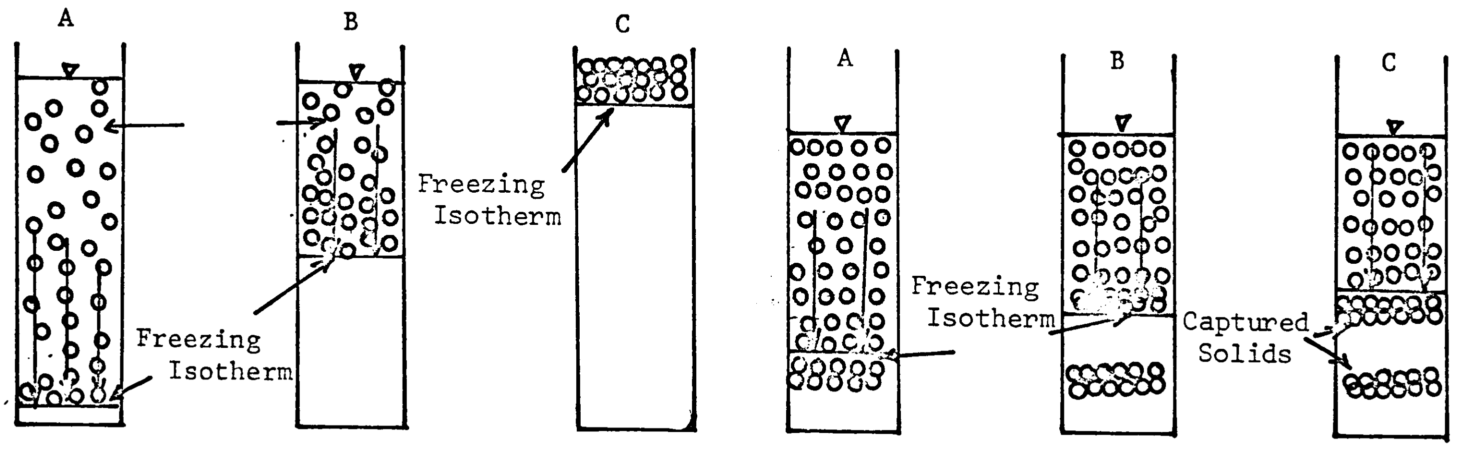
b. Frost Heave Theory (127, 128)--involves the separation of ice and soil particles into layers, due to the movement of water through soil in order to reach growing ice-layers or lenses.

c. Gross Migration Theory (117)--According to this theory, all the sludge solids are pushed upward in a freezing cylinder by the movement of advancing freezing ice structure until all the solids are concentrated and dehydrated at the top.

Logsdon (117) contradicted the previous capillary theory and, on the basis of the frost heave theory, proposed the following mechanism for the basis of solids migration:

a. Gross Migration Mechanism--Logsdon (117) assumed that for a sample of sludge placed upon a cold surface and frozen slowly, as the freezing isotherm moved up the sample, the water in the system froze. Due to the lesser specific resistance offered to the movement of the freezing isotherm, i.e., by solids accumulation, solids continued to be pushed upward by the ice formed until all of them reached the top, as schematically shown in Figure 9(i). The removal of water from the solids caused consolidation of gelatinous floc due to the increased moisture tension in the floc pores. This happened in the absence of any compressive forces. The rate of freezing in the above was slow and dewatering was very effective.

b. Micromigration Mechanism--(Figure 9(ii) When the rate of freezing was much faster than a) but not in the flash freezing range, growth of ice at a rate that exceeded the rate water could be supplied to the interface could cause particle trapping. This can be described as follows: 1) because of enough water to the ice to prevent solids capture, sludge solids were concentrated ahead of the ice; 2) some of the moisture in the sludge close to the ice was removed by capillary forces during the freezing process and resulted in dewatering. Dewatering and cake build up could decrease


A
B
C
Freezing Isotherm
Freezing Isotherm
A
B
C
Freezing Isotherm
Captured Solids

(i)

Mechanism of Gross Migration

A. Freezing Starts

B. Water flow remains good as freezing continues

C. All solids are pushed to top

(ii)

Mechanism of Micromigration

A. Water flows rapidly

B. Poor water flows--result of high specific resistance

C. Freezing isotherm jumps to new location for favorable water flow

Figure 9. Mechanism of solids migration. (Logsdon, 117)

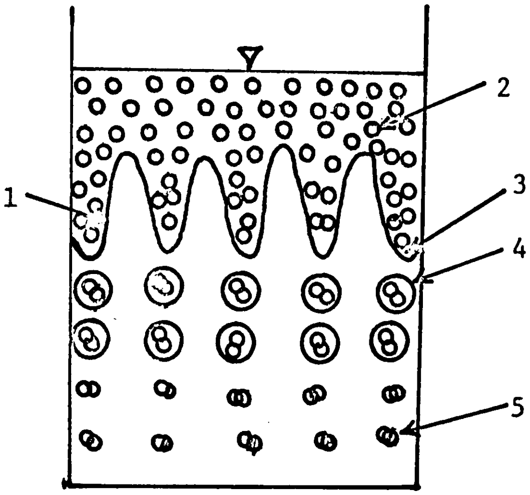
the ability of water to flow (increase in specific resistance), so that a layer of solids became trapped by the ice; and 3) when the condition in 2) was established, the freeze isotherm advanced to a location where conditions more favorable for water were again encountered.

Good dewatering could occur under the conditions of micromigration in spite of solids capture, which was evidenced by results obtained in this type of freezing.

c. Effect of Flash Freezing (117)--When "flash" freezing occurred, there was a minimum of time for the suspended sludge solids to separate from the water. With the greater reduction in the migration, sludge particles could not consolidate into larger particles that settled well and separated from the liquid phase after thawing.

4. Effect of Additives: (117)

a. Electrolytes--The situation in the case of high specific conductance of sludge (high total dissolved solids) (Figure 10) was different from micromigration phenomenon (Figure 9(ii)). The advancing ice rejected impurities, suspended and dissolved solids. If the solute



1. advancing unstable ice-water **interface, which captures** liquids and solids.

2. possible frozen sites.

3. Zone of increased electrolyte concentration and depressed freezing point.

4. captured liquid and solids.

5. possible dewatering site, if trapped solution solidifies

Figure 10 . Influence of Electrolyte concentration on freezing pattern (117).

could not diffuse away rapidly enough, it remained concentrated near the interface and depressed the freezing point of the liquid ahead of the ice causing an unstable situation. The amount of super cooling (cooling of liquid below its freezing point) increased and then decreased as the distance from the interface increased. This situation was called "constitutional super-cooling." Breakdown of this cooling caused freezing to occur at some distance from the ice interface rather than adjacent to it. This freezing caused solids and unfrozen liquid to be trapped, resulting in vertical and horizontal bands of frozen solids. This type of freezing resulted in poor dewatering. The chances of instability and subsequent solids capture became greater as the concentration of solute in the sludge liquid increased.

b. Effect of Polymers on Freezing--(117) Addition of polymers caused a more open pore structure in the sludge, permitting higher flow rates and thus higher freezing speeds without solids capture. Freezing speeds of 40 to 60 mm/hr gave good dewatering.

Freezing As A Conditioning Aid for Biological Sludges

This summary consists of three parts: 1) The composition of biological sludges, 2) The processes utilized and studied, and 3) The mechanism of conditioning.

1. Composition of Biological Sludges: This type of sludge is most commonly waste-activated sludge, which is the product of biological multiplication of microorganisms feeding on soluble and suspended organic matter in the presence of dissolved oxygen. This is mostly bacterial cells but it may contain protozoa, rotifers, fungi, sludge worms and larvae (24). According to Dungan *et al*. (25), most of the bacteria in the waste-activated sludge are floc-forming Zooglea, which are related to Pseudomonads. Up to 90 percent of the Zoogleal mass is extracellular jelly secreted as bacterial capsules. This gelatinous mass entraps small particles and organisms in flocs that settle with bacteria, leaving a clarified, final effluent. According to Kincannon and Gaudy (26), the overall composition is 53.1 percent carbon, 8.3 percent hydrogen and 10.7 percent nitrogen, accounting for 72.1 percent of the volatile suspended solids.

Sludge contains almost all of the metal ions that are discharged to sewers or extracted from plumbing (1). Heavy metal occurring in the sludge in quantities which are significant in foods include zinc, copper, nickle, cadmium, mercury and lead. Arsenic, selenium, manganese and molybdenum may occasionally be present in significant quantities from industrial sources. In addition to the above, they may contain some pathogens.

2. Processes Utilized and Studied: In 1929 Babbit and Schlenz (18), working with the problem of sludge disposal by application on sand beds at the experimental station, University of Illinois, discovered that the effect of natural freezing on digested sludge was an increase in the rate of filtration on sand beds. Also, a much better quality of cake, i.e. one easily separable from the sand beds, was obtained as compared to the untreated sludge. Later on they repeated the experiment using artificial freezing, i.e., an electric refrigerator. A poorly digested sample was frozen for nine days, while another similar sample was stored inthe laboratory for the same period. Drainage of the frozen sludge upon thawing resulted in a reduction to 50 percent moisture content in 50 seconds, while the lowest moisture content of the unfrozen sample was 58.4

percent after 28 hours of drainage. After 28 hours of drainage on sand beds, the moisture content of frozen samples was 30.7 percent. It was also observed that the rate of liquid separation was 3 to 7 times faster for the frozen samples as compared to unfrozen ones.

Microscopic examination showed that frozen sludge particles, after thawing, clumped together with widely separated groups, similar to the results of agglutination reaction. The original sludges showed a fairly complete dispersion of the particles throughout the field.

In 1939 Downes (19) found that freezing and drying destroyed the sliminess of the digested sludge and it allowed faster drainage of water. The cake moisture after drainage was about 65 percent and at this low-water content the sludge was, theoretically at least, self-burning (19).

In 1947, Forsyth (20), while working on the purification of humus and allied materials from soil organic matter at Macaulay Institute for Soil Research, reported that freezing completely destroyed the colloidal character of humus materials; they not only lost their water-holding capacity but also their general absorptive power.

In 1950, Clements, Stephenson and Regan (27), after reading the results of Forsyth (20) published in Nature, 1947, using digested sludge with and without chemical addition, conducted "test-tube" scale experiments which demonstrated great improvement in the filterability of digested sludge. After the initial experiments, a specially designed freezing machine, using methyl chloride in the heat exchanger coils, was devised. The two freezing pans containing sludge were located on the top of the coils. One pan acted as a freezing pan while the other acted as a thawing pan. A summary of results and conclusions follows:

a. The settling of all types of sewage sludge is promoted by freezing.

b. Settling was accelerated by freezing with chemicals, but the percentage settlement at the end of an hour was approximately the same, whether chemicals were used or not.

c. Filtration, after freezing with chemicals, was remarkably accelerated. Filtration times in the best cases were reduced to a few seconds and produced 3/8" cakes. The filter cakes were friable and of high solids content, being over 30 percent in some instances.

d. The chemicals used were chlorinated ferrous sulfate, chlorine gas, and aluminum sulfate, and doses were up to 1000 parts per million of Al^{+++}.

e. The best results were obtained by the use of aluminum sulfate, dry solids production reaching 350 $lbs/ft^2/hr$. In the case of chlorine, the maximum dry solids production appeared to be about 40 lbs/ft^2. Note: The dry solids production capacity of the Dorr-Oliver filter used in this experiment was 100 $lbs/ft^2/hr$, while typical vacuum filter dry solids production rate is 0.5 to 4 $lbs/ft^2/hr$ (41).

f. Complete freezing was essential. Freezing had to be fairly slow. "Flash" freezing was ineffective.

g. Some saving of latent heat of fusion was practicable in a suitable installation.

h. The method of thawing was immaterial as long as it was not associated with vigorous agitation.

i. The supernatant liquids on settlement were, on an oxygen absorption basis, not much worse than ordinary sewage.

j. Air drying rates of digested sludges were faster than those of activated sludge. The wet cake, as taken from the filter, was quite "short," porous, and free from the usual tendency to form an outside leathery coating on drying which interfered with further loss of water.

Clements (27) also studied the effect of freezing in thin films, using brine (dissolving 2.5 Kg of common salt in 10 liters of water) as refrigerant and freezing temperatures of -5, -10, -15, -20°C, while the sludge thicknesses to be frozen were 1/8", 1/4", 1/2". The results follow:

a. Even with substantial doses of aluminum sulfate, faster freezing in thin layers--say, in 7 to 10 min.-- led to poor results in settlement and filtration.

b. When the time of freezing is extended, either by use of a thicker sludge layer or by use of higher freezing temperatures, the effects on settlement and filtration were improved; this is true, in some measure, even of thinnest layers. When a half inch thick layer was frozen, involving a freezing time of 70 minutes, good results were obtained, whether the sludge was stored or not before thawing.

c. The adverse effects of quick freezing could be mitigated in some measure by storage for two hours before thawing.

d. There was no evidence that the presence of synthetic detergents had any marked effect on settlement and filtration in concentrations employed in the experiments.

e. Predictions of costs of filtration, etc. could not be made because no experiments with a filter-drum were carried out although the cost of the chemicals was available.

On the basis of laboratory experimental studies conducted by Clements (27), Bruce, Clements and Stephenson (28) in 1953 began full scale operation of sludge freezing at Northern Outfall Works, London, England. The objective was to produce one ton of ice per day and develop filtration techniques after thawing. The freezing machine (27) was modified to eliminate the use of latent heat of fusion, because of some practical problems, and so thawing was accomplished with steam and hot water. Methyl chloride was conducted through coils in a brine solution into which sludge containers were lowered for freezing. The operation did not produce the desired results since the brine solution temperature had to be raised between freezing batches to eliminate quick-freezing. They also experimented extensively with a large number of filter cloths on a large Buchner funnel apparatus, to determine the most suitable vacuum-filter material. Previous experimentation (27) with rotary vacuum filtration (Dorr-Oliver filter) and centrifugation proved these methods inadequate and not very successful. Synthetic filters of polyvinyl-chloride produced promising results with filtration times from 15 to 75 seconds, and dry cake solids levels ranging from 26.6 to 29 percent. The supernatant was black and colloidal with 0.5 percent solids, which were so finely divided that they passed through a nylon vacuum filter disc without staining it. However, the problem still remained unsolved because of three main reasons: 1) high cost and power consumption; 2) high capital and operating cost when using both refrigeration and vacuum filter equipment; and 3) frequent washing of filter media.

Katz and Mason (29) attempted to eliminate the problems faced by Clements (28) and others related to high cost of vacuum filter equipment and the filter-media blinding. They froze the activated sludge samples from the Milwaukee Water Pollution Control Plant in a commercial freezer and thawed them in a hot water bath. Thawed samples were gravity drained through a screen (40-80 mesh), placed in a 9 cm Buchner funnel and supported by an 18 mesh wire pad. Mechanical pressing, i.e., pressing with a rubber disc, or a 3 inch Hg vacuum applied for 10 seconds after gravity drainage was complete, produced the same results. The results obtained were very encouraging as in the case of other researchers. For a one percent raw solids sample, gravity and pressing was essentially complete in 50 seconds. Variation in feed solids concentration indicated that dewatering time decreased as solids increased for the same solids loading to the filter. Cake solids for the freezing process were determined to be comparable to those of conventional vacuum filters, ranging from 13 to 25 percent. Filtrate suspended solids ranged from 150 to 250 mg/l for a screen size of 40 to 80 mesh. The dissolved content increased from 1200 to 2000 mg/l. Dry solids production rates were on the order of 55 lbs/ft^2/hr. The filtrate and filter-cake quality produced from freeze conditioned sludge were equivalent to or better than that produced from vacuum filter operation.

Cheng, Updegraff and Ross (30) followed up the studies done by Clements (27, 28), and Katz and Mason (29), and attempted to solve the problem of high equipment and operating costs because of higher temperature differences and longer freezing times. Samples of primary (2.2%), activated (0.2%), return activated (0.3%), and digested sludge (1.6%) were frozen in rectangular canisters with sides 5 x 6 m^2 and either 1/4" or 1/8" spacing, holding about 42 or 21 ml of sludge, respectively. When loaded, the surface for heat transfer was about 290 cm^2. For freezing, the canisters were suspended in a stirred, controlled temperature bath of ethylene glycol. Alum, with varying concentrations from 20 to 200 p.p.m., was the conditioning chemical. Cheng observed that an ice film of small thickness possessed a thermal admittance of about 200 BTU/ft^2-hr-°F which is high enough to permit rapid removal of heat even at small temperature differences. With an average overall heat-transfer coefficient, U, of 12 BTU/ft^2-hr-°F, and a temperature difference from bath to sludge of -3° to -5°C, dry cake solids, after filtration, gave results comparable to those of previous investigators, while freezing time was reduced to ten minutes. Due to the increased agitation in the cooling bath, heat-transfer coefficient, U, increased to 29 BTU/ft^2-°F-hr and dry cake solids results were still the same; i.e., 20 to 30 percent, but freezing time was reduced to 5 minutes. Cheng (30) concluded that thin-film sludge freezing permits efficient dewatering of sludge in short times at low temperature differences (ΔT). The ice-film conducts heat with such rapidity that the external heat transfer mechanism controls the process. Chemical addition is necessary to dewatering by freezing. The distinct peaks after about 3 minutes in the profiles of temperature vs time revealed the presence of bound water that was released after the free water had been frozen.

On the basis of the encouraging results obtained by Katz (29), the Sewage Commission of Milwaukee (38) decided to investigate the freeze-conditioning of sludge containing 200 tons of dry solids/day, which was being chemically conditioned and dewatered mechanically. The annual cost of chemicals alone was $750,000. The research was conducted by Internal Rex Chainbelt, Inc. (39) on behalf of the sewerage commission and funded by the Environmental Protection Agency.

Bench scale and field tests were conducted to investigate the effect of different parameters and the results were as follows:

a. The effect of storage times of 0, 11, and

24 hours before freezing adversely affected the cake solids and caused an increase in soluble C.O.D. and soluble phosphates in the filtrate. Filtrate suspended solids were not affected by up to 11 hours, but there were detrimental effects by storage of liquid sludge for 24 hours before freezing.

b. While investigating the effect of thawed sludge storage times, 0, 8 and 24 hours, it was noted that the filtrate soluble phosphates and C.O.D. increased with increased age after thawing, but the filtrate suspended solids and drainage rate remained unaffected by up to 24 hours of thawed sludge storage. Therefore, it would be advantageous in full-scale operation to dewater the sludge as quickly as practicable after thawing.

c. The effect of storage times of up to 28 hours on the sludge in a frozen state (1/4" thin sheets) enhanced the dewatering properties of the thawed sludge. Although frozen sludge storage was desirable from a process standpoint, it was felt to be impractical on a full scale basis (e.g., at Milwaukee about three million gallons of waste activated sludge are processed daily).

d. The effect of freezing time (few seconds to 16 hours) on the sludge dewatering properties showed that the freezing time of 12 hours and storage of frozen sludge for 24 hours before thawing, was optimum from the standpoint of drainage time, drainage rate, and cake solids (10 to 13%). In general, it was indicated the increased freezing time improved the dewatering properties of thawed sludge to a great extent. Again, from a practical standpoint, this would result in greater volume requirements and increased capital costs of freezing equipment.

e. Partial freezing was not very helpful.

f. Sludge frozen by the Turbo Principle (liquid sludge flowing over a stationary cold plate or cold drum rotating in a vat of liquid) would not be applicable for freeze conditioning of waste-activated sludge.

g. Addition of $FeCl_3$ (54.2 lbs/ton of wet sludge) prior to freezing not only improved the dewatering characteristics, but also appreciably reduced the filtrate soluble phosphate content (90 mg/l) from that observed in the sludge prior to freezing (190 mg/l), and from freezing alone (250 mg/l). Addition of chemicals after thawing adversely affected the sludge properties.

h. During the investigation it was noticed that shapes and configurations (large blocks, small cubes, thin sheets) were important factors in the overall heat transfer process. In case of large blocks, as the freezing progressed the area for heat transfer and overall heat transfer coefficient decreased, resulting in a progressive decrease in the freezing rate. Furthermore, the rate of thawing was slow, because of relatively low surface area to volume ratio involved.

On the other hand, freezing in relatively thin sheets (1/8", 1/4", 1/2", 1" thick) had the following advantages: i) area for freezing and overall heat transfer coefficient remained essentially constant during the freezing process; ii) thin sheets lend themselves more readily to a continuous freezing process; iii) by breaking the frozen sheets into small chards, more surface area per unit volume for faster thawing may be obtained; iv) faster feedback information was available for process quality control; and v) faster freezing times per unit weight of sludge may be used resulting in lower equipment cost.

i. Relatively faster freezing produced sludge more sensitive to handling and this sensitivity increased with decreased freezing time. Good sludge dewatering properties were observed at fast freezing times when handling of the thawed sludge prior to gravity filtration was reduced to a minimum.

j. Out of the two available thin sheet freezing systems, namely, pan conveyor freezing and belt freezing, belt freezing (belts consisting of 4' wide and 12' long sections, brine solution as coolant, and sludge freezing thicknesses of 1/4" to 1/8") was more flexible and convenient.

k. Economic analysis showed that freeze conditioning, for handling 200 tons of solids/ day, was 80 million dollars (excluding site or housing cost), where conventional chemical conditioning handling of the same solids would cost $5.1 million dollars (including housing and installation).

1. The overall cost of freeze-conditioning process could be reduced by reducing operating cost, ($77 to $79/ton of dry solid), by conserving energy, by refrigeration work and by recovering energy.

On the basis of the above findings, the project was discontinued for further research work towards other dewatering techniques.

Alter (60) pointed out that low temperature was a natural resource that was readily available throughout a large part of the world.

Wood and Allanson (42) patented dewatering equipment that included freezing sludges between moving belts. Feed sludge in thin layers with 5 percent solids concentration was fed in at one end between the two moving belts and then passed through an electro-osmosis apparatus to remove moisture and concentrate the sludge to 20 percent. It then passed through a freezing and then a thawing section (thawing done by electrical heating). Finally, thawed sludge passed through a second electro-osmosis apparatus, thus concentrating the sludge to 30 to 40 percent dry solids by weight.

Gruber (43) also patented a technique for sludge freezing in 4 mm layers on a drum in Germany.

Baskeville (50) found that the effectiveness of sludge conditioning by freezing and thawing was highly dependent on the amount of shear which sludge experienced. With organic sludges, the floc was fragile and the freezing and thawing method was not thought to be feasible for conditioning unless chemical conditioning also was provided. With inorganic sludges, such as metal hydroxides, the technique was successful when the dissolved solids content of the associated liquor was low.

Klyachko (52) presented equations for calculating the thickness of sludge layers that could be frozen during winter.

Turovskii (51), while determining the relationship between the rate of drying (mg of $H_2O/min\text{-}cm^2$) and the moisture content (drying at 105°C) of raw solids and waste activated sludge, used the first critical point in the rate of drying curve as a measure of free water. Later on they found that freezing and thawing of sludge samples increased the free water content from 96.3 to 99.2 percent and decreased the bound water content from 1.7 to 0.8 percent.

Keith (53) noted that the solid particles of sludge were more closely coagulated after freezing and thawing. The waste sludge was centrifuged and the centrifugate was frozen. The thawed sludge was again centrifuged with still more separation of water.

There was considerable interest during 1973 in altering physical properties of sludges by freezing and thawing. Penman and Van Es (54) described a dewatering technique at Winnipeg, Canada, using drying beds without underdrains. The process consisted of two operating conditions: summer and winter. In summer, digested sludge was pumped to seven, 4-acre, 5 ft. (1.5 m) deep drying beds where solid-liquid separation took place. After 3 to 4 days supernatant was pumped back to the treatment plant. After every withdrawal of supernatant, 9" of sludge was pumped onto the bed and this procedure was repeated until 2 to 3 ft. of thick sludge (20% solids concentration) existed. The beds were then allowed to freeze during winter, until they could support heavy earth moving equipment, which was used to rip up and remove the sludge to a stockpile or it was trucked to nearby farmland for crop application. The typical winter operation consisted of pumping sludge to seven, 8-acre (24,000 m^2), 10 ft. (3.0 m) deep drying beds. Winter sludge was stored to a depth of about 8 ft. During the following summer supernatant was drawn off and pumped back to the treatment plant, while the remaining sludge was allowed to freeze once again for winter removal. The operating cost was \$0.84/cubic yard of sludge, excluding the costs of land, piping, and pumps.

Conditioning of waste activated sludge by the freeze-thaw method using natural refrigeration was considered by Tilsworth (55) to be effective and economically attractive in northern areas. Estimated costs of sludge handling by a lagoon system making use of winter freezing and summer drying were \$48/ton of dry solids. This was less than the estimates for all other types of systems considered.

Schmidt _et_ _al_. (56) reported that when Kraft mill sludge was thawed after having frozen in a lagoon during winter its volume diminished by a factor of 40.

Murdoch (58) developed a patent relating to sludge conditioning in a freeze-thaw cycle and solids were separated by vacuum filtration. The sludge was frozen in droplets. Neyhart (57) also developed a patent relating to the freeze-conditioning of waste activated sludge.

3. _Mechanism of Conditioning_: The mechanism discussed here will be mostly related to microorganisms,

especially bacteria.

a. Bacterial structure--The organisms consist of the following structural constituents (Figure 11).

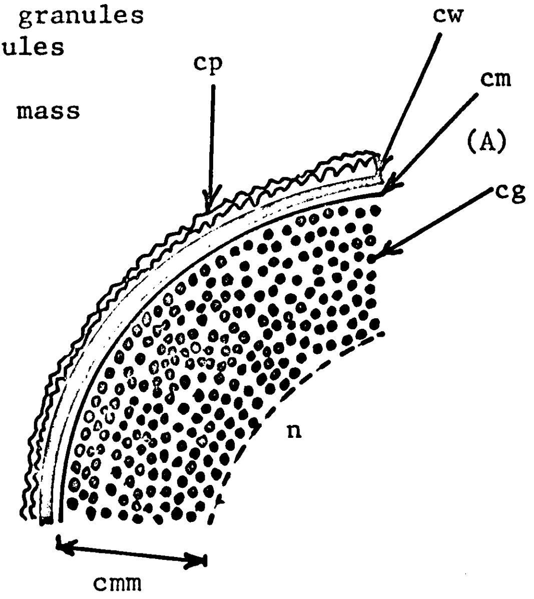
  i) gelatinous capsule (cp)
  ii) cell wall (cw)
  iii) cytoplasmic membrane (cm)
  iv) cytoplasmic mass (cmm)
  v) nucleus (n)

b. Biological damage--To understand the phenomenon of biological freezing, it is very important to understand the role of water in living systems. There are two categories of water associated with the cell; namely, "free water," which constitutes from 80 to 92 percent and will freeze as ice crystals on freezing, while the other portion is called the "bound water," which is about 7 to 10 percent of the total water and is not freezable.

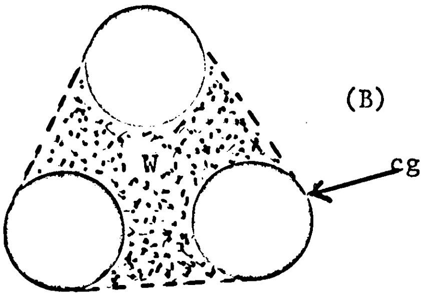
Several theories and mechanisms by which freezing injures biological materials have been proposed. The more tenable of these are:

i) The mechanical destruction theory: Cells are said to be disintegrated by mechanical compression, either on freezing

cp -- gelatinous capsule
cw -- cell wall
cm -- cytoplasmic membrane
cg -- cytoplasmic granules
W -- water molecules
n -- nucleus
cmm-- cytoplasmic mass



(A) One quadrant section



(B) Enlarged cytoplasmic granules and molecules of water

Figure 11. Simplified Bacterial Structure

due to ice-crystal growth or by thawing [Lepeschkin (61)], or the surface of the cell is said to be destroyed [Maximov (62)].

ii) The Chemical or Dessication Theory: It is known that in some cases water is removed from the cell and freezes around it. This may lead to a concentration of solutes within and around the cell resulting in protein denaturation; changes in pH; dehydration sufficient to precipitate from solution; and close contact between neighboring proteins, thereby permitting abnormal cross linkage.

The biological damage related to the above theories is either due to intracellular or extracellular freezing. The difference between the two is explored in the following discussion:

i) Extracellular freezing: Slow cooling rates (<1°C/min) tend to encourage the growth of a few ice crystals to very large size. When these develop in the extracellular spaces, the extracellular fluid becomes hypertonic as water is frozen out, causing intracellular water to pass out of the cells. The ultimate end of such a process is dehydration of cells and the development of external ice crystals, which may be many times the size of individual cells (See Figure 12). Chambers and Hale (69) found that ice would form on the outside of single frog muscle cells at about -1.2°C but did not form inside until a temperature of -1.6°C had been reached. Since the melting point of intracellular fluids is being depressed by increasing concentration, the temperature of spontaneous freezing (t_{sf}), is being proportionally reduced and intracellular nucleation prevented. Cell lysis occurs, irreversibly.

ii) Intracellular Freezing: If the diffusion of cell water is inadequate, due either to a very rapid rate of extracellular crystal growth caused by rapid cooling rates (>1°C/min) or to relative impermeability of the cell membrane, then the temperature of spontaneous freezing (t_{sf}) of the intracellular water may remain high relative to its temperature and intracellular nucleation can result.

Mazur (70), while describing the immediate effects of low temperature on E. coli in nonprotective media, summarized by plotting survival

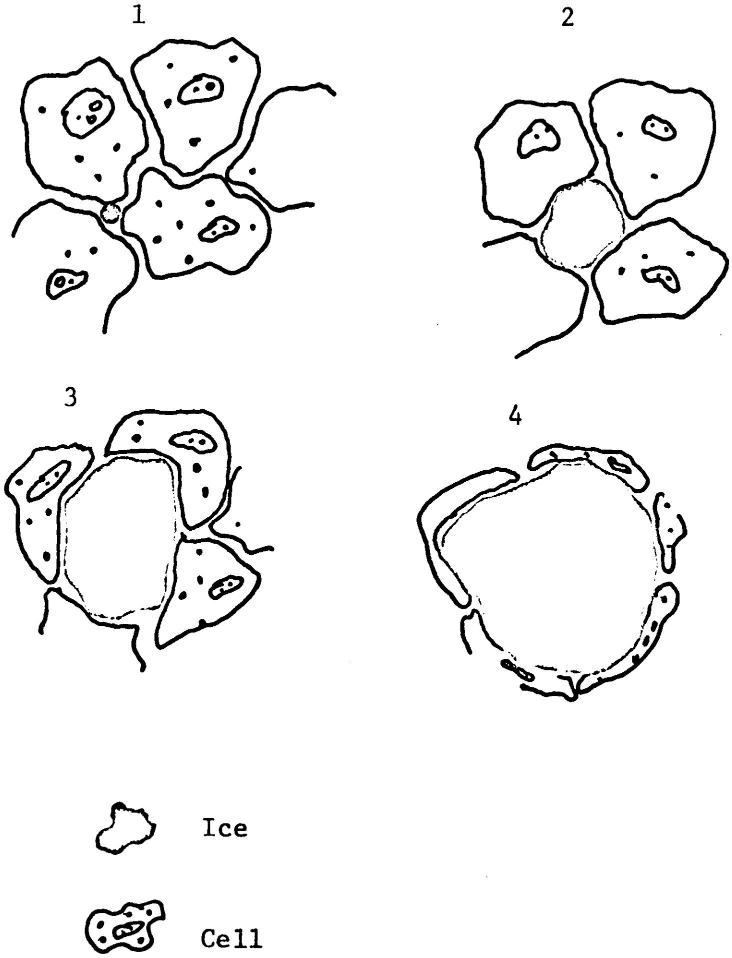


Figure 12. Diagrammatic representation of growth of extra-cellular ice (continuous black area) during freezing of muscle tissue, showing the progressive dehydration of cell (Meryman, 64).

as a function of cooling velocity (See Figure 13). He concluded that the curve dropped below 1°C/min. because very slow cooling is "equivalent to storage" and increasing durations of such "storage" have been very destructive to single celled micro-organisms. Survivals remained high at higher cooling velocities when warming was carried out rapidly, which could be explained by the fact that at higher cooling rates smaller and more imperfect ice crystals were formed thereby causing less damage, but were more sensitive to alterations and growth during warming. Mazur (70) proposed a hypothetical model (Figure 14) to explain the cause of the damage from intracellular freezing. He considered two membraneous intracellular compartments "L" and "R", filled with cytoplasm and connected by a narrow pore. He considered two cases: (A) rapid cooling (>1°C/min< 400°C/min) and rapid thawing, and (B) ultra-rapid cooling (>400°C/min) and slow thawing.

In the case of (A) he supposed that the water in "L" froze, but water in "R" remained supercooled. If the capillary pore was too narrow to permit the growth of ice from "L" to "R" at temperatures near 0°C, supercooled water will flow from "R" to "L" in response to vapor pressure differential and will freeze in "L". The volume of ice in compartment

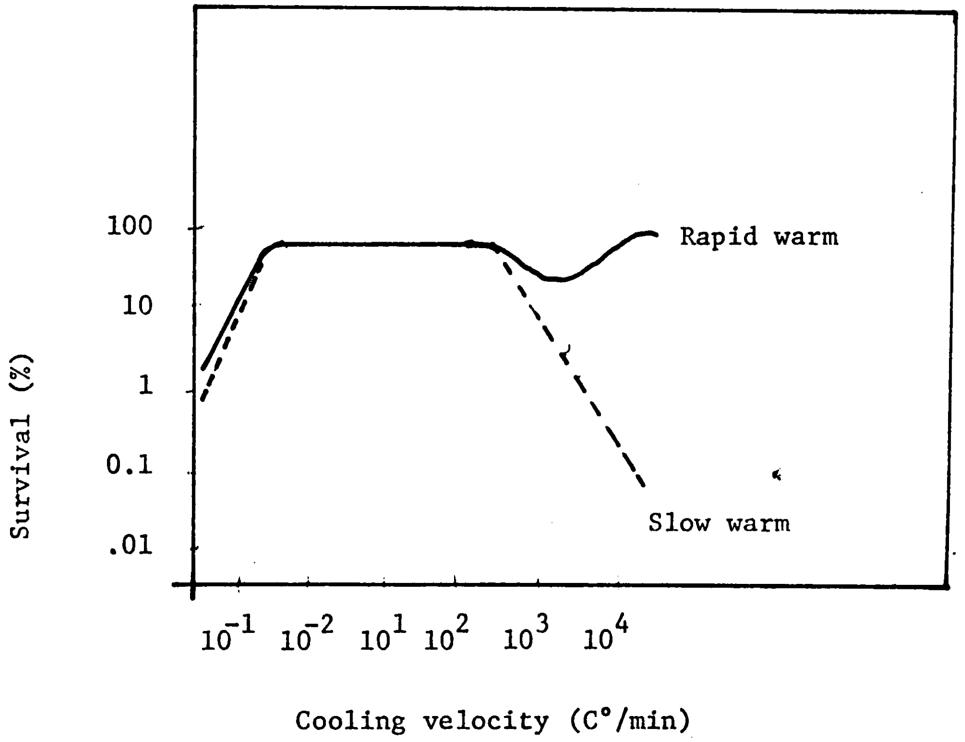


Figure 13. Approximate survival of E. coli as function of temperature. The curve for slow warming is hypothetical. The tic marks on the axes are omitted to emphasize that curves are approximate. (Mazur, 66, 67, 68).

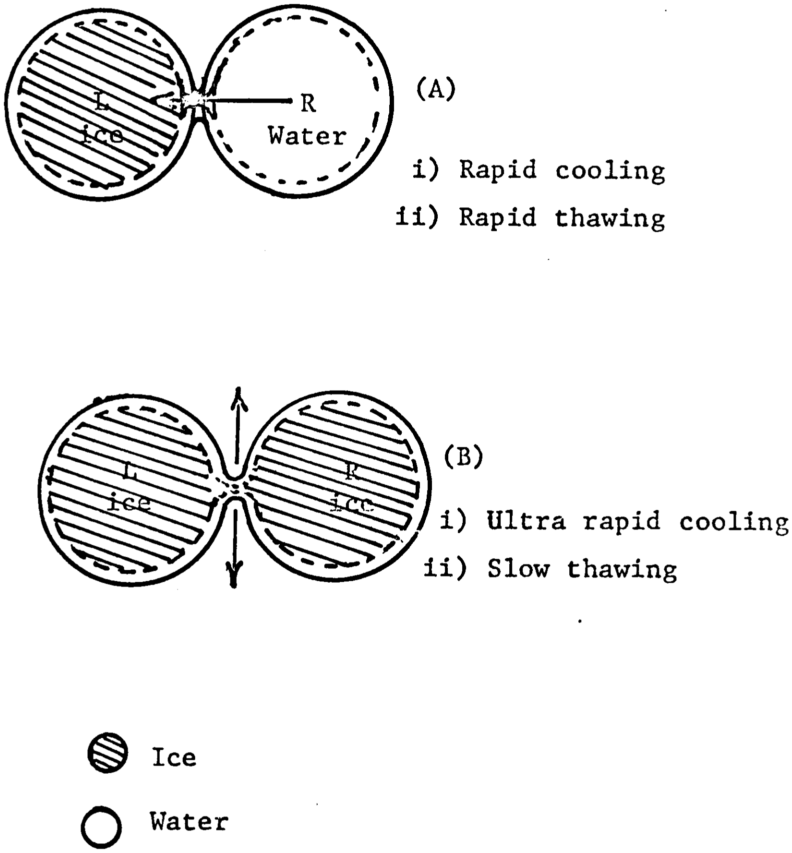

L
ice
R
Water
(A)
i) Rapid cooling
ii) Rapid thawing
L
ice
R
ice
(B)
i) Ultra rapid cooling
ii) Slow thawing
Ice
Water

Figure 14. Hypothetical model of cause of damage from intracellular freezing (Mazur,70).

"L" will grow and this growth will cause the lethal rupture of the membrane. Jackson and Chalmers (71) and Everett (72) explained that this process caused the frost heaves in clay soils. In the (B) process, if the cooling velocity was ultra-rapid, the water in "R" would freeze, either spontaneously or by nucleation from "L", before it was able to flow into "L" and freeze there. In this case there would be no damage by rupturing of cell membrane. Now, if there was very slow warming (<1°C/min), ice would migrate into the neck region causing it to thicken. Such thickening could cause the membrane annulus that delimits the neck to rupture. But, if the cell were warmed rapidly, all the ice would melt before the neck region had time to grow and no irreversible damage would occur (summarized in Figures 15 and 16).

a. Mechanical Injury: It is difficult to prove any direct mechanical injury resulting from the extracellular ice crystals alone in cells or animal tissue. The fact that cells and tissues will survive extracellular freezing under proper conditions demonstrates that the physical presence of extracellular ice crystals is not necessarily lethal, whereas intracellular ice crystal growth may be more

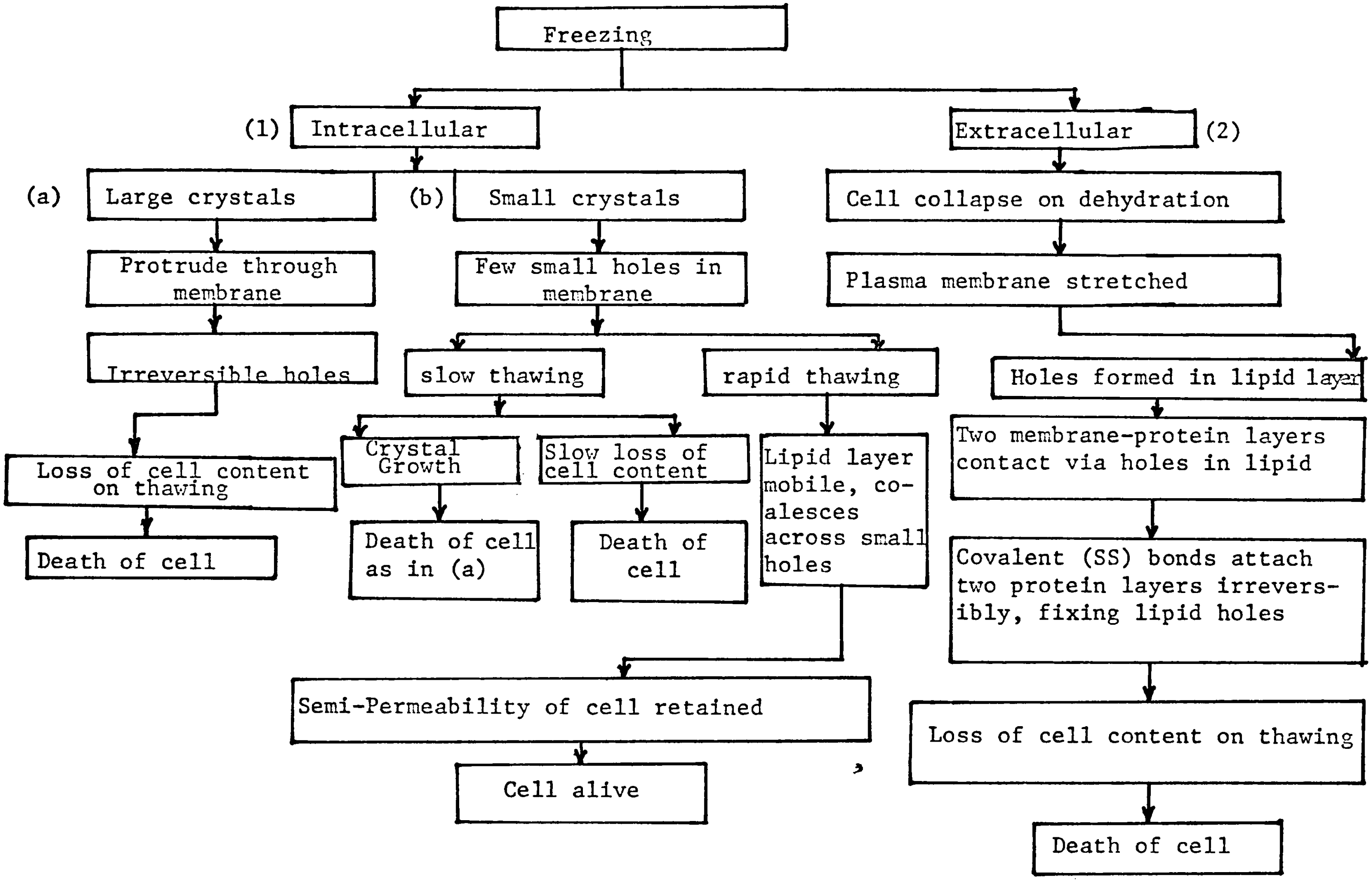

Freezing
(1) Intracellular
Extracellular (2)
(a) Large crystals
(b) Small crystals
Cell collapse on dehydration
Protrude through membrane
Few small holes in membrane
Plasma membrane stretched
Irreversible holes
slow thawing
rapid thawing
Holes formed in lipid layer
Loss of cell content on thawing
Crystal Growth
Slow loss of cell content
Lipid layer mobile, co-alesces across small holes
Two membrane-protein layers contact via holes in lipid
Death of cell
Death of cell as in (a)
Death of cell
Covalent (SS) bonds attach two protein layers irrevers-ibly, fixing lipid holes
Semi-Permeability of cell retained
Loss of cell content on thawing
Cell alive
Death of cell

Figure 15. Proposed mechanism of freezing injury by Levitt and Dear (59)

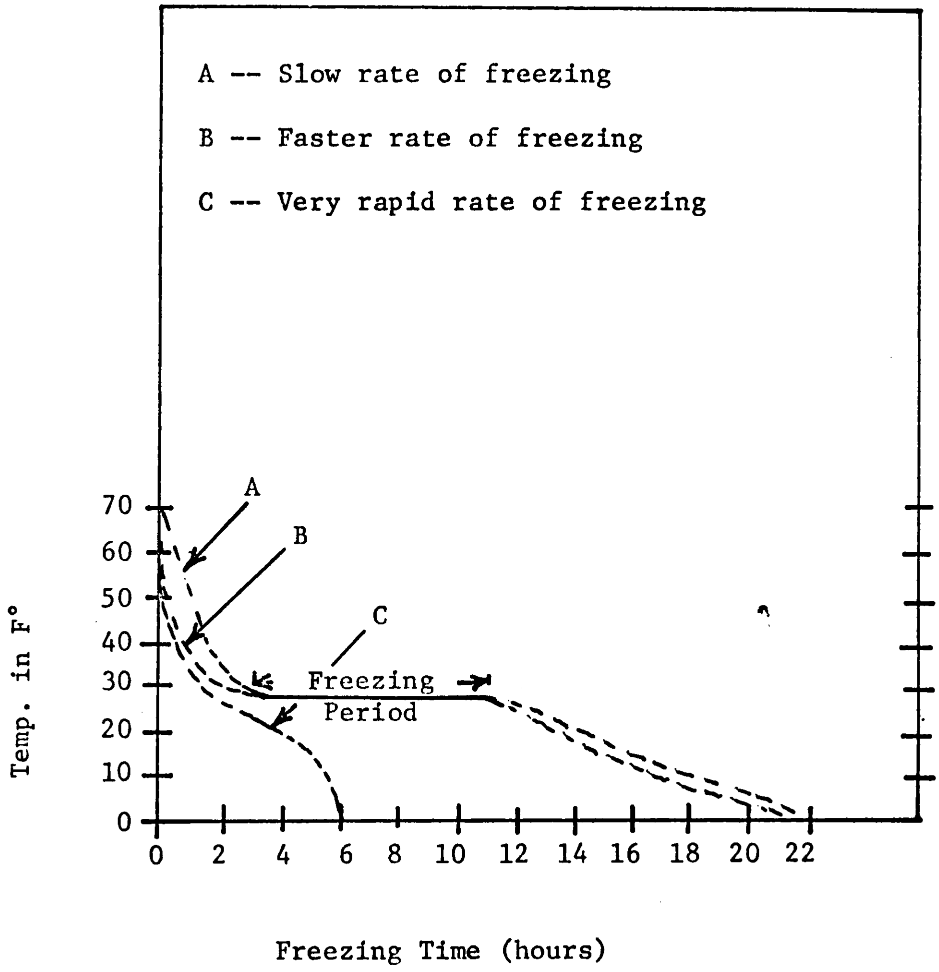


Figure 16. Typical freezing curves for the rate at which the temperature of the food falls when the food is subjected to different rates of freezing. (Gortner, 65)

lethal to cells and animal tissue in specific cases (77), because of an increase of cell volume by 5.4 percent (Haines, 91).

b. Biochemical Injury: Lovelock (73) suggested that lipid-protein complexes may be the weak link in many cells challenged by freezing. Unlike most simple proteins, lipoproteins are not held together by strong co-valent bonds, but by much weaker associations. Lovelock described these complexes as "inherently unstable and probably maintained in living cells by continuous synthesis." It was proposed that they dissociate following small changes in the environment which would be harmless to the more stable co-valent macro-molecules. Among the changes which might occur are:

(i) Increase in electrolytic concentration and resulting increase in ionic strength in suspending medium

(ii) Changes in pH

(iii) Sufficient removal of water to bring cells and their structures into actual physical contact (Lovelock, 73).

Further identification as to causes of biochemical injury are noted as follows:

i) Solute concentration: There is no conceptual difficulty in noting how gross alterations in the concentration of intra- and extracellular solute could be lethal. Lovelock (73) thoroughly documented the relationship between salt concentration and increased membrane permeability in the red cells, demonstrating a sudden increase in the loss of phospholipid from the cell at concentrations of NaCl above 0.85 M (5%). The loss of phospholipid was suggested to render the cell membrane permeable to cations. When the ionic strength is suddenly reduced with thawing, the cell suffers osmotic lysis.

ii) pH Change: Finn (75), while investigating the denaturation of ox muscle juice by freezing observed that there was a definite relationship between the amount of denaturation and pH. Lea and Hamak (76), while working on the sensitivity of principal protein of egg yolk to slow freezing, found that the reduction in pH from 6 to 4 for the frozen samples at -3°C resulted in complete precipitation of the protein. Rapid freezing would prevent denaturation of samples at pH 6.8 though not at pH 5.2.

iii) Dehydration and Molecular Contact: Lovelock (73) proposed another mechanism of injury to cells. While working on the denaturation of B-lipoprotein in human plasma frozen to -25°C or lower, he concluded that the progressive removal of water resulted in the concentration of lipoprotein molecules until they were in actual physical contact, which permitted the formation of undesirable cross linkages leading to distortion or rupture on rehydration. This phenomenon may happen in single celled microorganisms. Levitt (59) proposed a more specific reaction. His model presumed both the opposition of surfaces and folding of protein molecules as a result of removal of their aqueous suspending medium. Levitt proposed that oxidation of the sulfhydryl group or an SH ⇄ SS interchange results in the formation of sulfide bonds between adjacent proteins or portions of the same protein. On rehydration, these SS-bonds remain unbroken and the protein molecule is distorted or weaker bonds are ruptured. After freezing there was an increase in the SS-bonds content. It was also proposed that dehydration caused the breaking of hydrogen bonds in lipoproteins. Possibly those bonds between water and protein stabilized those sensitive molecules and prevented their interaction.

c. Non-related Injury:

i) Storage death--Weiser and Osterud (85) defined it as cell death resulting from the exposure of cell to a given sub-zero temperature for a certain period of time. For example, the cells begin to be exposed to concentrated solutes the instant ice forms in the aqueous media, and they continue to be exposed to solutes during subsequent storage or maintenance at that temperature. Haines (91), Straka and Stokes (92) and Woodburn and Strong (93) reported that death rates decreased in storage temperatures between -1°C and -30°C in a variety of bacteria, including species of *Pseudomonas*, *E. coli*, *Staphylococcus*, *Salmonella* and *Streptococcus* (see Figure 17). Haines (91) also concluded that storage at -2°C of a frozen solution of native cellular proteins of *B. pyocaneus*, extracted at low temperatures, led to rapid coagulation of one fraction of protein. Such flocculation was

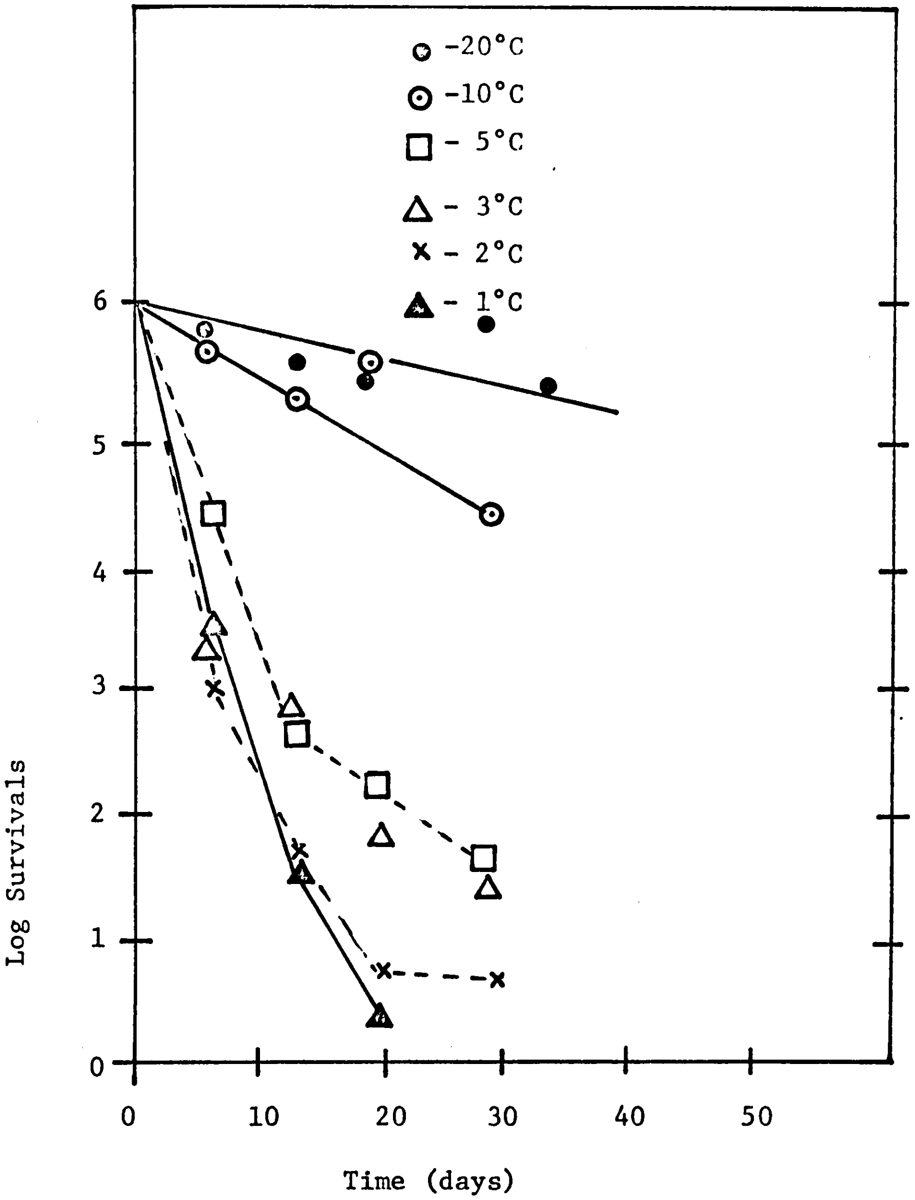


Figure 17. Survival of bacteria as a function of length of storage at immediate temperatures (Haines, 91).

negligible at -20°C. It was also pointed out that such a change leading to the flocculation of cellular proteins was not mechanical, but was chemical combined with a time lag.

ii) Immediate death--Weiser and Osterud (85) defined it as a cell injury resulting from the act of freezing or thawing itself. The causes of any injury resulting from "immediate" exposure to solutes during cooling are probably no different qualitatively from those operating during long-term storage or maintenance of that condition at constant low temperatures. Mazur et al. (86) concluded that intracellular ice crystals were the chief factor in immediate injury, although they obtained no direct microscopic evidence from volume measurements that ice actually formed in cells that were killed. Exposure to concentrated solutes appeared to have been a secondary factor in this type of injury.

iii) Effect of Cell Concentrations--Sato (87), Major et al. (88) and Bretz (89) showed that the survival of E. coli depended markedly on the concentration of cells in the suspension. Major et al., reported that 3.2 percent survived 7 days storage at -22°C when the suspension contained 10^9 cells/ml of broth, but only 0.006 percent survived when it contained 10^6 cells/ml. Similarly, Bretz found that 60 percent survived after 7 days storage at -9°C when the original population was 2 X 10^9 cells/ml of buffer, but only 4 percent survived when it was 2 X 10^5 cells/ml. The authors suggested that protection at high cell densities was due to the solutes that escape from injured cells.

iv) Nature of Medium Around the Cell--Harrison (90) showed that in E. coli, when suspended in sodium chloride, immediate survivals were minimal but the case was reversed in distilled H_2O.

Measurement of Conditioning Effects

Sludges generated from water and wastewater treatment facilities need to be concentrated and/or dewatered before final disposal (See Figure 1). The dewatering characteristics of sludges with or without treatment are measured by different parameters such as rates of settling (separation of solids from liquid), filtration and drainage. These parameters will be discussed in the following paragraphs.

Settleability

The most common measure of settleability is the sludge volume index (S.V.I.) which was introduced in 1934 (164). The sludge volume index is defined as the volume, in milliliters, occupied by one gram of sludge, after settling in a one liter graduate for 30 min (165). However, Dick and Vesilind (166) concluded that two sludges could have the same index value, but could exhibit grossly different settling characteristics because the rate of subsidence is influenced by temperature, cylinder depth, cylinder diameter, sludge depth and type of treatment (166, 167). Because of these problems many workers prefer to graph interface layer subsidence versus time or use sludge settling velocity (ft/hr) which is calculated from the graph. Higher velocities are indicative of better settleability.

Filterability

There are three general factors which contribute to the filtration characteristics (169) of sludges:

1) The filter media, which is characteristic of the equipment used,
2) The characteristics of the sludge,
3) Treatment of the sludge prior to treatment.

Of the three factors, the character of the sludge is the most important.

One of the most widely used methods of dewatering sludges is by vacuum filtration, the performance of which can be indirectly predicted by specific resistance measurements made in the laboratory, using a Buchner funnel (170). Review of literature reveals that Ruth (172) attempted to solve the problem of correlating actual experimentation with early theoretical derivations in filtrations. Carman (173) extended the work of Ruth to the point that the early formulations, generally derived for ideal, non-compressible sludges, could be applied to a variety of sludges under constant pressure conditions. This led to the concept of "average specific resistance," which is the resistance of a unit weight of cake per unit area at a given pressure and is commonly expressed in terms of sec^2/gm. The relationship is as follows:

$$r = 2\,\frac{P.A^2.b}{\mu C}$$

r = specific filtration resistance, sec^2/gm

P = pressure of filtration, gm/cm^2

A = filter area, cm^2

b = slope of T/V versus V, sec/cm^6

μ = filtrate viscosity in centipose

C = ratio of gms of dry solids per ml of liquid before filtration = gms/ml.

The above equation assumes the following:

1) The sludges are compressible

2) Resistance of the medium is negligible

3) Pressure differential "P" across the cake is constant

Carmen's work was confirmed by Coakley (170) and Coakley and Jones (171) who conducted laboratory experiments to determine the accuracy of specific resistance in describing the results of filtration tests.

Specific resistance measurements are a useful means of comparing the effectiveness of various methods of conditioning of sewage sludges and also of measuring the optimum quantity of coagulant required in conditioning sludges. Smaller specific resistance values means better filtration characteristics of the sludges. It has been shown (170) that a reduction in specific resistance corresponds to an improvement in dewatering on drying beds. This indicated that specific resistance measurements are applicable to drainage problems where applied pressure is small. Coakley (170) found that ferric chloride addition to a 12 percent solids content digested wastewater sludge decreased specific resistance by a factor of 100, which was further decreased by a factor of 10 by the freeze-thawing process.

Scott and Cornwall (174) reported their sludge filterability results in terms of specific resistance using filter-leaf and as filter yield. Randall, Moore and King (47) expressed filterability in terms of filtration rates.

King et al. (118) concluded that specific resistance was a qualitative measure of sludge dewaterability for polyelectrolyte conditioned aluminum, ferric sulfate and lime sludges respectively. There are other researchers (175, 119) too, who have used specific resistance as a useful parameter for determining relative rates of filtration and dewaterability of sludges.

Coakley and Jones (171) reported that specific resistance could be used to predict yield on large-scale filters by using the following equation:

$$L = .0357 \left(\frac{100 - C_f}{C_i - C_f}\right) \left\{\frac{mPC_i(100-C_i)}{\theta R\mu}\right\}$$

L = yield of dry cake solids lbs/ft^2/hr

C_i = initial moisture content of sludge %

C_f = final moisture content of sludge %

m = proportion of time for suction (usually 50 to 83% of the cycle time)

θ = time for one revolution of filter drum--min. (usually 6 min.)

P = average suction pressure--lbs/in^2

μ = viscosity of filtrate--centipoises

$R \times 10^7$ sec^2/g = specific resistance.

Jones (171) reported that in some cases there was agreement between actual filter yield and the value predicted from the above equation, but in many instances the difference in results between actual and predicted values was 200 percent. He attributed this to the differing composition of sludges and types of filters used. There was always a discrepancy between the values from full scale vacuum filtration operation and the predicted values. In the specific resistance equation (170), it was assumed that the pressure differential across the cake was constant, but Gale (176) pointed out that most of the sludges encountered in waste-treatment are compressible and the specific resistance of a sludge cake was being influenced by pressure differential variation across the cake. Empirically, it was found that

$$r = R_c \cdot \Delta P^{s^o}$$

r = specific resistance, sec^2/gm

R_c = cake constant

s^o = compressibility coefficient

$$\log r = \log R_c + {}^o s \log \Delta P$$

A log-log plot of specific resistance determinations obtained at different pressure differentials gives the coefficient of compressibility and cake-constant, as the slope and intercept where $\Delta P = 1$.

The compressibility coefficients quoted by Dahlstrom and Cornell (177) for sludge were under 0.4, while Trubnick and Mueller (178) reported coefficients of 0.79 and 1.10, respectively for fresh and digested sludges. Understanding of this "coefficient" is essential to understanding the behavior of a sludge on the filter. The values of this coefficient vary greatly for different sludges and different methods of conditioning (170). Bakerville and Gales (179) developed an instrument to measure "capillary suction time" (CST) which could be correlated to the specific resistance, but it could not be used to estimate the coefficient of compressibility. Another convenient way of obtaining information on the filterability of sludges is the "leaf test," in which if the conditioning procedures of sludges, vacuum level, form time (time involved in cake formation) and drying time are the same, the yield of the filter is given by (182)

$$Y = \frac{W}{A_T \cdot t_c}$$

Y = filter yield, weight of dry solids/ft^2/unit time

W = weight of solids retained on the leaf

A_T = test-leaf area, ft^2

t_c = total cycle time

Schapman and Cornell (181) reported that the "leaf test" gave good correlation of different filter performance between the laboratory and full scale plants. Tebutt (186) pointed out that the specific resistance values were being reported in the units of sec^2/gm, considering the vacuum pressure in the filtration test as g(wt.)/unit area, whereas, in fact, it should be expressed as g(force)/unit area. Hence, using pressure units of Newtons/unit area, the correct units for specific resistance are cm/gm or m/kg. The Water Pollution Research Laboratory (186) adopted the practice of reporting specific resistance in the units of 10^{13} m/kg instead of 10^9 sec^2/gm. Within a 2 percent error, values expressed as 10^9 sec^2/gm can be converted to 10^{13} m/kg using the conversion factor 10^9 $sec^2/gm = 10^{13}$ m/kg or multiplying it by 10^4.

Drainability

A second method of sludge-dewatering before final disposal is sludge drying beds, which is by far the most common method of dewatering sludge at municipal waste treatment plants. The 1962 Inventory of Municipal Waste facilities (Glass and Jenkins, 182) indicated that two-thirds of the municipal plants in this country have drying beds. The beds usually consist of 6 in. of sand overlying about a foot of gravel in which open jointed tiles are placed for removal of filtrate.

The solids concentration, after initial filtration of a day or two, is 13 to 22 percent (183) and digested sludge normally dries to 25 to 45 percent solids (183).

Although there are several types of sludge drying models, i.e., open-drained, covered-drained, and open non-drained, yet the mechanisms responsible for the sludge dewatering are: 1) rate of drainage and total drainable water, and ii) evaporation.

Drainage rate is the most important when mechanical dewatering methods such as vacuum filtration are used, but on the other hand, total drainable water is the most important when gravity drainage methods, such as sludge drying beds, are used.

Randall, Turpin and King (9) reported that gravity drainage on sand beds was affected by the solids concentrations in the feed, B.O.D. of the mixed liquor, enzyme activity, type of microorganism in the sludge, change in cellular protein and carbohydrate content, and pH. Other researchers have found that drainage is affected by solids content (187, 191, 192), dosing depth (191), depth of supporting media (191), sand-grain size (188), degree of paving (190, 191, 9) and presence or absence of coagulants or conditioning prior to dewatering (190).

Quon et al. (189) observed there was an inverse relationship between the two main mechanisms, i.e., drainage and evaporation, and that maximization of one retarded the other. Jennett (190) reported that out of the two, drainage was more significant and important. Quon et al. (193) reported that in case of poorly drainable sludges, evaporation became more dominating and was affected by factors such as air temperature, wind velocity and humidity. The two main factors responsible for the loss of the sludge moisture by evaporation were the physical state of the sludge and the evaporative potential of the air. The moisture loss was approximated to the removal rate from a free water surface, provided there was free sludge surface moisture (194). The phenomenon of evaporation for sludge dewatering takes place in two separate phases, the constant rate drying period and the falling rate drying period.

In case of constant rate drying, the free moisture keeps on moving to the top surface by the internal transport phenomenon, and evaporation continues until free surface moisture is exhausted. The constant rate transitions through CMC (critical moisture content), which is influenced by dosing depth and sludge transport rate) to decreasing fall rate, which may or may not be a linear relationship with time and depends on the nature of the dewatering material, and environmental conditions (194). Nebiker (194) indicated that the sludge evaporative rates would be modified by the darker sludge surface, which would absorb more radiant energy or atmospheric heat and increase moisture, while the presence of dissolved solids, oils and fats on the top portions of the sludge would suppress evaporation losses. Greater applied depths of sludge resulted in higher critical moisture content values, but once the CMC was reached, the variation in applied depths of sludges did not make any difference.

Quon *et al.* (193) reported that in case of faster drainage rates, constant rates were of very short durations and hence, in such cases, most of the moisture loss was due to the combined effects of drainage and falling rate period evaporation loss. Jennett *et al.* (187) concluded that the viscosity of the entrapped water in the sludge particles affected both drainage and evaporation processes.

Summary

The review of literature reveals that sludges generated from water and wastewater treatment are becoming an ever-growing problem, and one of the most important factors before final disposal is conditioning of the sludge. Of all the conditioning procedures developed during the past 10-15 years, the most promising appear to be the physical conditioning processes, especially freezing, which seems to have application to a variety of sludges, with or without addition of chemicals. However, there is no real, practical, economical and well understood freezing process available as yet. The purpose of this research was to look into the feasibility of a direct freezing process by conducting experimental work and developing information to fill the gaps in current knowledge.

CHAPTER III

EXPERIMENTAL METHODS AND MATERIALS

The aim of experimental work in this research was to develop appropriate principles and techniques for conditioning and dewatering waste-activated sludge. The scope of the experimental procedures in this chapter can be divided into the following categories:

i) Description of direct freezing processes; i.e., batch and continuous;

ii) Measurement of chemical, physical and biological changes occurring during freezing; and

iii) Measurements of changes in filtration characteristics occurring during direct freezing, with different refrigerant contact times, different solids concentrations, and other variables.

Sources of sludge

The sludges used in the experiments were obtained from three different sewage treatment plants in Virginia, namely, the Interstate 81 Rest Stop plant (Sludge "A") near Radford, the Corning Glassworks plant (Sludge "B") near Blacksburg, and the Roanoke plant (Sludge "C") in the city of Roanoke (see Appendix I for the brief description of sewage treatment plants). The samples were collected from the outlet of the return sludge line in all three cases. The samples were transported directly to the laboratory and initial tests were run on the sludge and supernatants after the desired solid's concentration was obtained.

To concentrate the sludge samples from the sewage treatment plants they were allowed to settle for 4 to 5 hours in a constant temperature room at 20°C and the supernatant was siphoned off to obtain initial solids concentrations of about 1.5%, 0.8% and 1.4% for Sludges "A", "B", and "C", respectively. To obtain higher solids concentrations, an air flotation unit was used. Nevertheless, the maximum obtainable concentrations were only about 1.5% to 1.6%. An alternate procedure of repeated aeration for 6- to 8-hours and settling (under refrigeration at 4°C to 5°C) resulted in maximum obtainable concentrations of 3.6%, 2.0% and 2.3% for Sludges "A", "B", and "C" respectively. This process of concentration took from 3-7 days. Concentrated samples were sometimes stored for later use.

Sludge Characterization Studies

Characterization studies were employed to enable comparison of the sludges produced at different sewage treatment plants.

Total, volatile, fixed and suspended solids analysis, and B.O.D., and C.O.D. determinations were conducted according to Standard Methods (165). A Beckman 215 analyzer was used for total carbon measurements and pH was measured using a Leeds and Northrup probe.

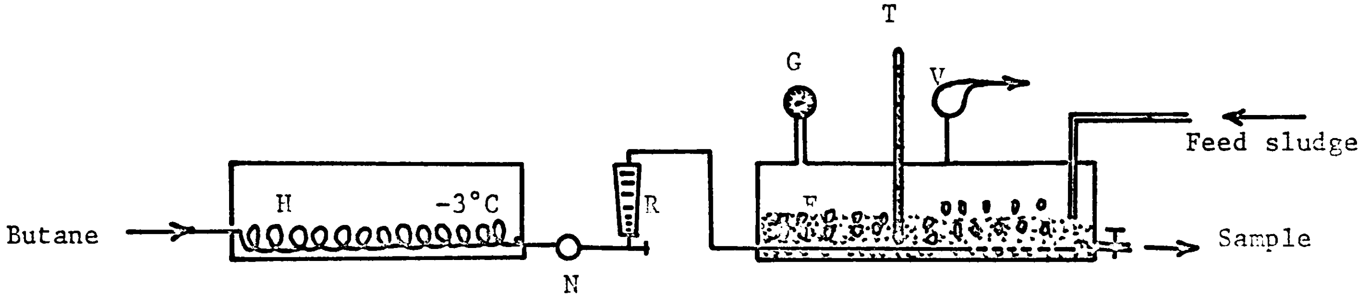
Freezing Processes and Experimental Design

The following freezing systems and techniques were used during the course of the investigation:

1. Batch freezing system (see Figure 18)

   The initial experimental sludge selected was Sludge "C". After concentration by settling to 13,500 mg/l, 1500 ml sample volumes, precooled to 3°C to 4°C, were placed in the batch freezer "F", which was a rectangular tank constructed of 3/4" plexiglas with dimensions of 6" x 18" x 18". Liquid butane was then bled from a storage tank at an outlet pressure of 16 p.s.i., through a -3°C heat exchanger and into the bottom of the sludge freezer where it vaporized into the mixed liquor from a copper tube diffuser. Flow was measured by a rotameter. The heat of vaporization was extracted from the sludge, freezing was induced, and ice slurry was formed. The freezer was operated under a vacuum of 3 cm of Hg to lower the boiling point of butane to -1.5°C and insure complete freezing of the sludge. The actual freezing point of the sludge was -0.5°C.

   The liquid butane rate of flow was 30 ml/min/1500 ml of sludge and butane contact times of 10, 20, 40, and 60 minutes were used for separate experiments.


Butane
H
-3°C
N
R
G
T
V
F
Feed sludge
Sample

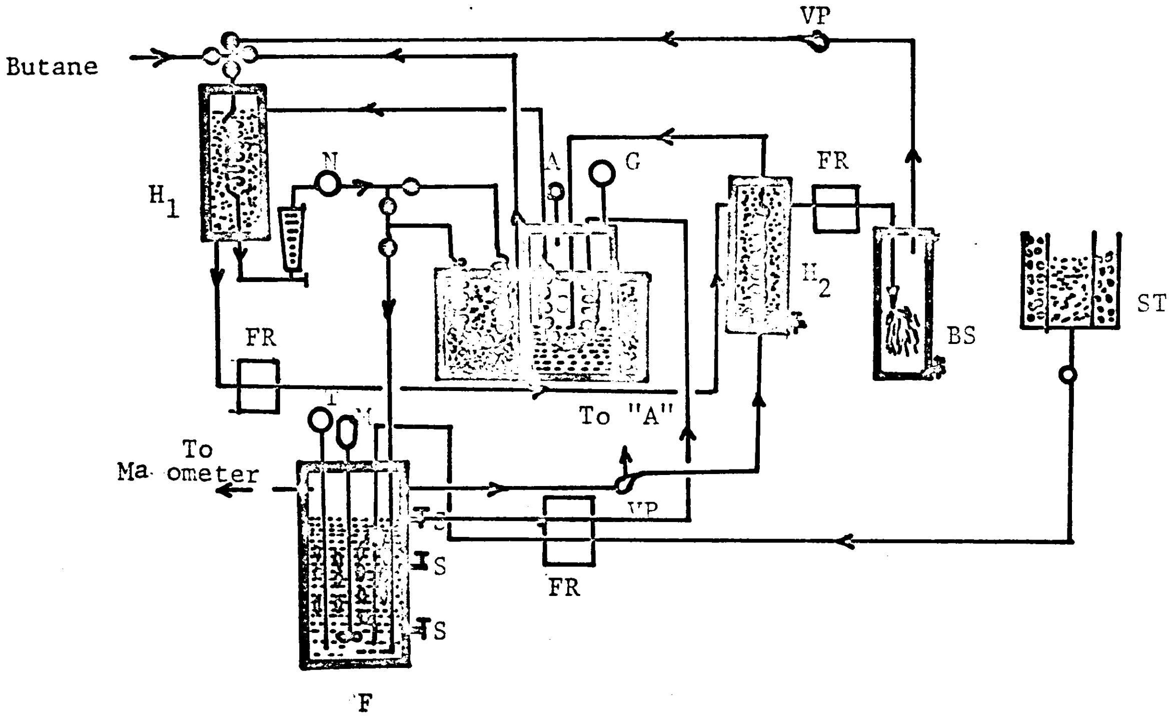
H--Heat exchanger
F--Sludge freezer
N--Non-return valve
R--Rotameter
T--Thermometer
V--Vacuum pump
G--Pressure gauge

Figure 18. Sludge freezing by batch process.

After freezing the sludge was allowed to thaw at room temperature. For these experiments the butane vapors were discharged to the atmosphere after bubbling through the sludge. For later studies, a continuous flow apparatus was developed for the study of butane recovery and reuse. Some sludge samples were frozen indirectly for 36 hours in the refrigerator for comparison with direct freezing.

2. Continuous Flow Apparatus (see Figure 19)

For continuous flow studies, the experimental sludge at a certain solids concentration was allowed to flow from a sludge tank "ST" (surrounded by ice) through a flow regulator "FR," into the freezer "F," where liquid butane, flowing through the heat exchanger "H_1" and flow regulator "R," came into contact with the sludge (intimate contact was achieved by mechanical mixing). After heat-exchange between butane and sludge, the slurry frozen sludge was pumped through the condenser coil "C_1" to the heat exchanger "H_1", from where it flowed to heat exchanger "H_2" and finally to the butane stripper "BS" for recovery of dissolved butane from the supernatant for reuse, if necessary. The hot-vapors of butane from the freezer "F" were compressed by vacuum-pressure pump "VP" and condensed on the condenser coil "C_1"


Butane
H1
N
A
G
FR
VP
H2
BS
ST
FR
To "A"
To
Ma ometer
T
M
VP
FR
S
S
F

A--Automatic Pressure Switch
G--Pressure gauge
VP--Vacuum Pressure Pump
M--Mechanical Mixer
T--Built-in-thermocouple
R--Rotameter
BS--Butane Stripper
FR--Flow regulator
ST--Sludge Tank
S--Sample Point
C--Condensing Coil
N--Non-return Valve
F--Freezer

Figure 19. Butane Recovery and Continuous Flow Apparatus.

and recovered as liquid for reuse in the freezer. The slurry frozen sludge in heat exchanger "H_1," condenser coil "C_1," and heat exchanger "H_2" liquified the butane vapors.

3. Operation of Continuous Flow Unit

For the initial series, sludge "B" at a solids' concentration of 8000 mg/l and flow rate of 3 to 5 ml/min. was allowed to flow into the freezer. At the same time, without any lag time, liquid butane at the flow rate of 5 to 7 ml/min. was allowed to flow into the freezer and mix with the sludge by mechanical mixing. To achieve a certain contact time the sludge was allowed to fill up to that depth, before sludge withdrawal. The vacuum in the freezer initially was 3 cm. To vary the butane contact time (sludge-butane mixing time or sludge retention time in the freezer) for studying the effects on conditioning of sludge, the sludge depths in the freezers were varied to give 6, 12, 24 and 36 hrs. of contact times. After the attainment of desired contact times the slurry frozen sludge withdrawal operation was started. The rates of inflows to and outflow from the freezer were the same. The sludge volumes used during the operation were 18 to 20 liters. When the sludge depths increased in the freezer, the vacuum in the freezer was increased to a maximum of 7cm, to insure the boiling point of liquid butane below the freezing point of the sludge. The slurry frozen sludge was pumped from the freezer to heat exchanger "H_2" after it had flowed through the condenser coil "C_1" and heat exchanger "H_1." The slurry frozen sludge was allowed to thaw in the heat exchanger "H_2" before sampling. The time taken between the moment the slurry frozen sludge came out of the sludge and the sampling for analysis was 18 to 20 hrs. A second series was run using a contact time of 12 hours, a sludge "B" (8000 mg/l) feed flow rate of 3 to 5 ml/min, and different butane flow rates of 5, 15, 25, and 40 ml/min. For a third series, a butane flow rate of 5 to 7 ml/min was maintained and different feed sludge concentrations from 0.8% to 3.6% of Sludges "A," "B," and "C" were used separately with varying butane contact times to determine optimum results. At low solids concentrations ($\leq$ 1.0%), subsequent thawing was accomplished in the heat exchangers, but when the solids concentrations were higher thawing was carried by very slow stirring, because the volumes of concentrated samples were insufficient to maintain the system in equilibrium.

4. Effect of Variation of Influent Temperature of Feed Sludge

To evaluate this effect, sludge "C" samples with solids concentrations of 4000 mg/l were adjusted to three separate temperatures, 0°C, 4°C, and 27°C, and were placed in the freezer. After freezing and thawing, vacuum filtration tests were run to see the difference in the filtration characteristics. A record of time and filtrate collected was maintained. Rates of filtration were the same for all three influent sludge temperature levels.

Tests and Procedures Employed for Sludge Conditioning Evaluations

1. Sludge Filterability Test

The specific resistance test as described by Coakley and Jones (171) was adopted as one of the primary measurements of improved dewaterability. Using a 7.0 cm Buchner funnel with Whatman No. 1 filter paper, applied vacuum of 12" Hg, and maintaining one solids concentration, the sample volumes (in the Buchner funnel) were varied from 50 ml to 150 ml to study the effects of volumetric loadings on specific resistance. To study the effects of applied vacuum on the coefficient of compressibility, the applied vacuums were varied from 12" Hg to 24" Hg, using a sample volume of 50 ml. During batch studies, sample volumes placed in the Buchner funnel were 50 ml and a constant vacuum of 12" Hg was applied.

2. Settling Characteristics

The rate of sludge settling before and after freezing was determined by calculating the interfacial settling velocity (ft/hr) and the sludge volume index (S.V.I.) from data obtained by settling the sludge in a one liter graduated cylinder.

3. Sand-Bed Studies

The second method of measuring the dewatering characteristics of sludges, with or without freezing, was by dewatering on gravity sand beds. The gravity drainage apparatus consisted of a box constructed of 3/4" plexiglas with outside dimensions of 1' x 1' x 1' and a filtrate collecting trough 2" deep fitted with an outlet pipe for sample collection. The box was subdivied into smaller sections of 1.75" x 1.75" (batch studies) and 3" x 2" (continuous studies), using 1/4" to 1/8" plexiglas partitions. The filter media consisted from top to bottom of a 2" depth of fine sand (effective size = .0232") and a 1" layer of crushed gravel (effective size = .0469"), supported by a wire mesh with 1/16" openings overlying a 1/8" wire mesh. For batch experiments, each smaller bed section was washed about 4-6 hours before use, while for the continuous flow studies the sections were washed for about a day before loading the beds. Only 50 ml of sample volumes were applied to the sand beds (smaller sections) during batch studies, while volumes of 400, 600 and 800 ml* were applied separately for each sludge from the continuous studies. After applying a certain volume, time to collect different volumes of filtrate was noted. Amount of filtrate collected at the end of 24 hours was noted and, later on, samples from the cake on the sand bed were taken after 3, 5, and 7 days for moisture content determination. Gravity drainage was considered to be complete after one day while the moisture reductions after 3, 5, and 7 days were considered to be due to air drying. To study the effect of solids loading on the cake-quality, different volumes of settled and concentrated samples (after freezing and thawing) were applied to sand beds. The solids loading varied from 1.5 lbs/ft to 4.5 lbs/ft^2 of sand beds. The sludge used was "B."

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*These volumes were approximately equivalent to 4", 6" and 8" hydraulic heads on the beds.

4. Gravo-Vacuum System for Solids Production

To study the rate of solids production (lbs/ft^2/hr), an 80-mesh micro-screen was placed in a 3" funnel fitted to a filtrate collection apparatus, and also connected to the vacuum system. After placing a certain volume of sample in the screen, it was allowed to drain under gravity until most of the drainable water had been removed (it usually took a few seconds to a few minutes), then about 3" Hg vacuum was applied for 50 seconds for every solids loading. Higher concentrations of solids were obtained after settling of frozen and thawed samples. The solids loading varied from 0.5 to 1.5 lbs/ft of screen. Sludge "A" was used for these experiments.

5. Microscopic Examination

To study the physical and structural changes occurring in the sludge cells due to the direct freezing, an "olympus phase contrast microscope" was used to take photomicrograph pictures before and after freezing. The magnification and dilution used were 200 and 1/10 respectively.

6. Effect of Storage Time on Sludge Samples Before and After Freezing and Thawing

The following few experiments were run:

i) Sludge samples were stored for 1 to 7 days before freezing.

ii) Sludge samples were stored for 1 to 3 days after freezing, but without thawing.

iii) Sludge samples were stored after complete thawing for 1 to 3 days.

7. Wet Sieve Analysis (48)

The size of sludge floc before and after freezing was determined by wet sieve analysis using the method of Rivera-Cordero (48). Four sieves of 44, 75, 106, and 250 microns were used. About 10 ml of sludge sample was poured into the pre-weighed and dried (at 103°C) sieves, and lightly shaken for almost five minutes while partially submerged in distilled water. The sieves were re-dried at 103°C for about 2 hours and weighed. The weight of sample retained on each sieve was plotted against the sieve number.

Butane Recovery and Stripping

Theoretically butane is immiscible in water but researchers (136, 137, 138, 140) have shown that 50 to 150 mg/l will remain in solution at temperatures ≤ 0°C. Therefore, for economic considerations, butane stripping and recovery became very important. Thus, the butane recovery study was divided into three sections:

i) Recovery of butane vapors from the freezer, for reuse.
ii) Vacuum stripping of butane trapped or dissolved in the sludge supernatant, for reuse.
iii) Air-stripping of butane from sludge supernatant, not for reuse.

To evaluate the extent of butane stripping from the sludge supernatant, the sludge temperature was lowered to about 0 to -0.5°C for a few minutes, but solid freezing was prevented to avoid dissolution of cellular structure which might have interfered in the stripping phenomenon.

1. Recovery of Freezer Vapors

An ordinary vacuum-pressure pump was used. The vacuum was about 3 to 7 cm Hg, while pressure was 16 to 18 p.s.i.g. The butane vapors from the freezer were compressed and condensed on coil "C_1" through which slurry frozen sludge flowed. The temperature in the condenser, which was in the constant temperature bath, was about -1.5°C to -2°C. Butane recovery using single compressor was 40 to 60%, which could be increased to 70 to 80% using a secondary compressor in series with the first one.

2. Vacuum Stripping

The sludge supernatant from the heat exchanger "H_2" was pumped into the butane-stripping flask "BS" at flow rates of 30, 60, and 84 ml/min for each applied vacuum. The stripper vacuums used were 3, 10, 30, and 50 cm Hg. One series of runs was made with supernatant temperature maintained at 0 to 1°C throughout stripping. A second series was run wherein the supernatant was permitted to warm up to room temperature (27°C) before stripping. The stripped vapors were permitted to escape, but they could be recovered for reuse if desired. The total carbon in the samples was measured before and after stripping, as a measure of the effectiveness.

3. Air-stripping

The sludge supernatant at room temperature was aerated for 4 to 8 hours to strip off most of the butane into the atmosphere.

Evaluation of Freon as an Alternate Refrigerant to Butane

Freon-114 (1, 2-dichloro tetra flouro-ethane) which had a boiling point of 38.89°F, a density of 91.65 lbs/ft^3

and a heat of vaporization of 58.89 BTU/lb, was selected for study because of the following characteristics:

a) Low toxicity
b) No appreciable odor
c) Non-flammable
d) High liquid and vapor densities
e) Low corrosion rates in metal system.

Liquid freon was brought in contact with the sludge in the same way as the butane, and mechanical mixing was provided using an r.p.m. of 70 to 80. In spite of the procedure, a distinct interface persisted between the sludge and the freon. The temperature at the interface was below 30°F, but considerable thermal variation occurred in the other sections. An alternate method was tried in which sludge and freon were mixed in the form of a fine spray and this resulted in a gas hydrate formation (solid frozen sludge).

Application of Direct Freezing to Waste Sludges from Other Sources

1. Pulp and paper waste sludge

This sludge was obtained from the Wesvaco Pulp and Paper Mill at Covington, Virginia. The sludge contained total solids of about 13,300 mg/l with dissolved solids of about 4,000 mg/l. The following series of batch experiments were run, using 200 ml of sludge for direct freezing experiments. One experiment was run using a 500 ml sample volume to study the settling characteristics (using 500 ppm Al+++).

i) direct slurry freezing without chemicals

ii) direct slurry freezing using Al+++ coagulant dosages of 100 to 1500 ppm

iii) direct solid freezing without chemicals

iv) direct solid freezing with chemicals (Al+++ dosages of 100 to 1500 ppm)

v) original sludge with addition of chemicals without freezing.

Out of the above, i), iii), and v) showed similar results. The effectiveness of direct freezing was determined by specific resistance, cake moisture, rate of solids production and settling characteristics.

2. Aerobically Digested Sludge

This sludge was obtained from units in the research laboratory. The sludge samples were taken out of aerobic digesters maintained at temperatures of 20, 25, 30, 35, 40 and 45°C after digestion times of 11 days. Using 200 ml of each sample, the following series of direct freezing experiments were run and specific resistance and moisture content were used as a measure of improved filterability:

i) direct slurry freezing without chemicals

ii) direct slurry freezing with chemicals (Al+++ dosage--200 ppm)

iii) direct solid freezing with and without chemicals.

CHAPTER IV

EXPERIMENTAL RESULTS

The improvement in sludge dewatering or solid-liquid separation due to the conditioning effects of direct freezing was determined by measurement of settleability, specific resistance values, sand-bed filtration and rate of solids production. The effects of feed solids concentration, butane contact times, butane flow rates, variation in applied vacuum volumetric loadings and hydraulic loadings on the above parameters are reported in this chapter.

Sludge Characterization

The proper correlation of present, past and future research requires that all sludges, from different sources, be properly characterized. The reason for this is that no two sewage treatment plants produce sludges of the same composition, properties and characteristics. The characterization results for the three experimental sludges designated as "A", "B", and "C", are summarized in Appendix Tables A-1 to A-5. The sludge concentrations greater than 1.5% were obtained by repeated aeration and settling as previously described, but simple settling was used to obtain solids concentrations $\leq$ 1.5%. The solids concentrations of the sludges when fed to the freezing unit varied from 0.8% to 3.6%, depending upon maximum obtainable concentrations.

Sludge "A"

The sludge as collected had a total volatile solids content of 76%, and 98% of these solids measured as volatile suspended solids. After freeze conditioning, there was a 20% reduction in total solids, the percent total volatile solids was 78%, and 96% of the volatile solids were volatile suspended solids. The total and volatile solids in the vacuum filtrate after conditioning were almost entirely dissolved solids, but they had increased by 21% over the initial value. There was a slight increase in total and volatile solids in the supernatant after freezing, whereas the change in the gravity drainage filtrate was negligible. However, the solids values of this filtrate were higher than those of the vacuum filtrate.

The C.O.D. values of the mixed liquor suspended solids (MLSS) decreased about 10% with conditioning while the changes in filtrate and supernatant were very small. The pH values of the sludge, the filtrate, and the supernatant before and after conditioning were 7.9 to 7.95, 8.2 to 8.6 and 8.2, respectively.

Sludge "B"

Sludge "B" originally had a total volatile solids content of about 78%, of which 95% were volatile suspended solids. After conditioning, a 40% reduction in total solids had occurred. Of the total solids, about 90% were volatile solids of which 90% were volatile suspended solids. The total and volatile solids contents of the filtrates from both gravity drainage and vacuum filtration were increased by 40% to 50% after freeze conditioning.

Slurry freeze conditioning reduced the C.O.D. values of the MLSS by 40% to 50% while there was not much change in the filtrate and supernatant values. There were no significant changes in pH values, which ranged from 6.8 to 7, 8.2 to 8.4, and 7.2 to 7.4 for sludge, filtrate and supernatant, respectively.

Sludge "C"

The original sludge contained 70% total volatile solids of which about 70% were volatile suspended solids, while after conditioning the volatile solids were about 80% of the total and 68% of them were volatile suspended solids. The reduction in total solids after conditioning was about 40%. The filtrate and supernatant total solids increased, but the differences were not much. The C.O.D. values of the MLSS decreased by about 40%, while the filtrate and supernatant C.O.D. values changed very little.

The pH values of the sludge, the supernatant and the filtrate before and after conditioning were 6.9 to 7, 7 to 7.2, and 7.8 to 8, respectively.

Of the three sludges, the best quality of filtrate and supernatant after slurry freeze conditioning was obtained from Sludge "B", while the worst was obtained from Sludge "C".

General Observations of the Direct Freezing Continuous Flow Process

Some preliminary experiments were conducted to evaluate the nature of the continuous flow process, i.e., to determine temperature effects on settling characteristics and the proper mechanical mixing speed of the stirrer for effective slurry freezing. The following observations were made:

1) Butane flowing into the freezer must be liquid to produce optimum settling and specific resistance reduction. A partial vapor-liquid state would bring the temperature down, but would not accomplish freezing, and considerable foam would be generated in the upper portions of the freezer.
2) The temperature of the liquid butane should be only 1°F to 3°F below the freezing temperature of the sludge. Greater temperature differentials resulted in worse conditioning. The optimum temperature in the freezer was in the range of 28° to 30°F.
3) The freezer must be under a constant vacuum (3 to 7 cm of Hg) to maintain the temperature of butane low enough to encourage the heat exchange phenomenon between sludge and butane.

4) In spite of mechanical mixing, 25 to 30% of the sludge (that portion close to the freezer walls) would freeze solid, but it did not affect the settling characteristics as long as the temperature during settling was between 10°C and 15°C. At higher or lower settling temperatures, the rates of interface subsidence were inhibited.

5) Mechanical stirring speed during freezing needed to be varied from 15 to 45 r.p.m. for best results, with minimum speed in the beginning and highest during the final thickening stage.

6) Violent agitation and fast pumping rates during the process of thawing in the heat exchangers resulted in poor settling, but very slow stirring would enhance flocculation. Thus, instead of pumping the slurry frozen sludge from the freezer to and between the heat exchangers, gravity flow would be more appropriate.

7) Increased storage of samples before freezing and after thawing resulted in decreased settling efficiency and higher specific resistances.

8) During the process of thawing, samples of mixed liquor were taken at different time intervals and temperatures to study the optimum settleability. It was observed that the best results were obtained

if settling was carried out in the range of 10°C to 15°C. However, effective vacuum filtration and gravity drainage of samples gave better results at room temperature (23°C to 25°C).

Effect of Direct Slurry Freezing on Sludge, Supernatant, and Filtrate Properties

The initial series of experiments, which were conducted using the batch process, studied the effects of different butane, i.e., freeze conditioning, residence times on subsequent sludge dewaterability. The dependency is illustrated by Figures 20 and 21. Figure 20 shows that all periods of freezing improved vacuum filtration rates with a resulting reduction in the specific resistance values, but the improvement was a function of contact time. Freezing was not complete after 20 minutes, but it was after 40 minutes. The rate of improvement with residence time decreased after complete freezing occurred, but further improvement was observed. The reduction in the specific resistance was from 47×10^{13} to 20×10^{13} m/kg in 40 minutes, while a reduction to 18×10^{13} m/kg occurred after 60 minutes.

Similar improvement in gravity drainage was obtained by increased contact times (Figure 21). After a dewatering time of 2 minutes, the unconditioned sludge contained about 70% cake moisture, while the sludge conditioned for 60 minutes contained only 20% cake moisture.

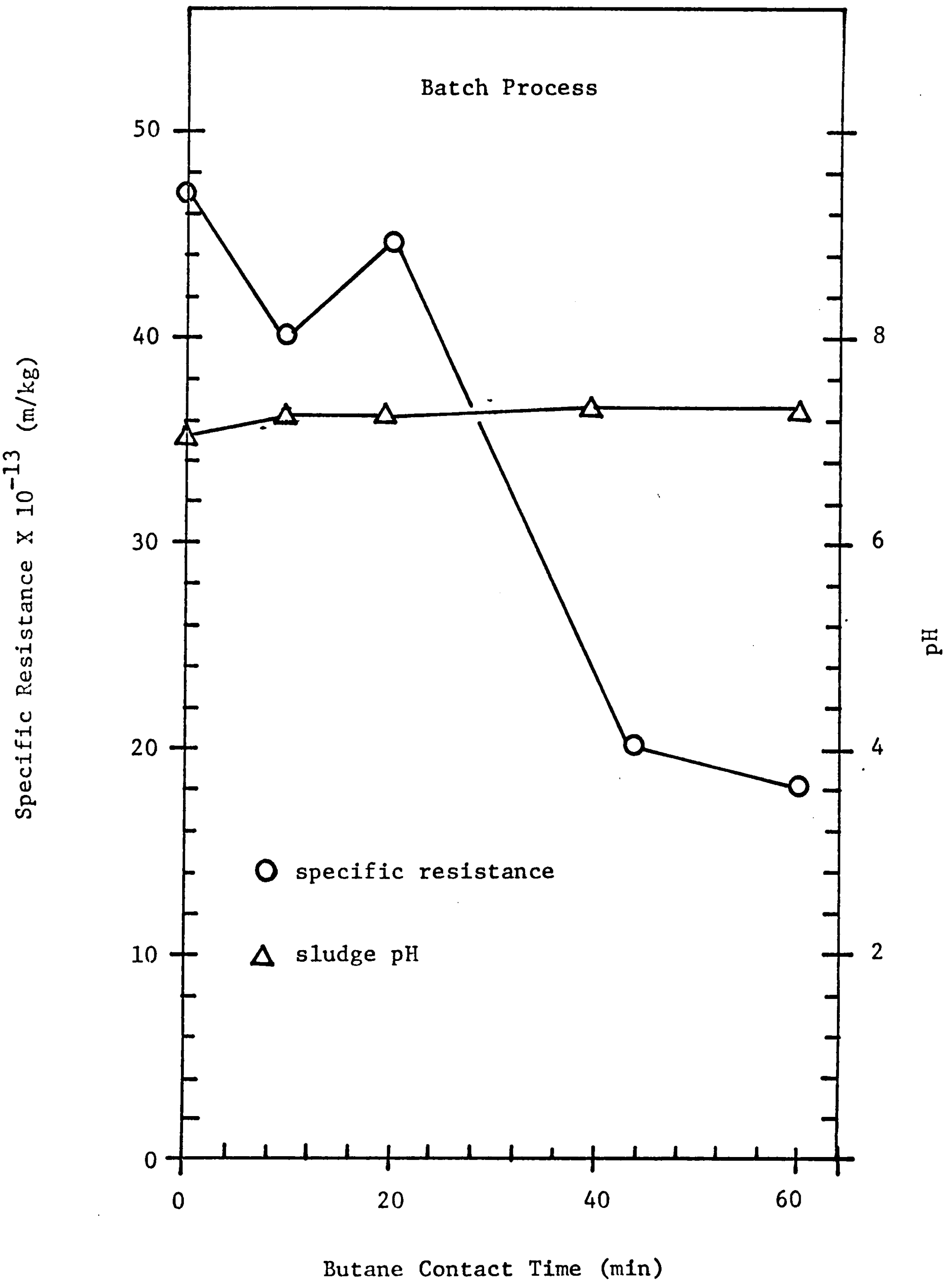


Figure 20 . Effect of butane contact time on specific resistance (Sludge "C")

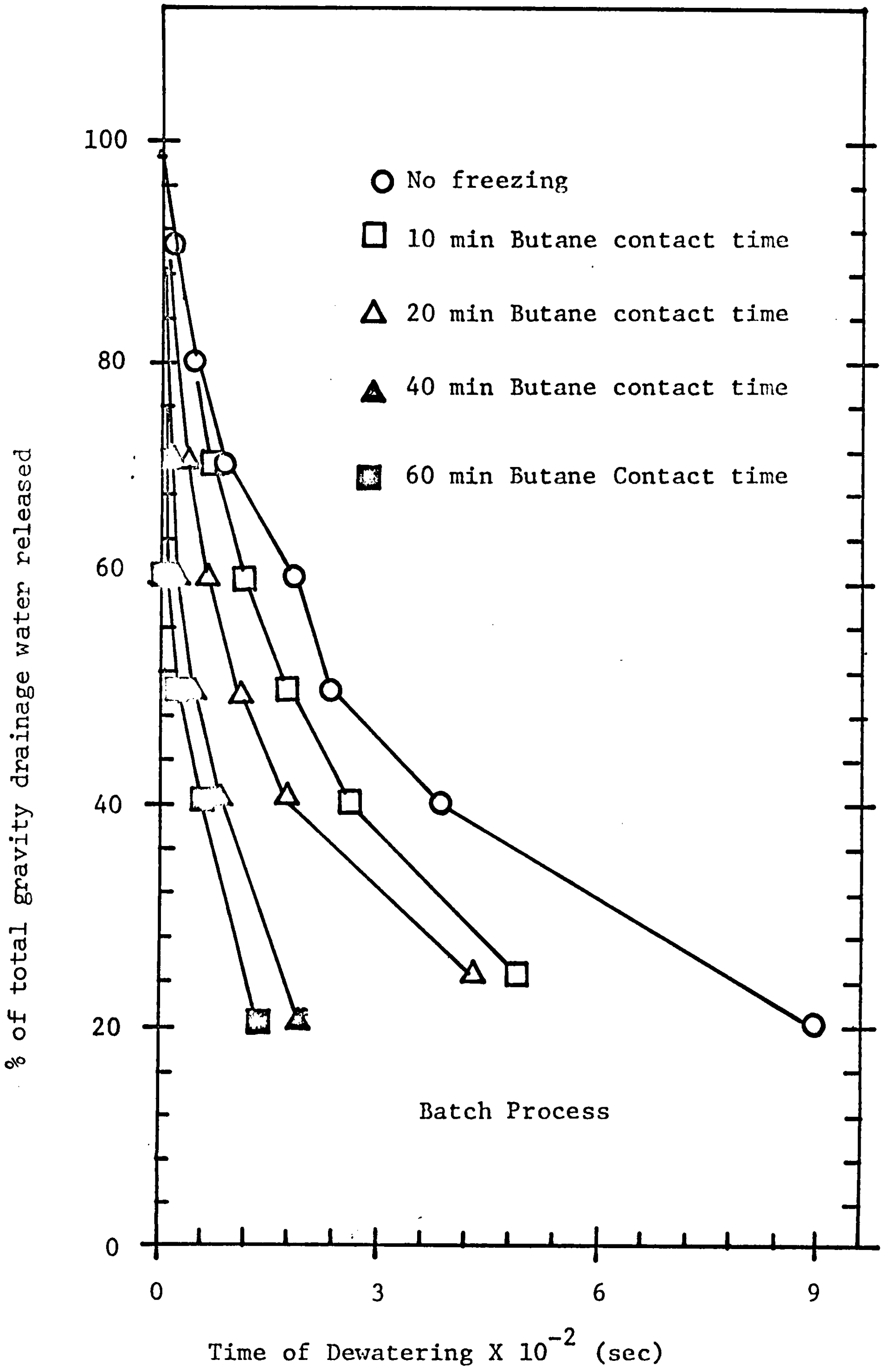


Figure 21. Variation of moisture content with time of dewatering by gravity drainage (Sludge "C").

It was also observed that improvements occurred with increases in contact times during the continuous flow experiments with Sludge "B". A specific resistance reduction from 8.5 x 10^{13} to 2.2 x 10^{13} m/kg occurred with a contact time of six hours (butane flow rate of 5 ml/min), while a further reduction to 1 x 10^{13} m/kg was observed after 36 hours of conditioning (Figure 22). Cake moisture decreased from about 99% to 60% after 36 hours, while a reduction to 80% was observed after only 6 hours. There was not much improvement between 6 and 24 hours (Figure 23).

The settling results showed that sludge settleability is greatly dependent on the butane sludge contact times. The sludge settled to about 200 ml in 3 minutes after 36 hours of contact time, while it settled to only 650 ml in the same settling time with a contact time of 6 hours (Figure 24). The initial settling rate of sludge conditioned by indirect freezing for 36 hours was faster than that conditioned by direct freezing for an equal amount of time, but its final settled volume was only 310 ml. This volume was reached after only 3 minutes and the unconditioned sludge had not settled at all during this time. The interfacial settling velocity (Figure 25) was greater than 16 ft/hr after 36 hours of contact time, while it was less than 4 ft/hr after 6 hours of contact time. The sludge volume index decreased from slightly less than 60 to 24 (Figure 25) with an increase in contact time from 6 hours to 36 hours.

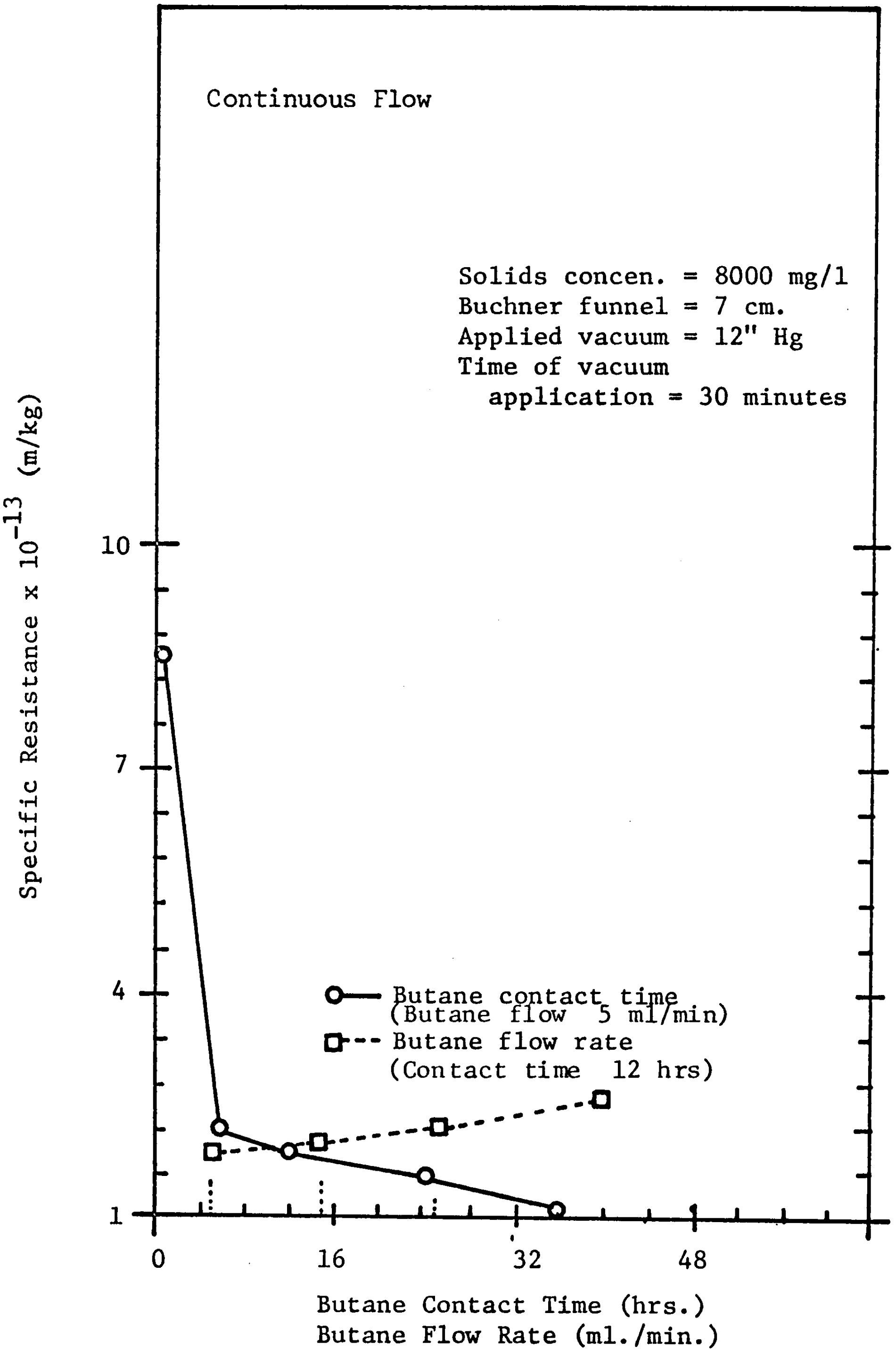


Figure 22 : Effect of Butane Flow Rate and Contact Time on Specific Resistance (Sludge "B").

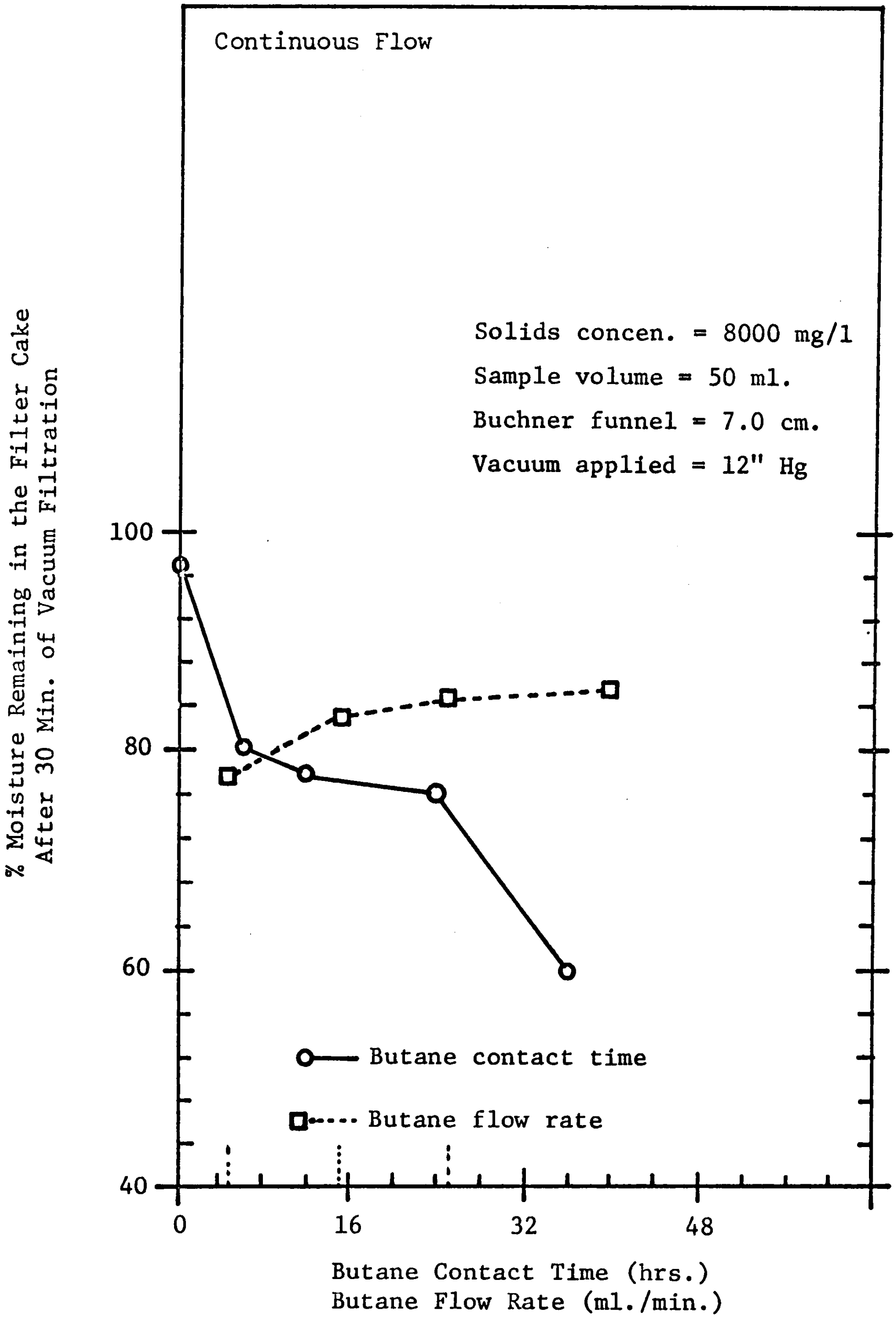


Figure 23 : Effect of Butane Flow Rate and Contact Time on the Quality of Cake (Sludge "B").

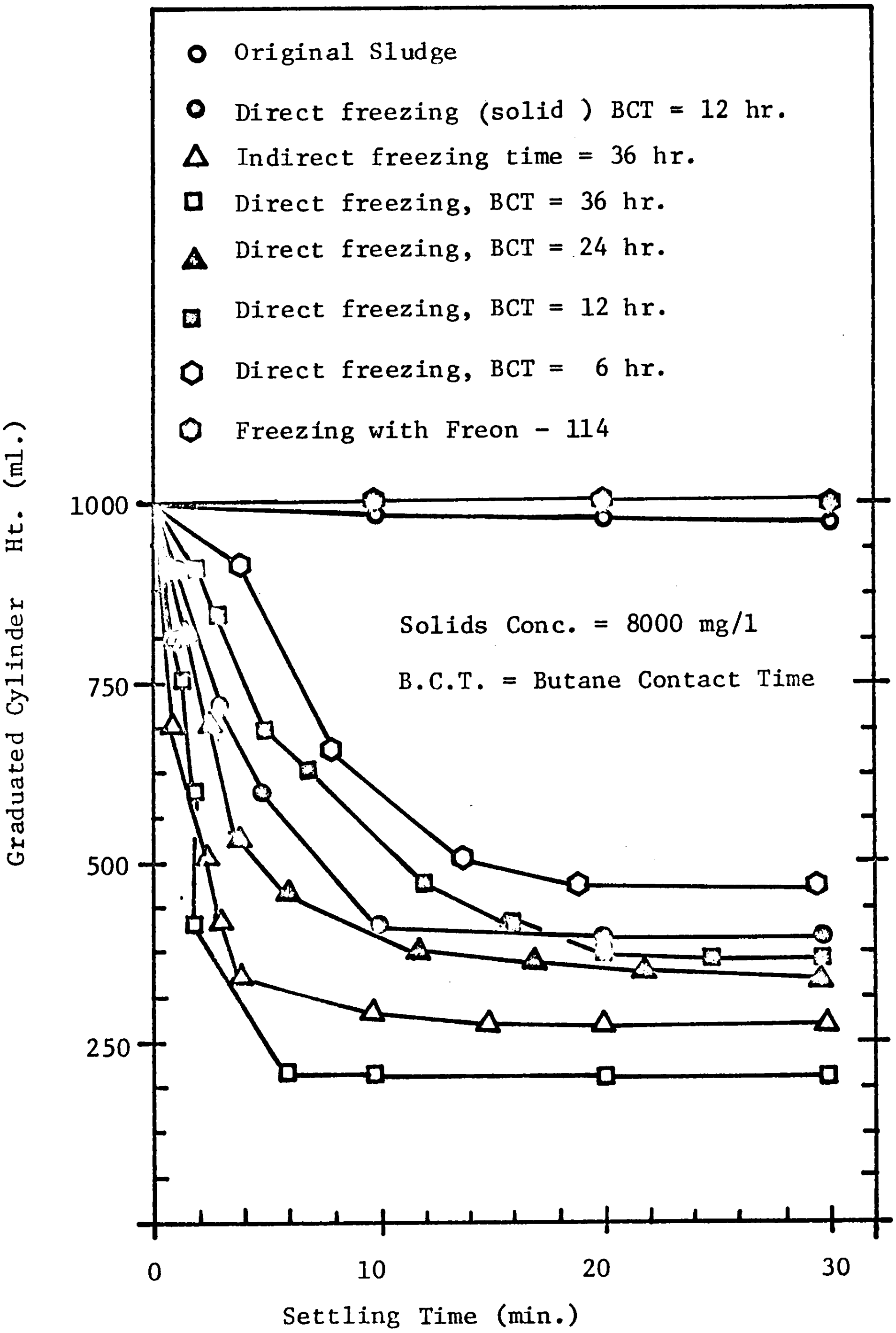


Figure 24: Effect of Butane Contact Time on Sludge Settleability (Sludge "B").

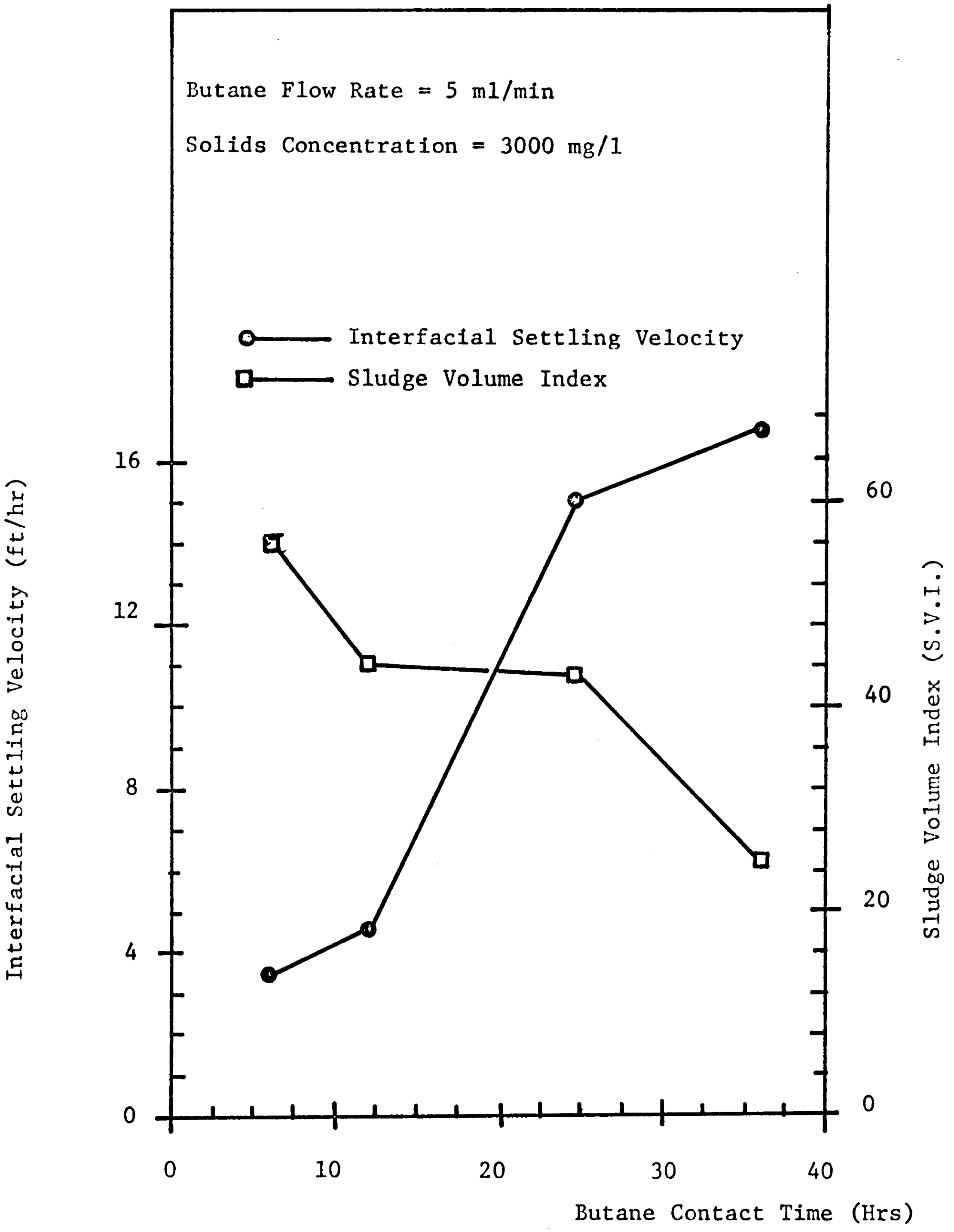


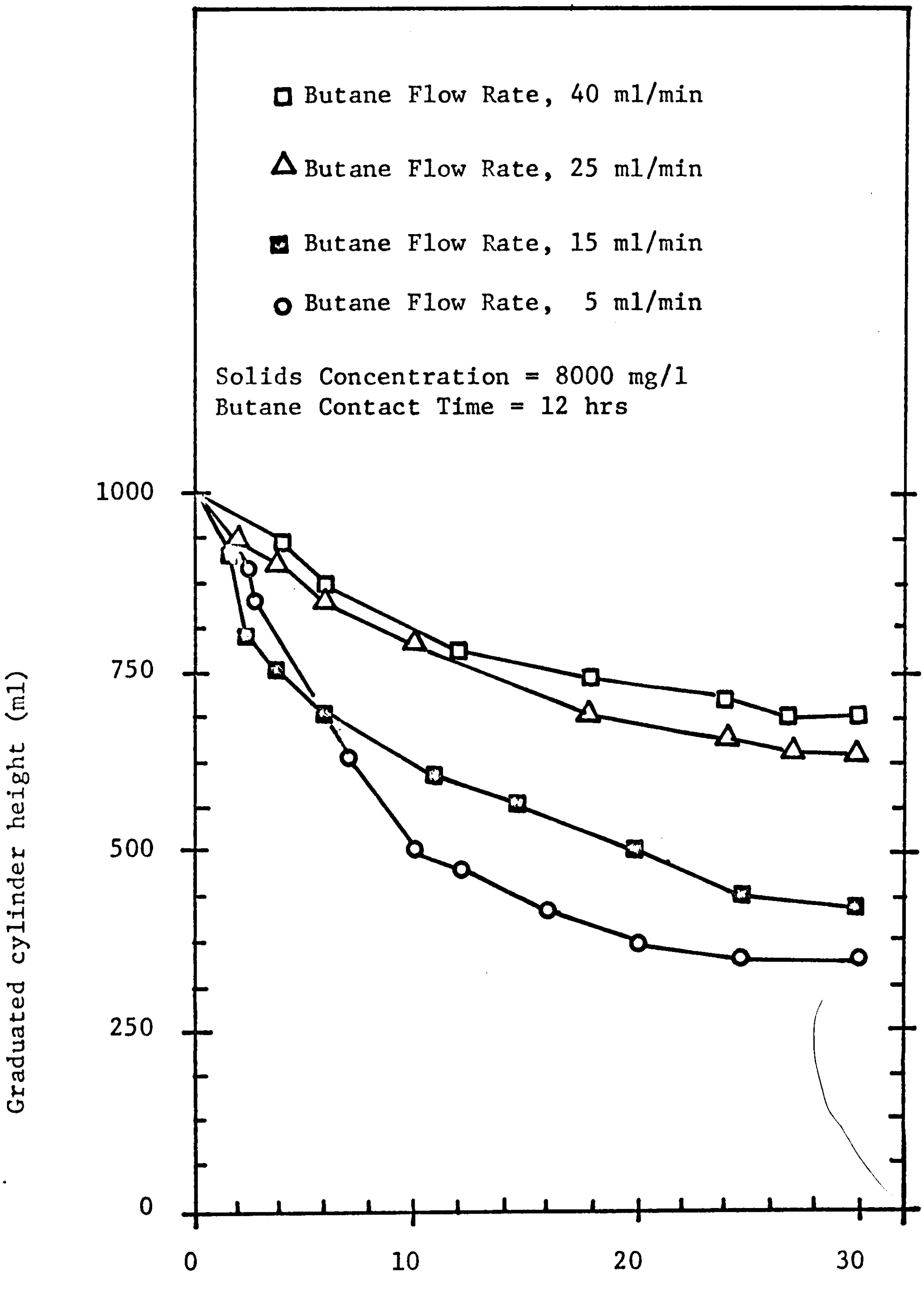
Figure 25. Variation of interfacial settling velocity and S.V.I. with Butane contact time (Sludge "B")

Effect of Butane Flow Rates

When the butane flow rate was increased from 5 ml/min to 40 ml/min using a 12 hour contact time, the specific resistance increased from 2×10^{13} to 2.8×10^{13} m/kg (Figure 22) and the cake moisture content increased from 78% to 85% (Figure 23). The settling characteristics were also greatly affected (Figure 26). After 30 minutes of settling, the settled volume of the sludge treated with the 5 ml/min flow was about 325 ml resulting in a 67.5% reduction in volume, while after treatment at 40 ml/min the volume was 700 ml for a reduction of only 30%. The interfacial settling velocity decreased from 4 to 1.5 ft/hr, while the sludge volume index increased from 40 to 87 (Figure 27).

Comparison with Other Processes

It was observed that the initial rate of settlement after direct solid freezing (Figure 28) was faster than the rate after slurry freezing, but the final settled volume was about the same. Both slurry and solid freezing resulted in a 65% reduction in the sludge volume after 30 minutes of settling, after which no further settlement occurred. Most of the settling occurred during the first 10 minutes, with a reduction of 57% at that time, while the remaining 8% reduction took 20 minutes to occur. The solids concentration of the feed and the contact time for the above experiment were 0.8% and 12 hours, respectively. By comparison, the



Settling Time (min)

Figure 26. Effect of butane flow rate on sludge settleability (Sludge "B")

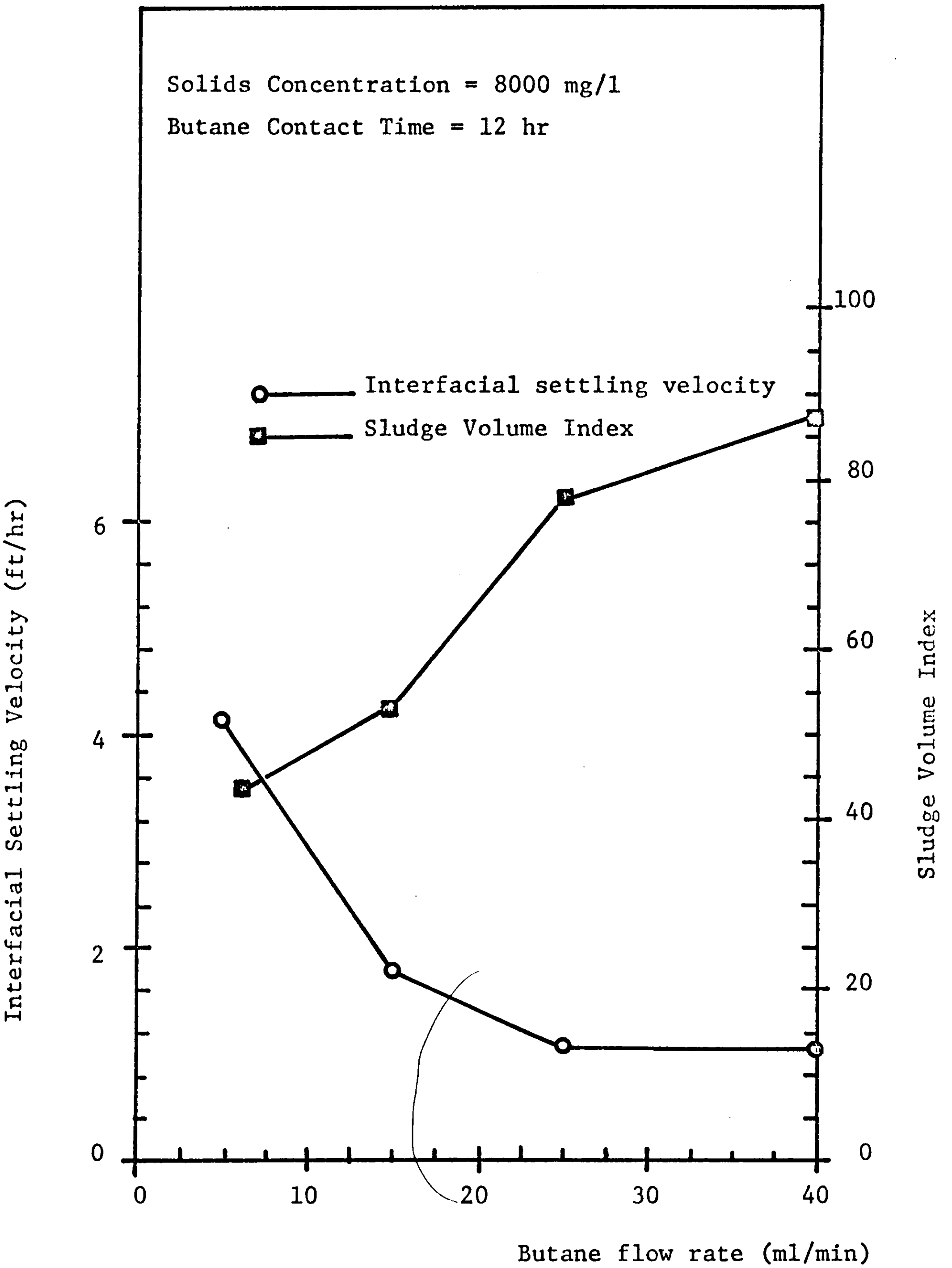


Figure 27. Variation of interfacial settling velocity and S.V.I. with different butane flow rates (Sludge "B").

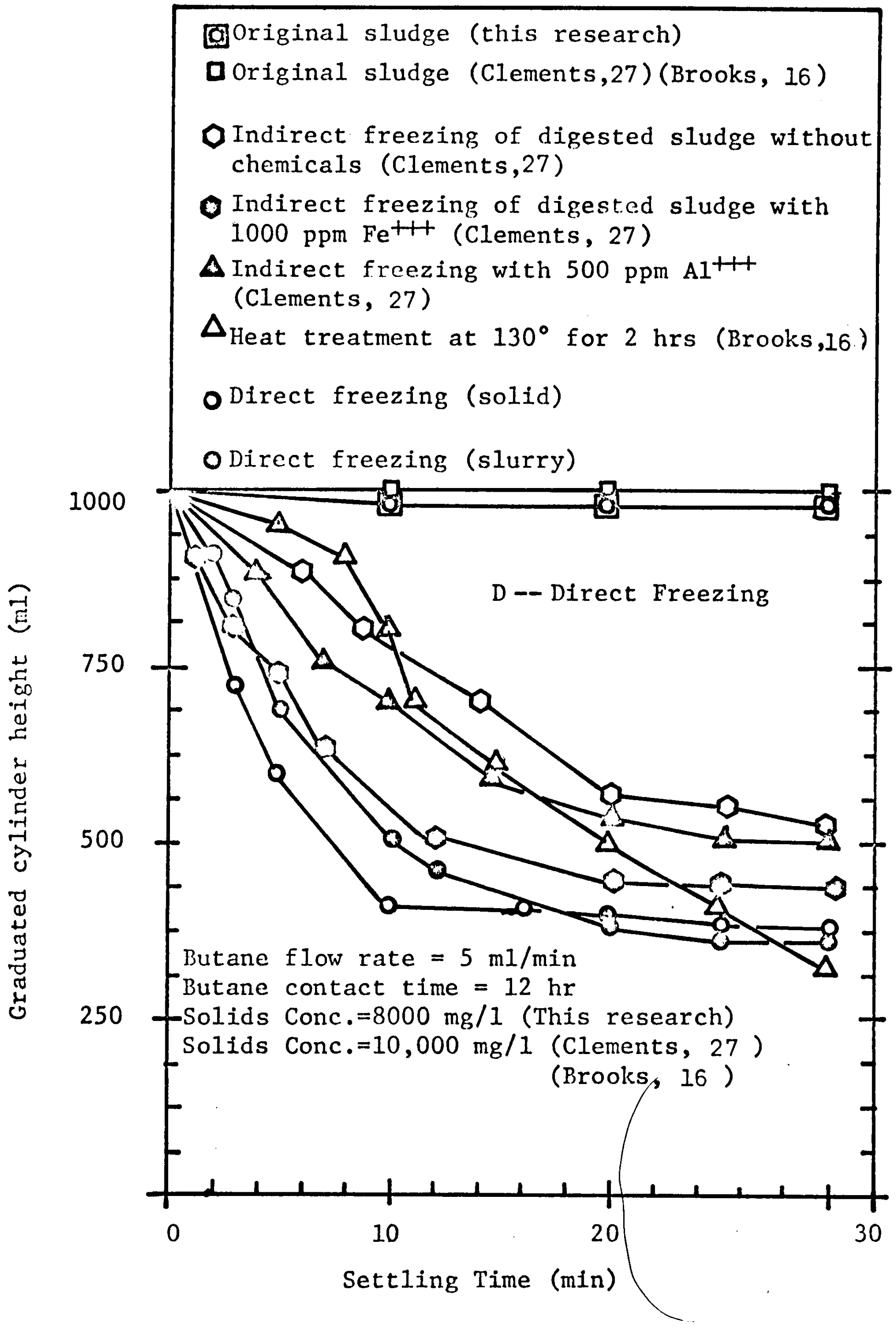


Figure 28. Comparison of direct freezing method to others--sludge settleability as criteria (Sludge "B").

literature states that for indirect freezing using a sludge concentration of about 1%, a 45% reduction in volume was obtained without chemicals, a 50% reduction was obtained with 500 ppm of Al+++, and a 55% reduction was obtained with 1000 ppm of Fe+++ (27). Heat treatment (16) gave settling characteristics to the sludge (solids concentration 1% and temperature of 130°C maintained for 2 hours) such that very slow settling occurred initially followed by a very fast rate which continued even after 30 minutes. Prior to conditioning, the sludge used in the direct freezing system settled about 2% after 30 minutes while no settling occurred with the unconditioned sludge used in the heat treatment (16) and indirect freezing (27) experiments.

Effect of Operational Procedures on Subsequent Dewaterability of Freeze Conditioned Sludge

The effects of changes in operational and handling procedures on the subsequent dewatering characteristics of the conditioned sludges were evaluated. Operation of the freezing unit was changed by varying the feed solids concentration whereas handling procedures were changed by varying the filtration vacuum, the solids loading rate and the storage time before dewatering.

Feed Solids Concentration

When the feed sludge solids concentrations were greater than 0.8%, (Sludge "B"), a 12 hour contact time in the continuous unit was insufficient for good conditioning, and it was evidenced by the subsequent rate and degree of settling. At a solids concentration of 0.8%, Sludge "B" settled to 350 ml (Figure 29) resulting in a 65% volume reduction in about 20 minutes, while for solids concentration of 1.0%, 1.2%, 1.426% and 2.0%, the volume reductions were 40%, 12.5%, 10% and 1% after the same settling time. Similarly, in the case of Sludge "A" (solids concentration 1.426% and butane contact time of 12 hours), 10% and 35% volume reductions were observed after 20 and 60 minutes of settling times, respectively (Figure 30). However, with a solids concentration of 2.05% and a butane contact time of 40 hours (butane flow rate 5 ml/min), settling was complete in about 15 minutes, resulting in a 75% reduction in volume. Again, when the sludge concentration (Sludge "A") was increased to 3.6% and a butane contact time of 40 hours was used, the rate of settling was about 4 times less than at a solids concentration of 2.05%.

When sludge "C" (concentrations of 1.2 and 1.727%) was subjected to butane contact times of 40 hours, considerable improvement occurred during the first 15 minutes of settling, but further settling was very slow. However, when the solids concentration was 2.3%, only a 50% volume reduction occurred during the time in which a 75% reduction was achieved at a lower solids content (Figure 31).

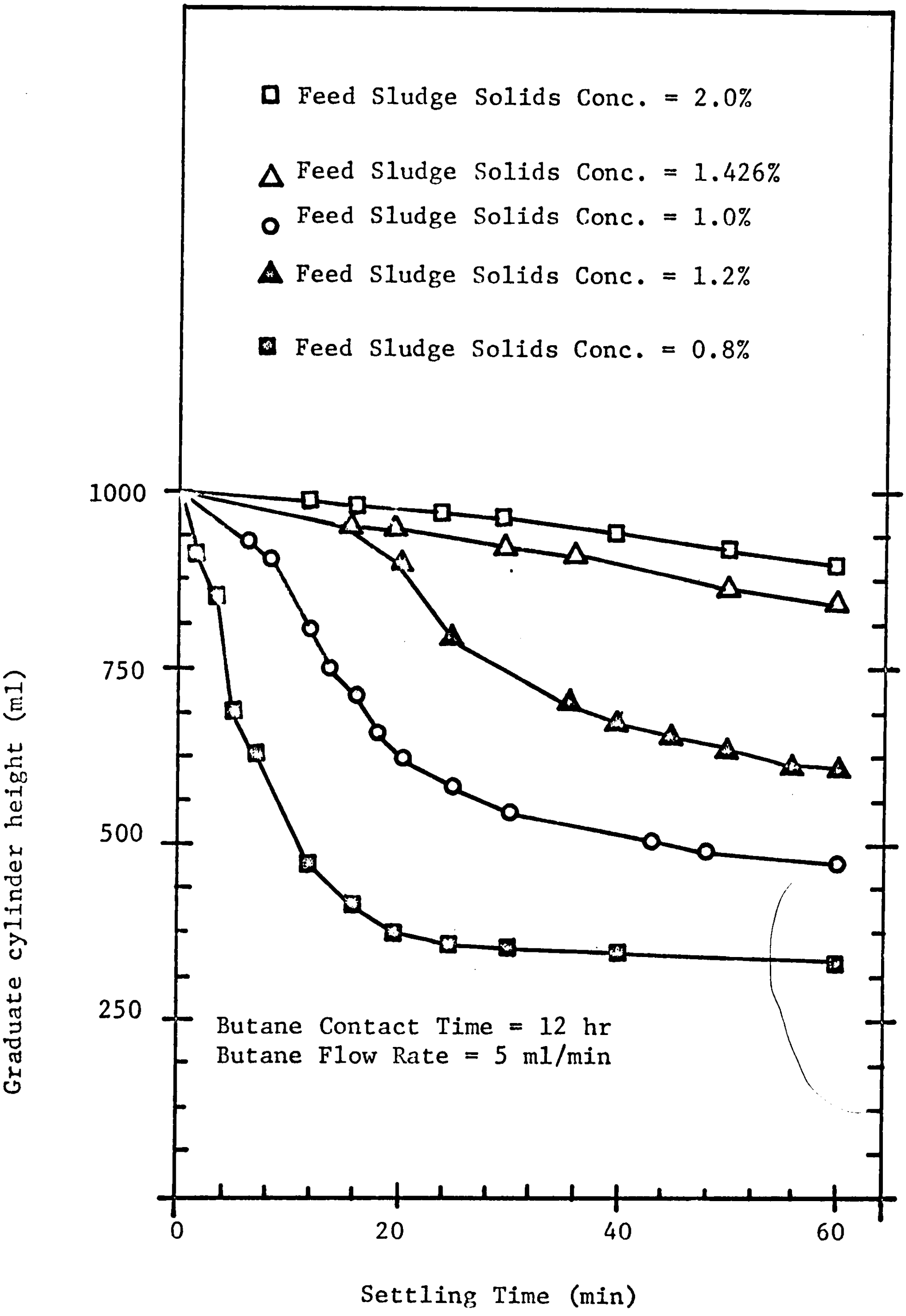


Fig 29 . Effect of feed sludge solids concentration on sludge settleability (Sludge "B").

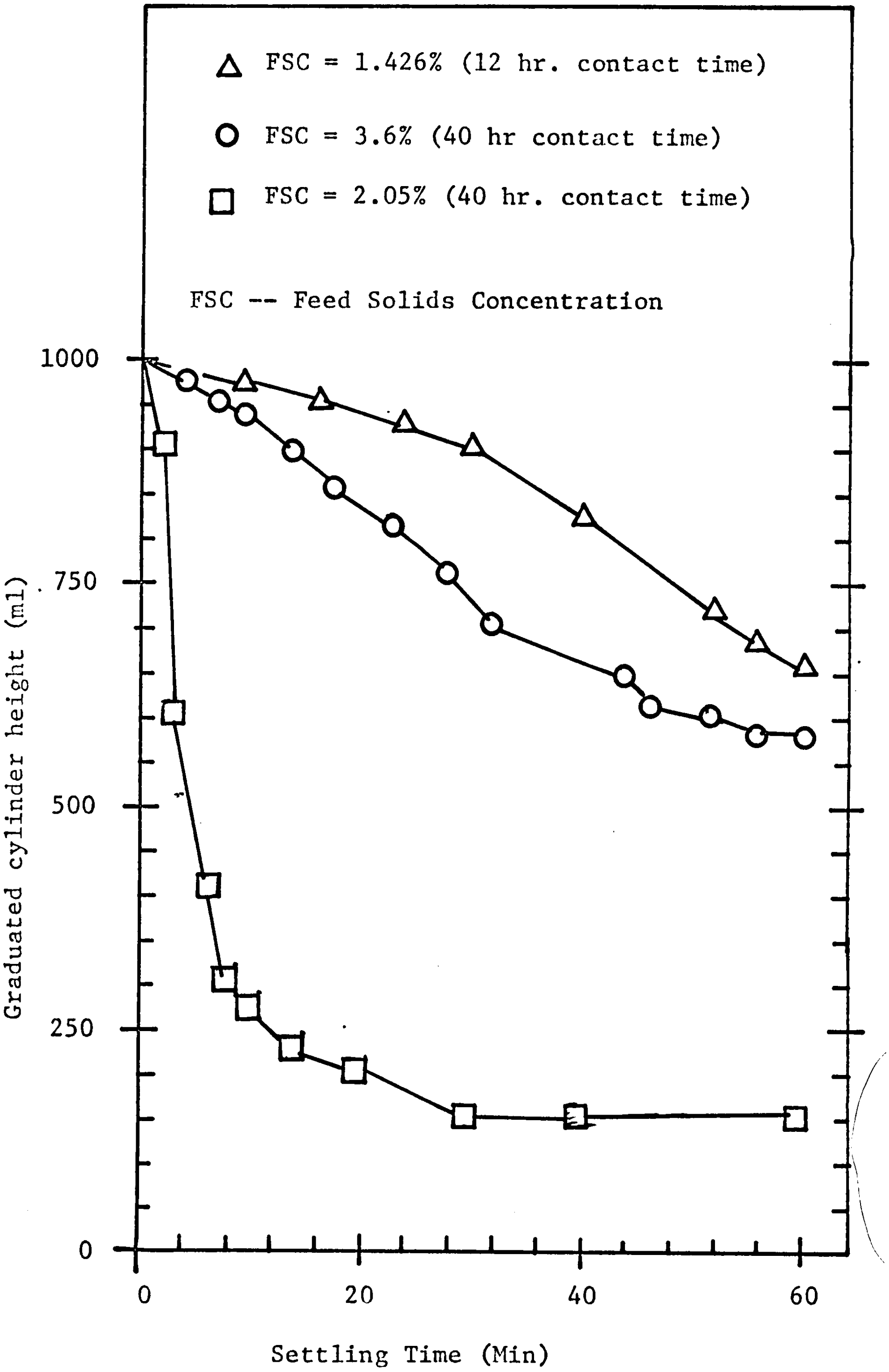


Figure 30. Effect of solids concentration on settling characteristics (Sludge "A")

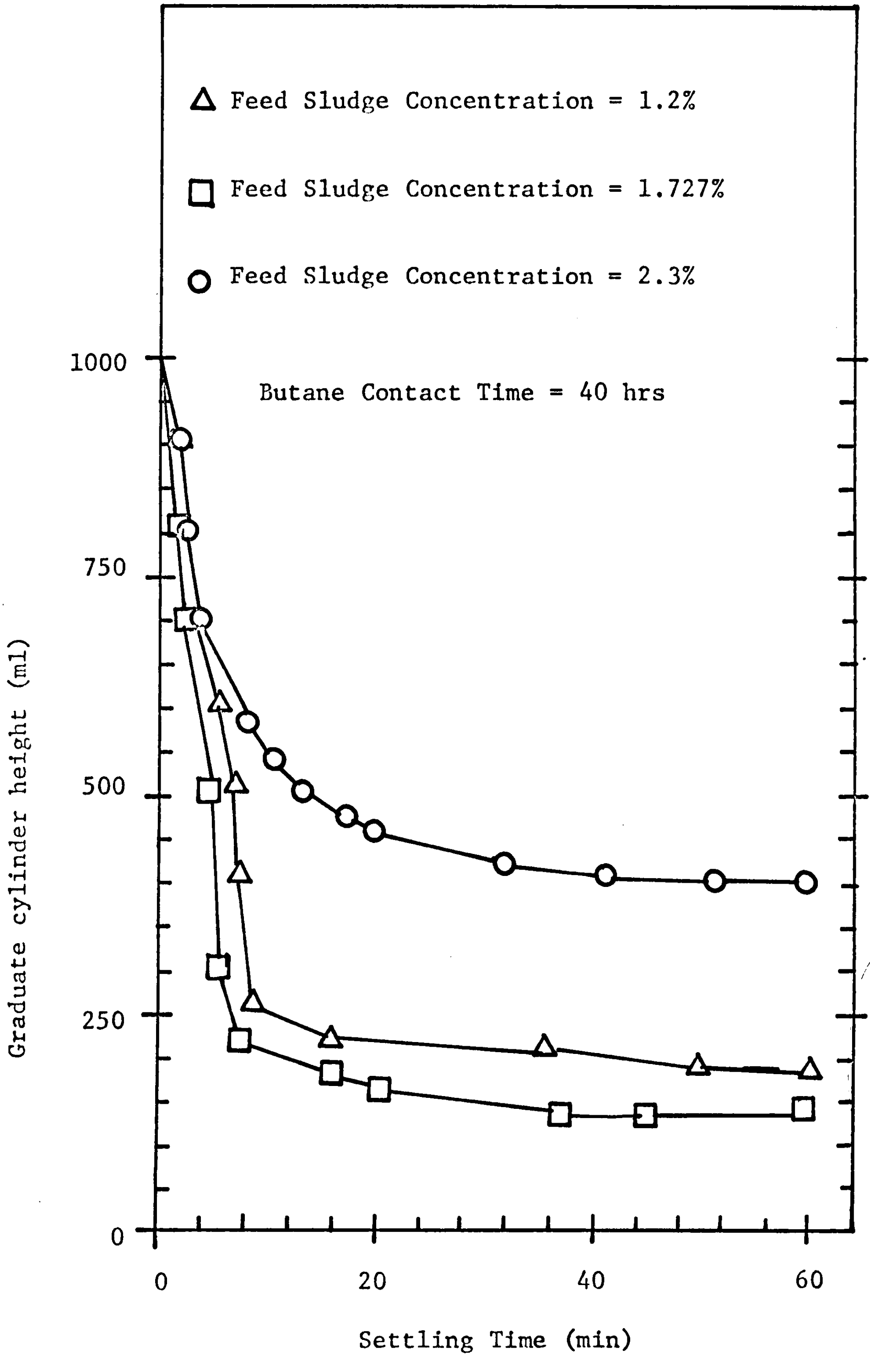


Figure 31. Effect of solids concentration on the settling characteristics (Sludge "C")

The interfacial settling velocity of Sludge "B" (contact time 12 hours) decreased from 3.75 to 0.15 ft/hr with an increase in sludge volume index from 40 to 60, when the solids concentration was increased from 0.8% to 2.0% (Figure 32). An increase in contact time from 12 to 40 hours improved the interfacial settling velocity from 0.4 to 10.4 ft/hr for a solids concentration of 2.3% (Figure 33). Higher solids concentrations decreased it to 0.8 ft/hr. Using a constant contact time of 40 hours for Sludge "A", a decrease in settling velocity from 8 to 2.4 ft/hr was obtained when the solids concentration was increased from 1.426% to 3.6%.

It was observed that to have some appreciable improvement in the dewatering characteristics and faster rates of settling at higher solids, the corresponding butane contact times must also be increased. The relationship could apparently be described by the following equation, assuming a butane flow rate of 5 ml/min:

$$B_{ct} = 24 + 8X_f^2$$

B_{ct} = butane contact time in hours
X_f = feed solids concentration in %

When the feed solids concentration of Sludge "B" was increased from 0.8% to 2.0% using an applied filter test sample volume of 50 ml, the specific resistance value of the conditioned sludge increased from 0.5×10^{13} to 1.6×10^{13}. When applied sample volumes of 100 ml and 150 ml were used,

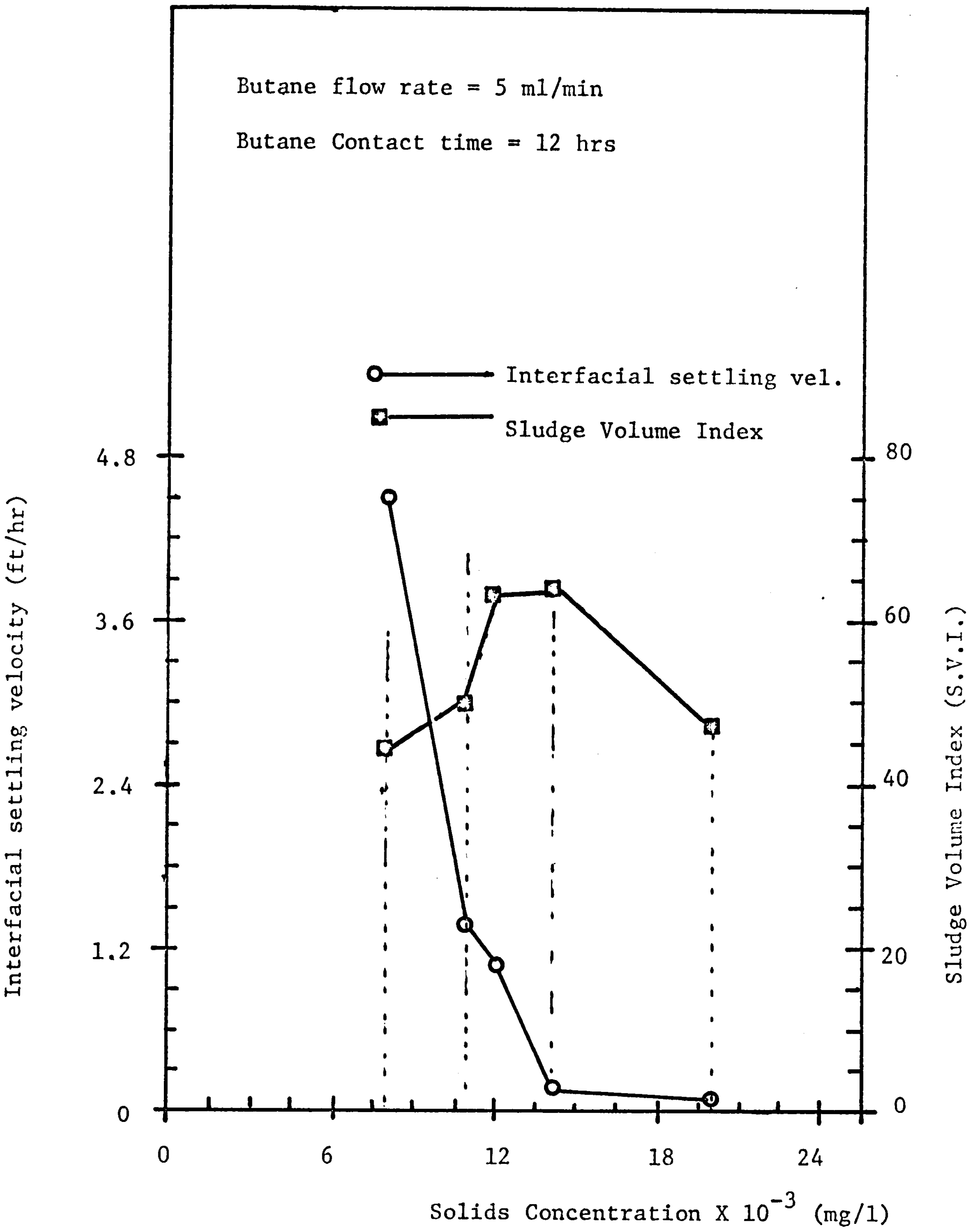


Figure 32. Effect of solids concentration in feed sludge on the S.V.I. and interfacial velocity (Sludge "B")

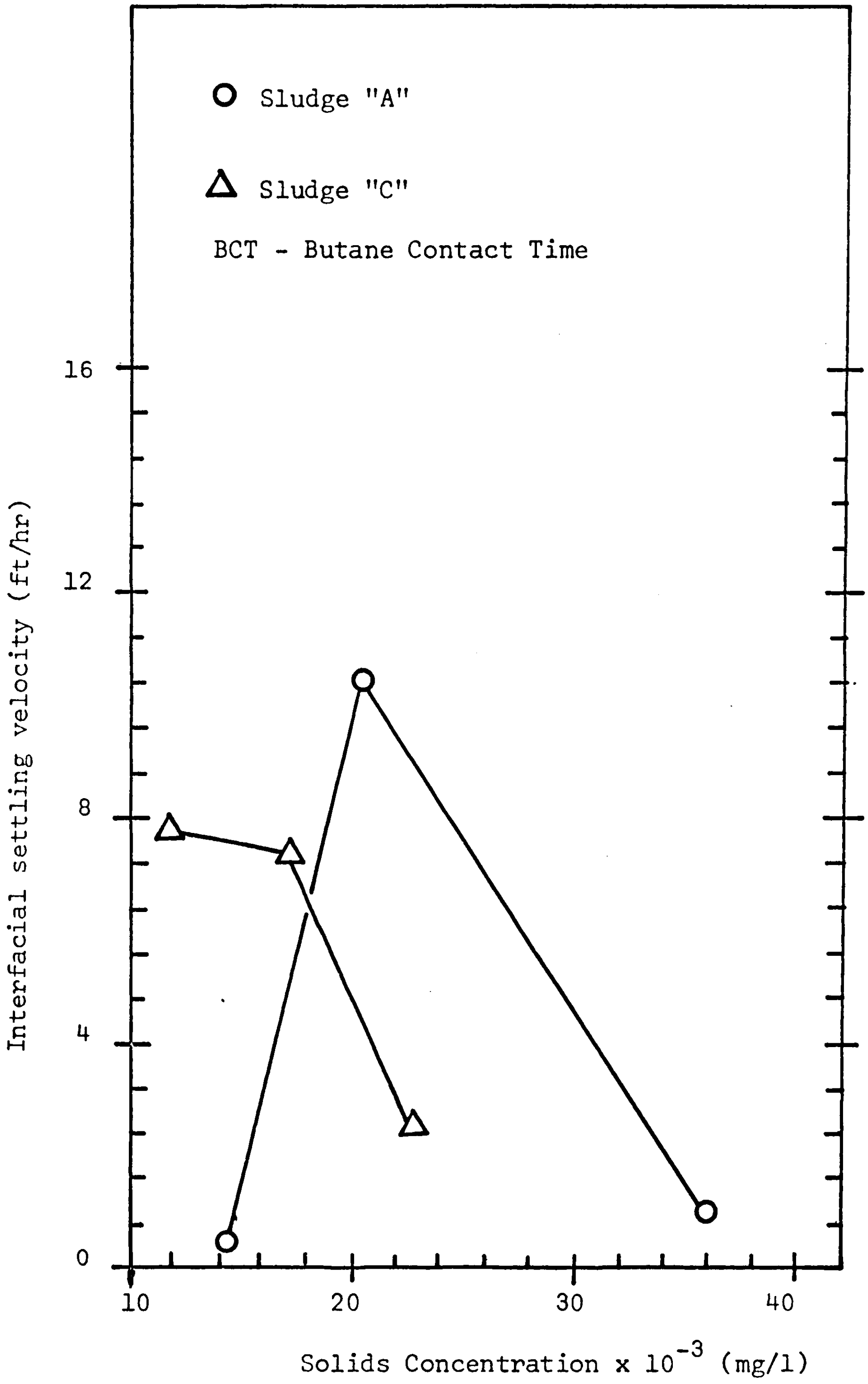


Figure 33. Variation of settling velocity with solids concentration (Sludge "A" and "C").

the specific resistance values of the conditioned sludge were 1.2 x 10^{13} and 2.4 x 10^{13} m/kg, respectively, when the feed solids concentration was 2.0% (Figure 34).

For Sludge "A" (Figure 35-A) using a sample volume of 50 ml and an applied vacuum of 12" Hg, the specific resistance increased from 0.5 x 10^{13} (solids concentration of 1.426%) to 4.9 x 10^{13} (3.6% solids), but this value decreased to 0.2 x 10^{13} m/kg at a solids concentration of 10%. As the applied vacuum was increased from 12" Hg to 24" Hg, the specific resistance increased from 0.5 x 10^{13} to 3 x 10^{13} m/kg for a solids concentration of 1.426%. It was observed that at a constant applied vacuum of 12" Hg, as the applied sample volume was increased to values of 100 ml and 150 ml, specific resistance reductions from 3.5 x 10^{13} (1.426% solids) to 2.5 x 10^{13} m/kg (2.05% solids) and from 5 x 10^{13} to 2.5 x 10^{13} m/kg were observed (Figure 35-B). These specific resistance values increased to 7 x 10^{13} and 8 x 10^{13} m/kg when a 10% solids concentration was used and the same volumes were applied. The effect of increased solids concentration on the unconditioned sludge was adverse, because the specific resistance increased from 9 x 10^{13} to 11.5 x 10^{13} m/kg when the solids concentration was increased from 1.426% to 3.6%.

Sludge "C" responded to solids concentration increases similarly to Sludges "A" and "B". Specific resistance increased from 3.25 x 10^{13} (1.727% solids) to 3.6 x 10^{13} m/kg

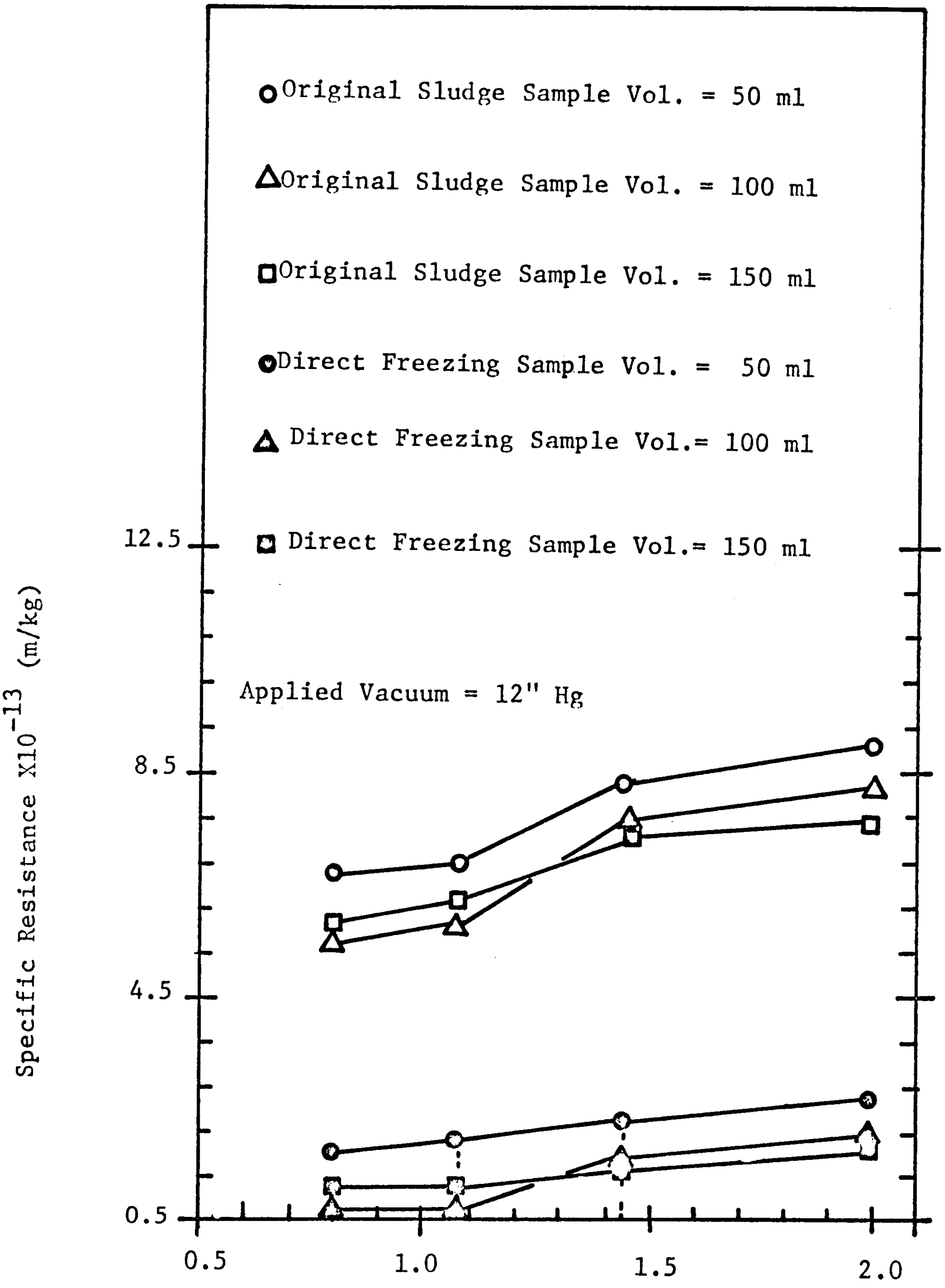


Figure 34 . Effect of feed sludge solids concentration on the specific resistance (Sludge "B")

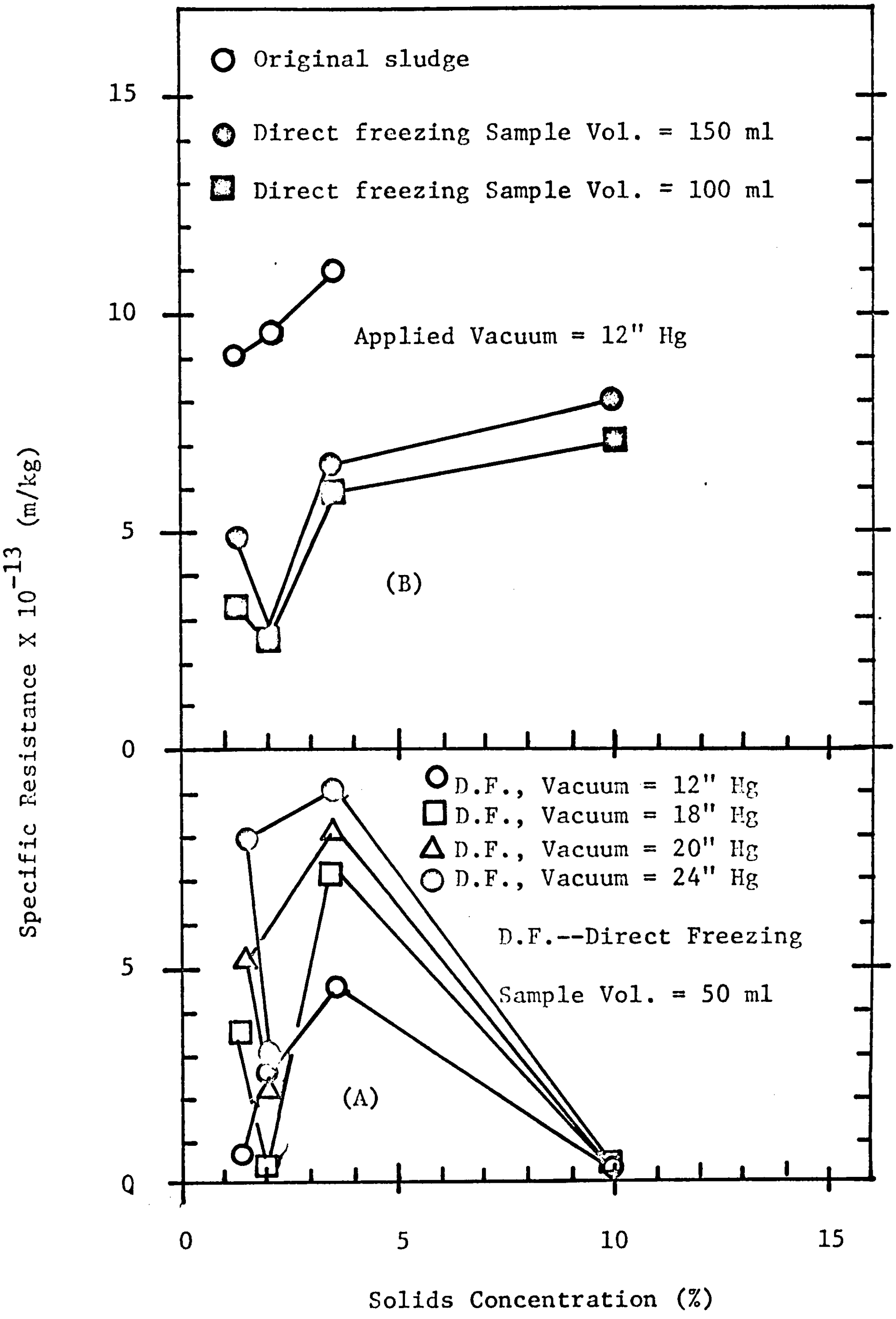


Figure 35. Effect of feed solids concentration on the specific resistance (Sludge "A").

(2.3% solids) and decreased to 1.25 x 10^{13} m/kg at a solids concentration of 14% (Figure 36). The unconditioned sludge showed adverse effects due to increased solids concentration with change in specific resistance from 4.8 x 10^{14} to 5.4 x 10^{14} m/kg for the same increase in concentration.

Filter cake quality decreased as the solids concentration and applied sample volumes were increased. Moisture content for Sludge "B" increased from 60% (0.8% solids) to 74% (2.0% solids) for applied sample volumes of 50 ml, from 70% to 90% for sample volumes of 150 ml (Figure 37). The unconditioned sludge moisture content was 98% and it did not change. The effect of the feed solids concentration on the cake quality of Sludge "A" was somewhat different from that on Sludge "B". At an applied vacuum of 12" Hg and a sample volume of 50 ml, the moisture content decreased from 90% (1.426% solids) to 87% (2.0% solids), then increased to 94% at 3.6% solids (Figure 38-A), and, with a further increase in solids concentration to 10%, decreased to 70%.

An increase in the applied vacuum from 12" Hg to 24" Hg resulted in higher cake moisture retentions. The moisture content increased from 88% to 97% as the feed solids concentration increased from 1.426% to 3.6%, but at a solids concentration of 10% the moisture was reduced to less than 74%. Higher applied sample volumes also resulted in greater moisture retentions (Figure 38-B). For applied sample volumes

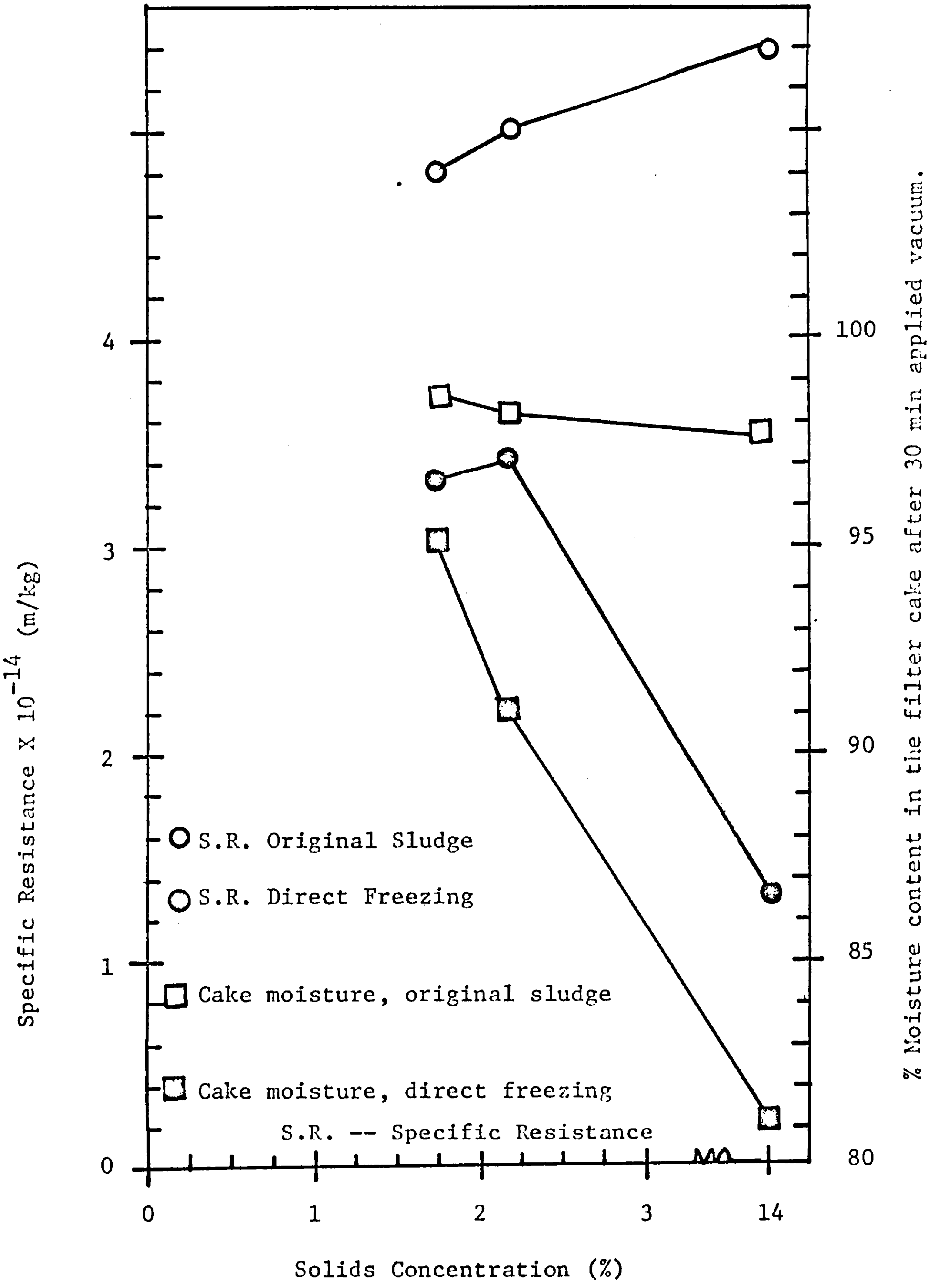


Figure 36 . Effect of feed solids concentration on specific resistance and moisture content (Sludge "C").

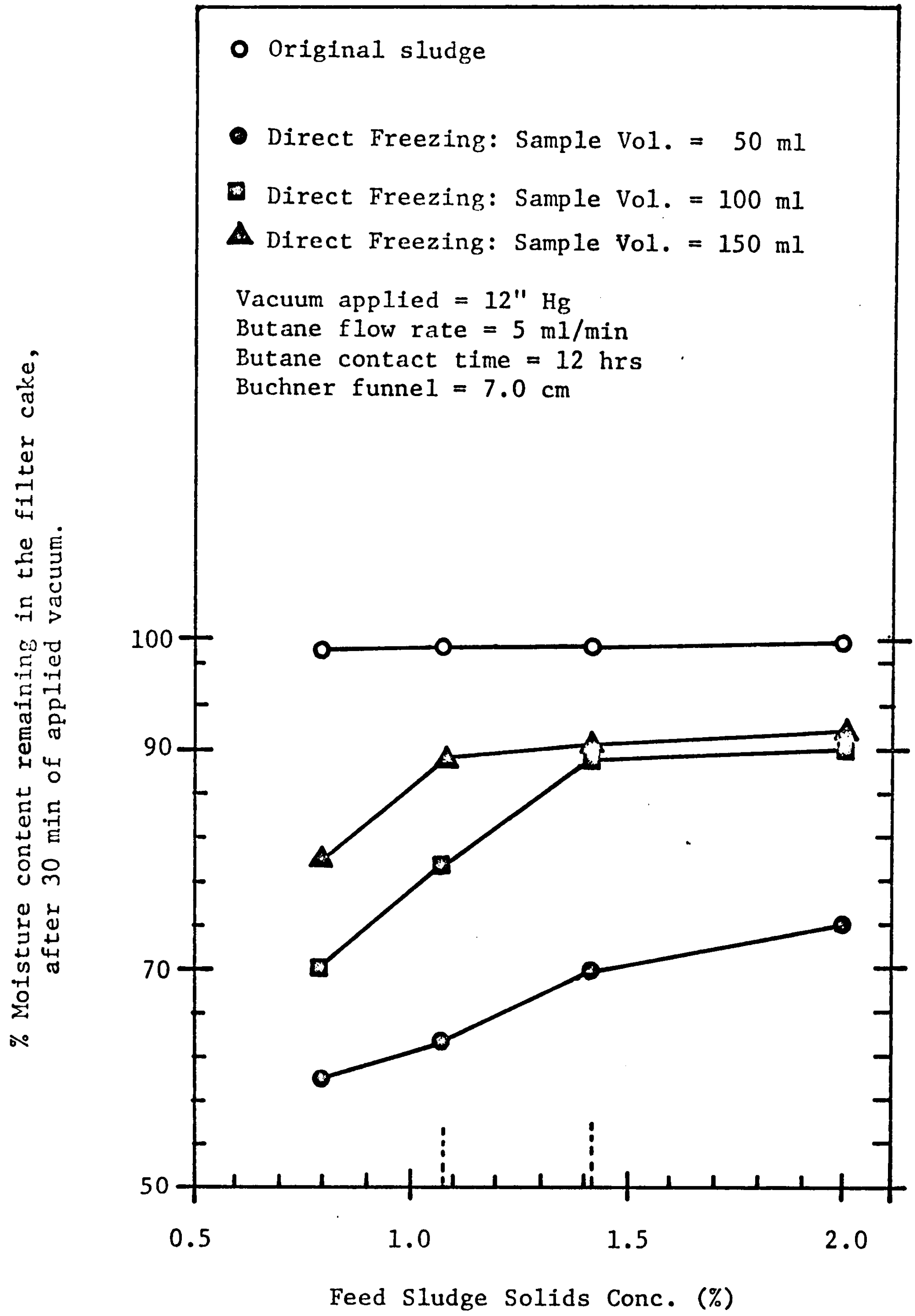


Figure 37. Effect of feed sludge solids concentration on the filter cake quality (Sludge "B").

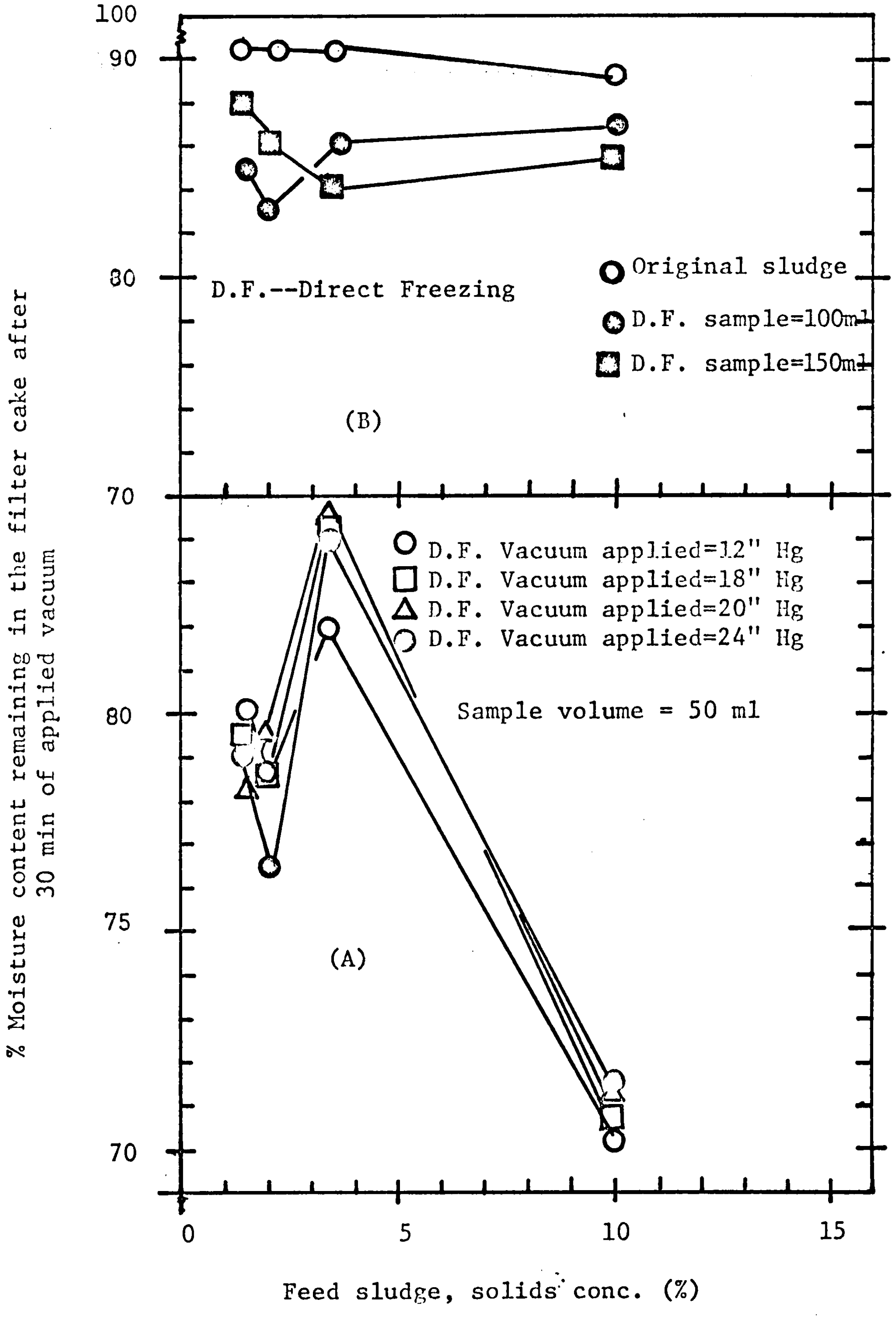


Figure 38. Effects of feed sludge solids concentration on the quality of cake (Sludge "A")

of 100 ml, the moisture content decreased from 95% (1.426% solids) to 93% (2% solids), and then increased to 97% when the solids concentration was changed to 10%. When the sample volume was 150 ml, the subsequent moisture content decreased up to a solids concentration of 3.6%, and then increased to 96% at a 10% solids concentration.

The cake quality of sludge "C" improved as the solids concentration increased, with the moisture content decreasing from 95% (1.727% solids) to 81% (14% solids).

Variation of Applied Filtration Vacuum

An increase in the applied filtration vacuum from 12" Hg to 24" Hg resulted in an increase in specific resistance. The conditioned Sludge "B" (Figure 39) showed a decrease in specific resistance up to 18" Hg vacuum, after which, with further increase in applied vacuum, the specific resistance increased. Higher specific resistances were observed at higher solids concentrations. The coefficient of compressibility values increased from 1.21 to 1.35 with a change in solids concentration from 1.075% to 2%, but the values decreased for higher solids concentrations. A similar increase in the coefficient of compressibility of Sludge "A" with an increase in solids concentration was noticed over the low range (Figure 40), but high solids concentration produced a decrease. The specific resistance values for Sludges "A" and "C" (Figures 40, 41) increased as applied vacuum

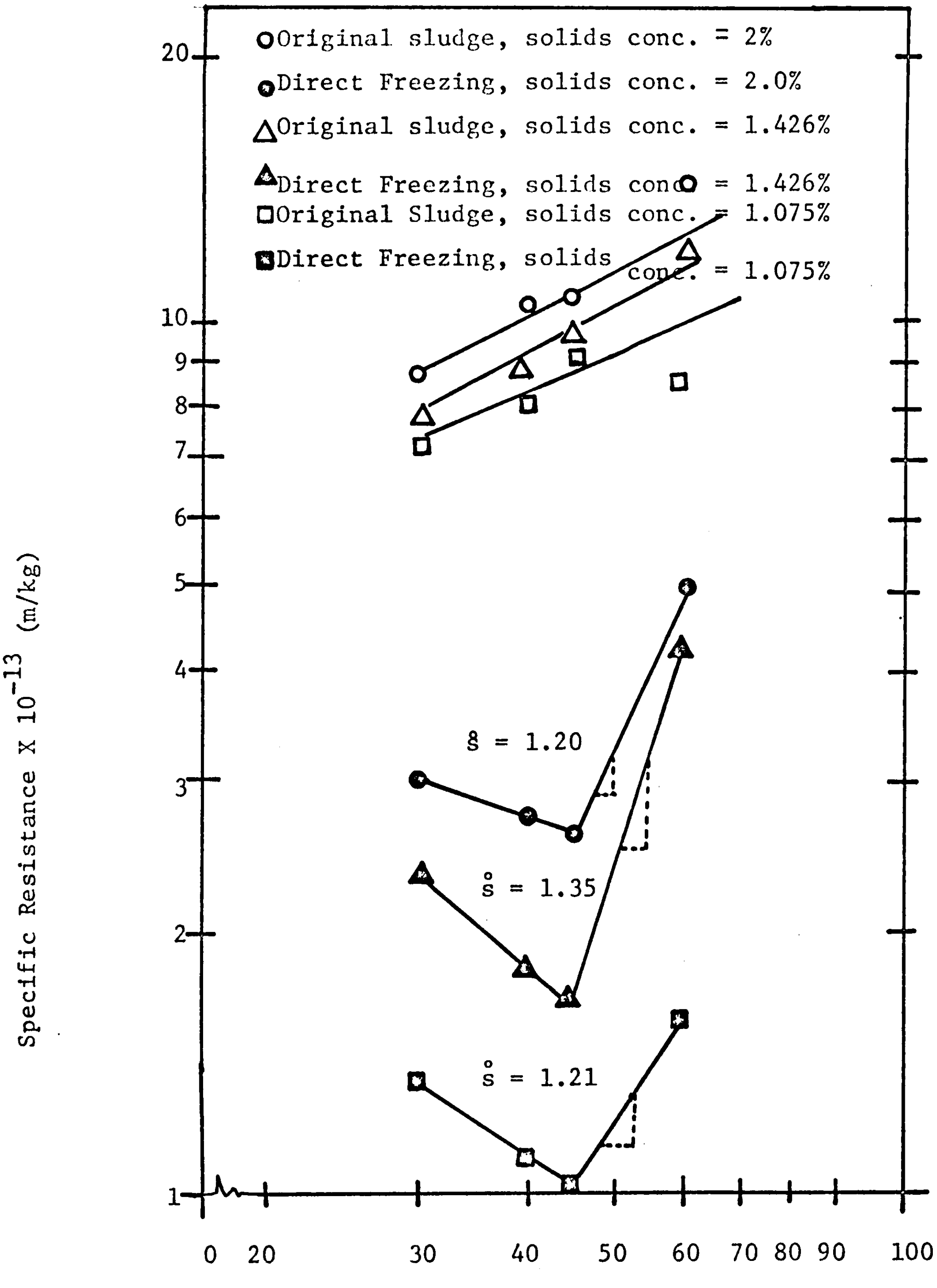


Figure 39. Effect of applied vacuum on specific resistance and coefficient of compressibility (Sludge "B")

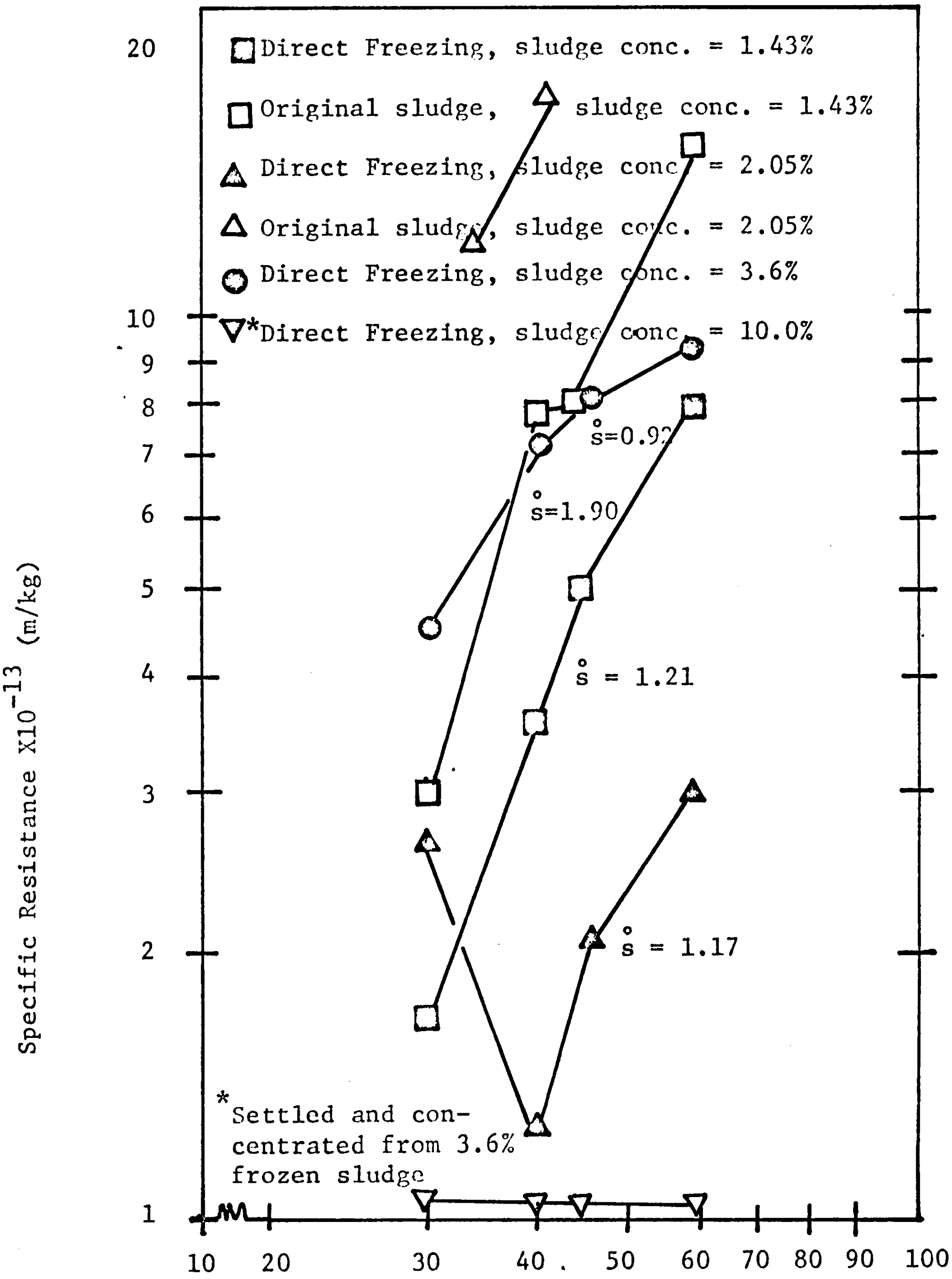


Figure 40. Effect of applied vacuum on specific resistance and coefficient of compressibility (Sludge "A")

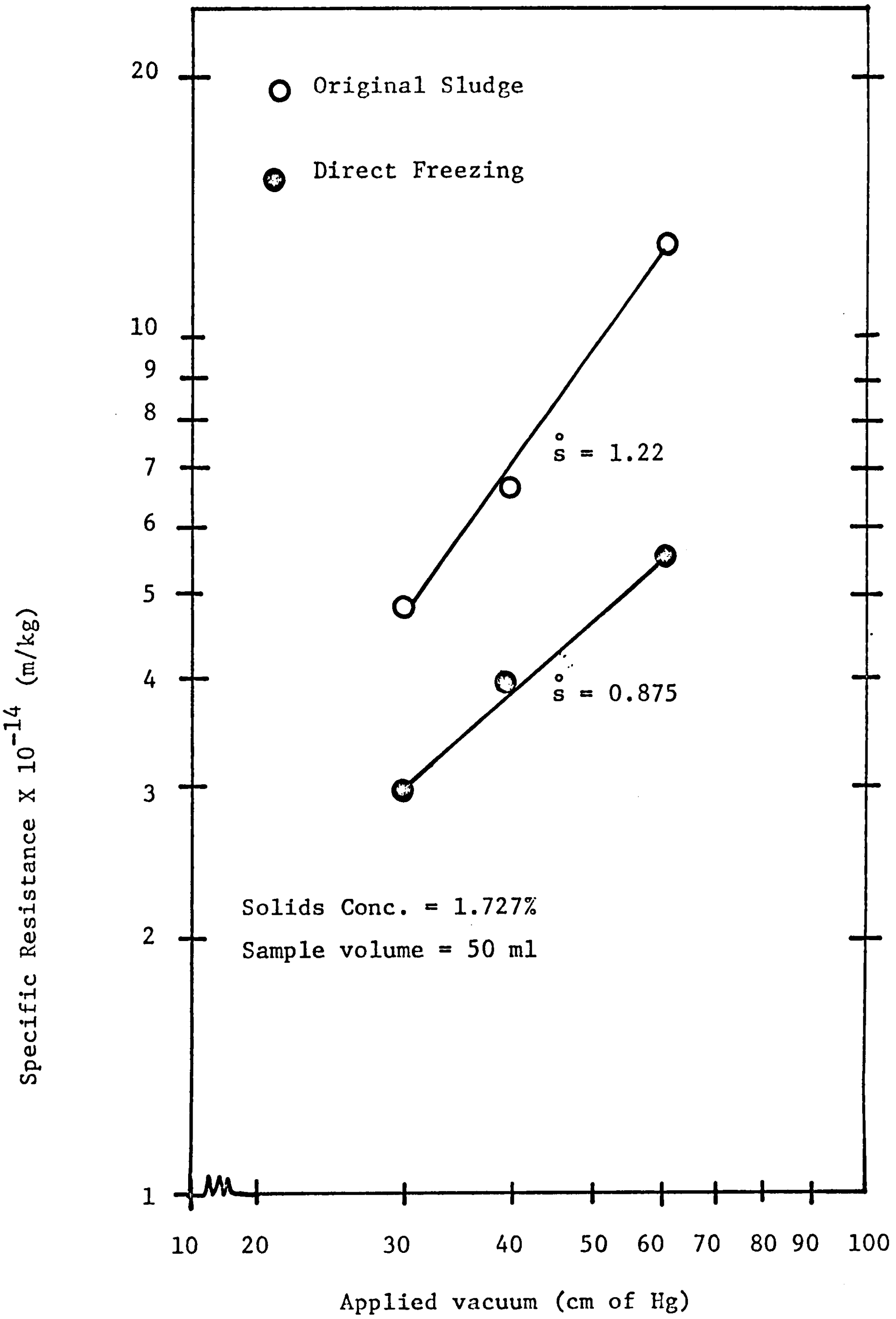


Figure 41. Effect of applied vacuum on specific resistance and coefficient of compressibility (Sludge "C").

increased with one exception. The specific resistance value of the 1.43% solids concentration of Sludge "A" decreased for vacuums up to 18" Hg, after which it increased.

Applied vacuums of 12" Hg to 18" Hg resulted in decreases in subsequent cake moisture contents of Sludges "A" and "B" (Figures 42, 43), but higher vacuums increased the moisture content. For Sludge "C" (Figure 44), higher vacuums improved the cake quality.

Effect of Solids Loading and Alum Addition (gravo-vacuum system)

As the solids loading was increased from 0.1 to 0.25 lbs/ft^2 of screen, the dewatering time for freeze conditioned Sludge "A" (with 200 ppm of Al+++) increased from 48 to 75 secs, while without chemicals it increased from 70 to 120 sec (Figure 45). The maximum solids loading used for conditioned sludge without chemical addition was 0.3, but it was increased to 0.5 with chemical addition.

Rate of solids production (lbs/ft^2/hr) increased from 7.5 to 18 for freeze conditioned sludge with chemical addition (Figure 46). The maximum rate of solids production was achieved at a solids loading of 0.3 lbs/ft^2, and it decreased to 12 lbs/ft^2/hr at a solids loading of 0.5 lbs/ft^2. Freeze conditioned sludge, without chemicals, had a maximum rate of solids production of about 7 at a solids loading of 0.2, after which the rate of production decreased.

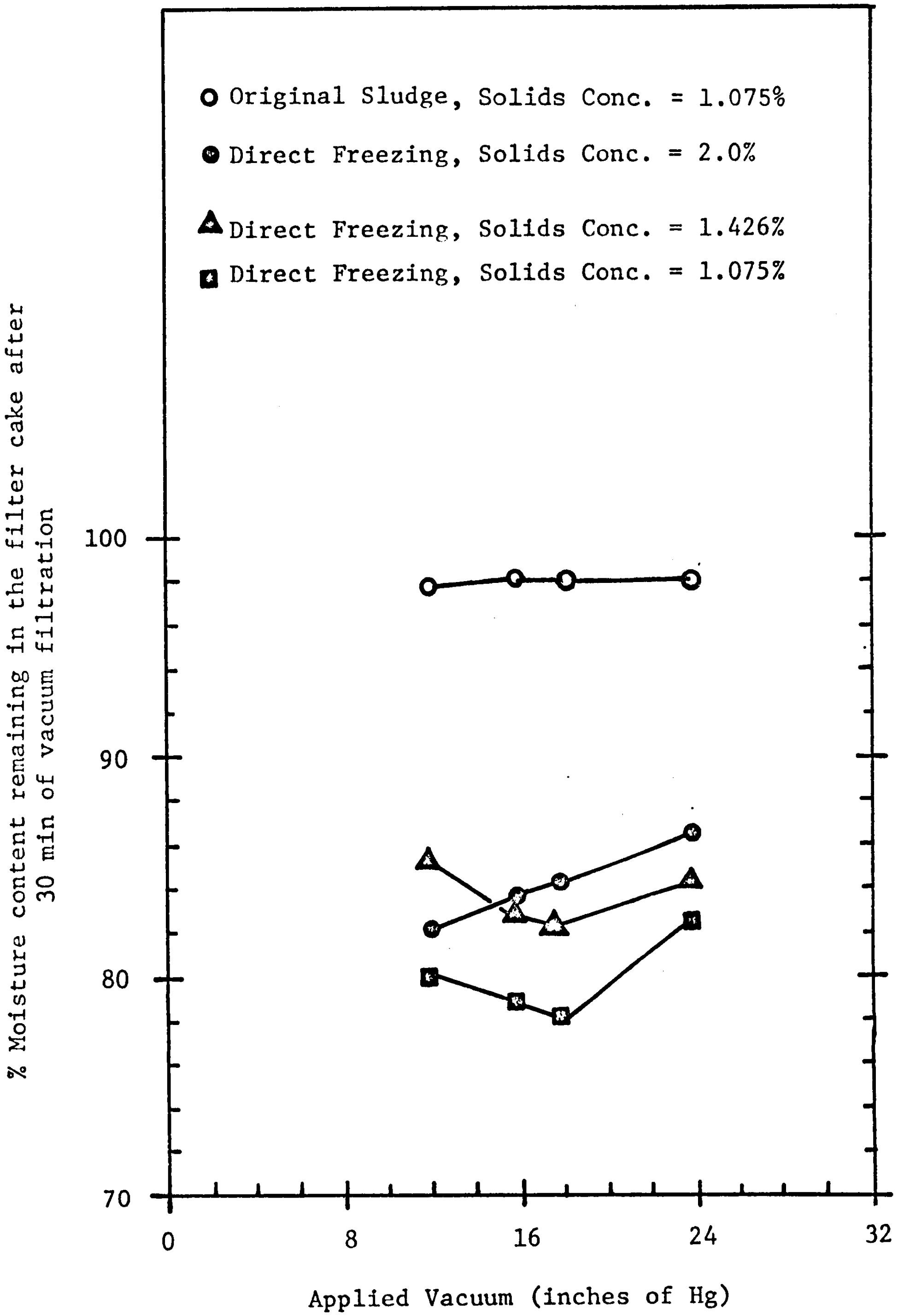


Figure 42. Effect of vacuum on the quality of filter cake (Sludge "B").

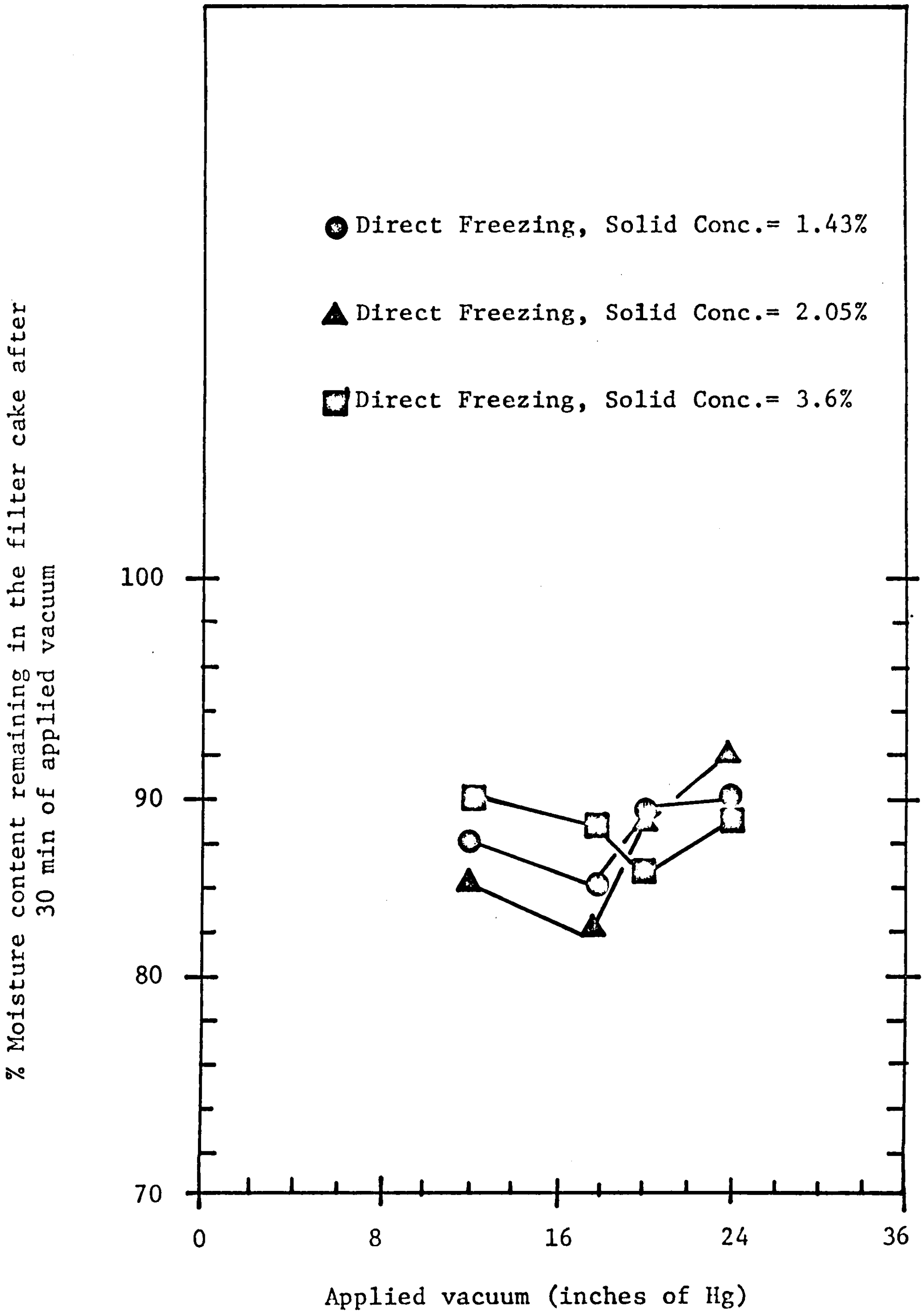


Figure 43. Effect of applied vacuum on the quality of filter cake (Sludge "A").

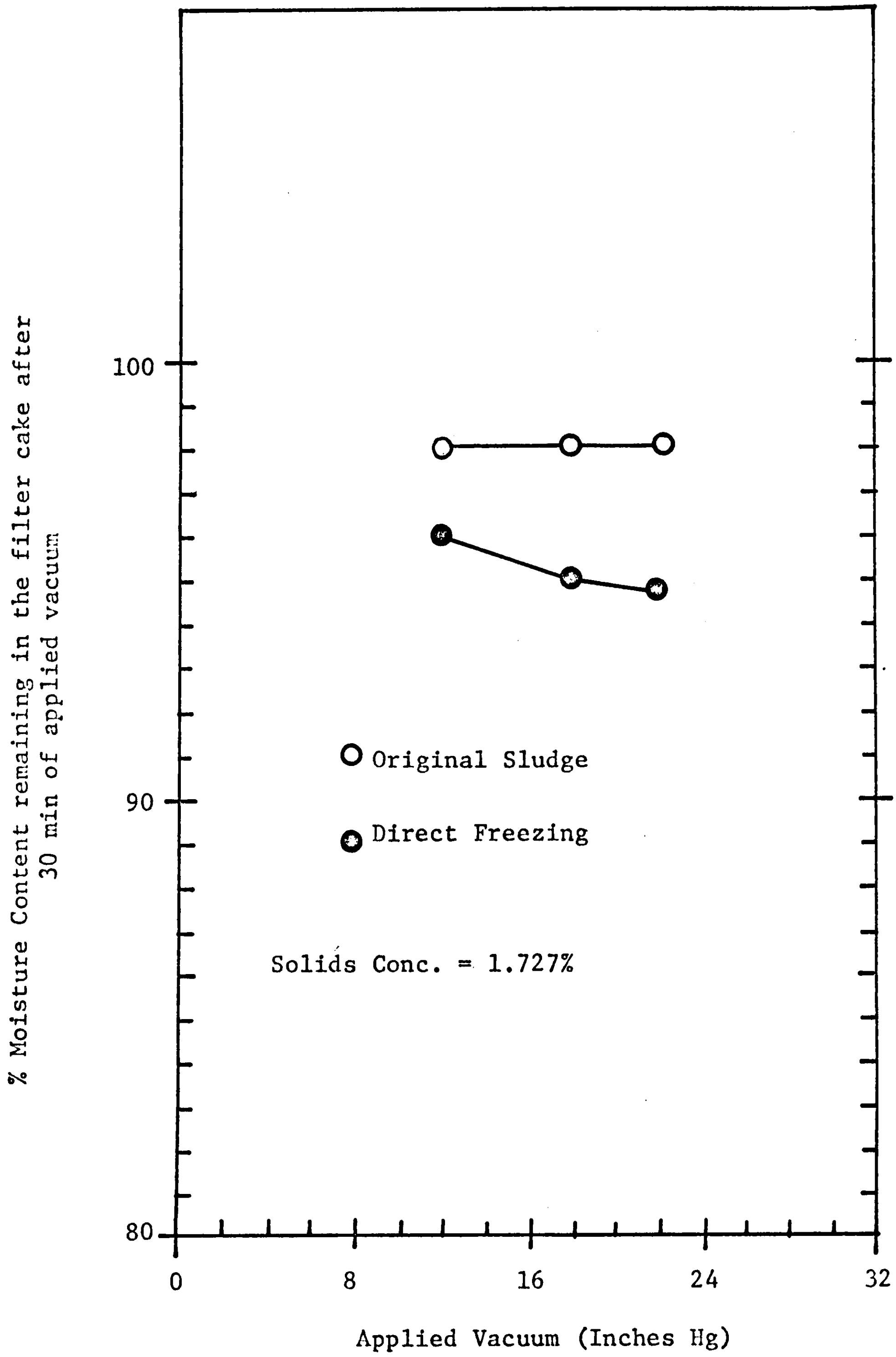


Figure 44 . Effect of applied vacuum on the quality of filter cake (Sludge "C").

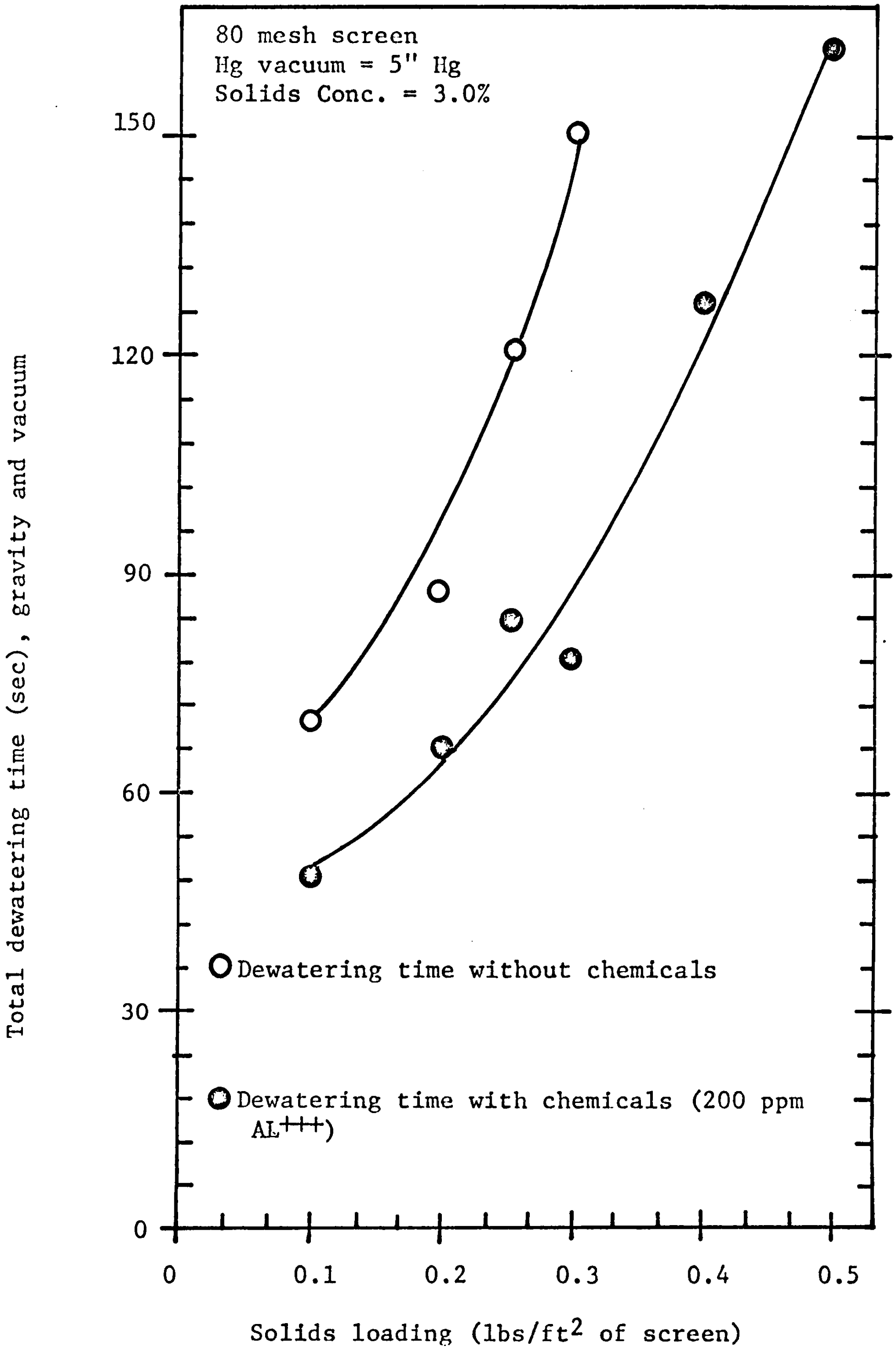


Figure 45. Effect of solids loading on dewatering time, after gravo-vacuuming (Sludge "A").

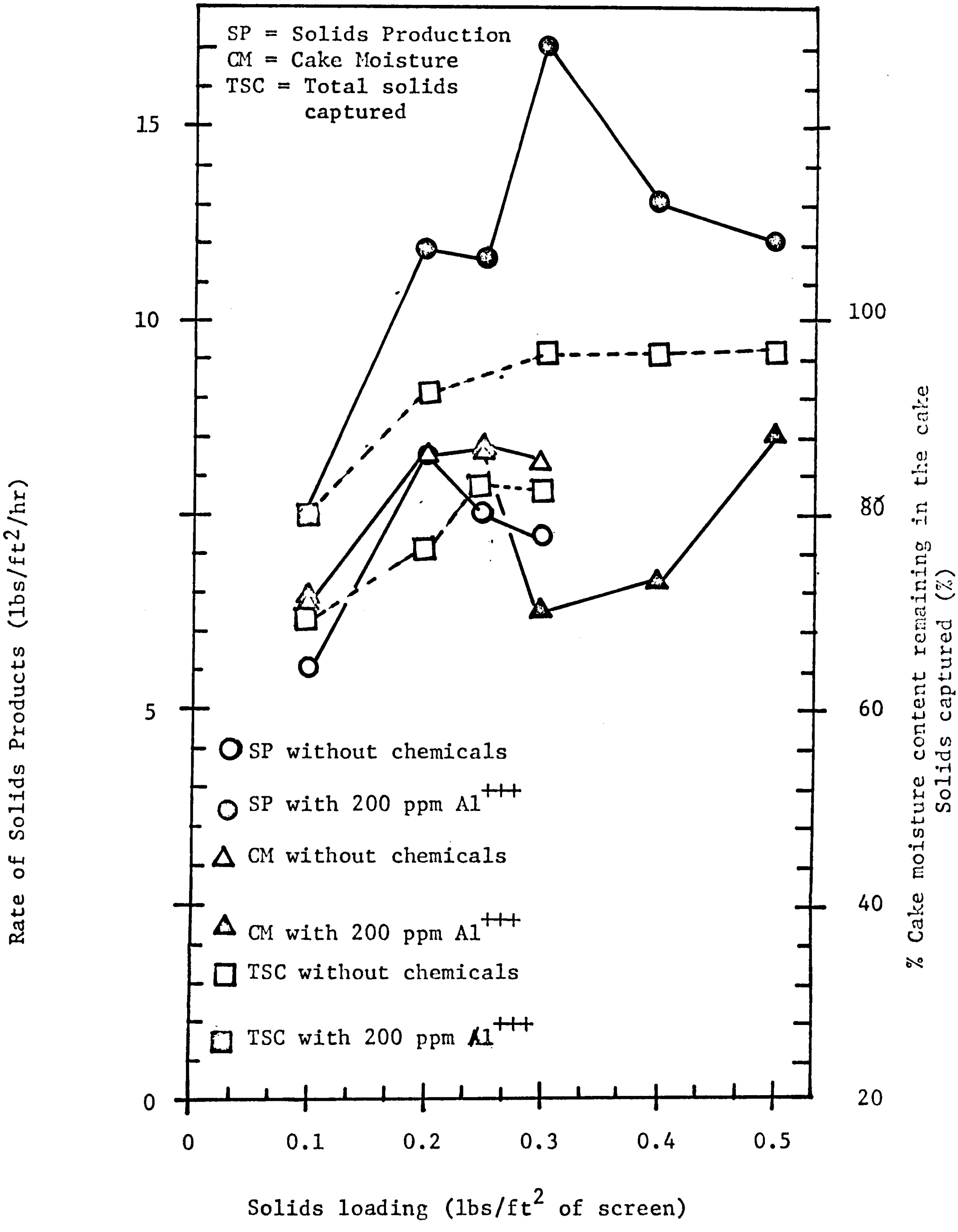


Figure 46. Effect of solids loading on the rate of production of solids and cake quality (Sludge "A").

The minimum moisture content for freeze conditioned sludge without chemical addition was 70% at the lowest solids loading of 0.1, but at the highest solids loading it increased to 84% with the addition of chemicals. The conditioned sludge moisture was also 70% at solids loadings of 0.1 and 0.3, but at other loadings the moisture contents were high. The addition of chemicals resulted in the capture of 98.5% of the solids, while without chemicals it was only 82%.

Effects of Storage Time on Subsequent Dewatering

A few batch experiments were run to study the effects of storage time before freezing and after freezing and thawing. It was observed that in both cases the storage time had detrimental effects on settling, filtration, and drainage characteristics. When stored after freezing, the subsequent characteristics were equal to or worse than those of the unconditioned sludge. The quantity of experimental data was small and it was not reported or plotted.

Dewatering Characteristics on Sand Beds

Gravity drainage on the sand beds was almost complete in one day, and the shape of the curve was approximately an S (Figure 47). Gravity drainage took place in two or three steps. A fast initial rate of drainage occurred during the first 30 minutes to one hour, followed by a slow rate, and a subsequent faster rate. The rate of drainage after 2 to 3

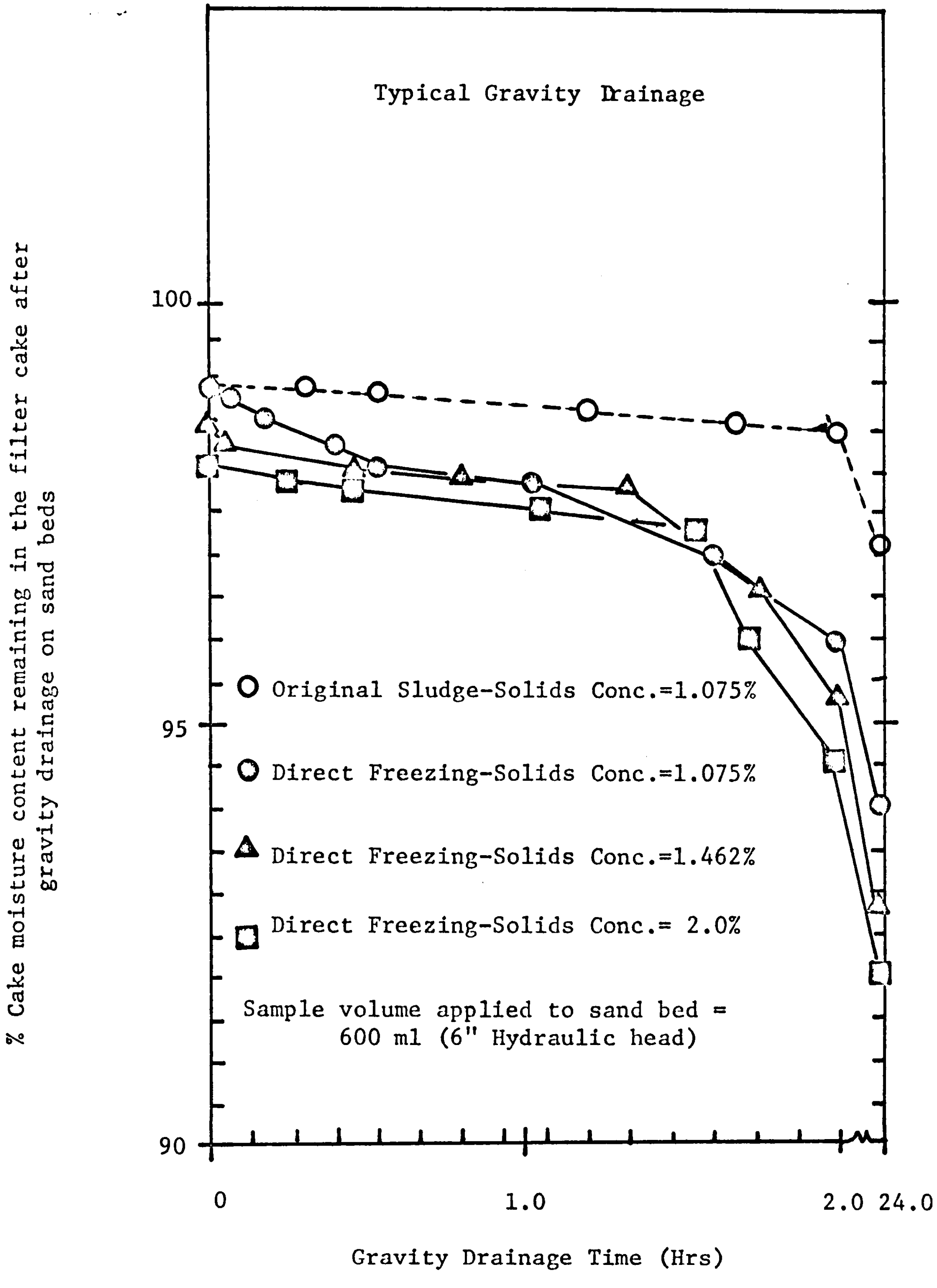


Figure 47. Bench scale sand bed studies--dewatering due to gravity drainage (Sludge "B").

hours was very slow. After one day of drainage, the sludge sample with the higher solids concentration contained the lower moisture content. Sludge "B" (Figure 47) contained 91% moisture at 2.0% solids, while the value was 93.5% at a solids concentration of 1.075%.

Air drying results in a relatively fast initial rate of moisture reduction, but it slows down with time (Figure 48). After 7 days there was no appreciable reduction in the moisture content with air drying. The sludge sample with the lowest concentration of solids had the lowest moisture content and, thus, the best quality of cake. Moisture content after 7 days of air drying for a solids concentration of 1.075% was 80%, while for a solids concentration of 2.0% the same value was 84%. The unconditioned sludge retained a moisture content of 91% after 7 days of air drying.

High solids concentrations in the feed sludge had adverse effects on the dewatering characteristics of Sludge "B" (Figure 49), Sludge "A" (Figure 50), and Sludge "C" (Figure 51). For a sample volume of 400 ml (2% solids) of sludge "B", the moisture retained was 79%, while for 600 ml and 800 ml volumes of the same concentration, the comparative values were 84.5% and 85.5%, respectively. At the solids concentration of 1.426%, filter quality improved by reduction in moisture content, while at other solids concentrations the values were higher. The cake moisture varied

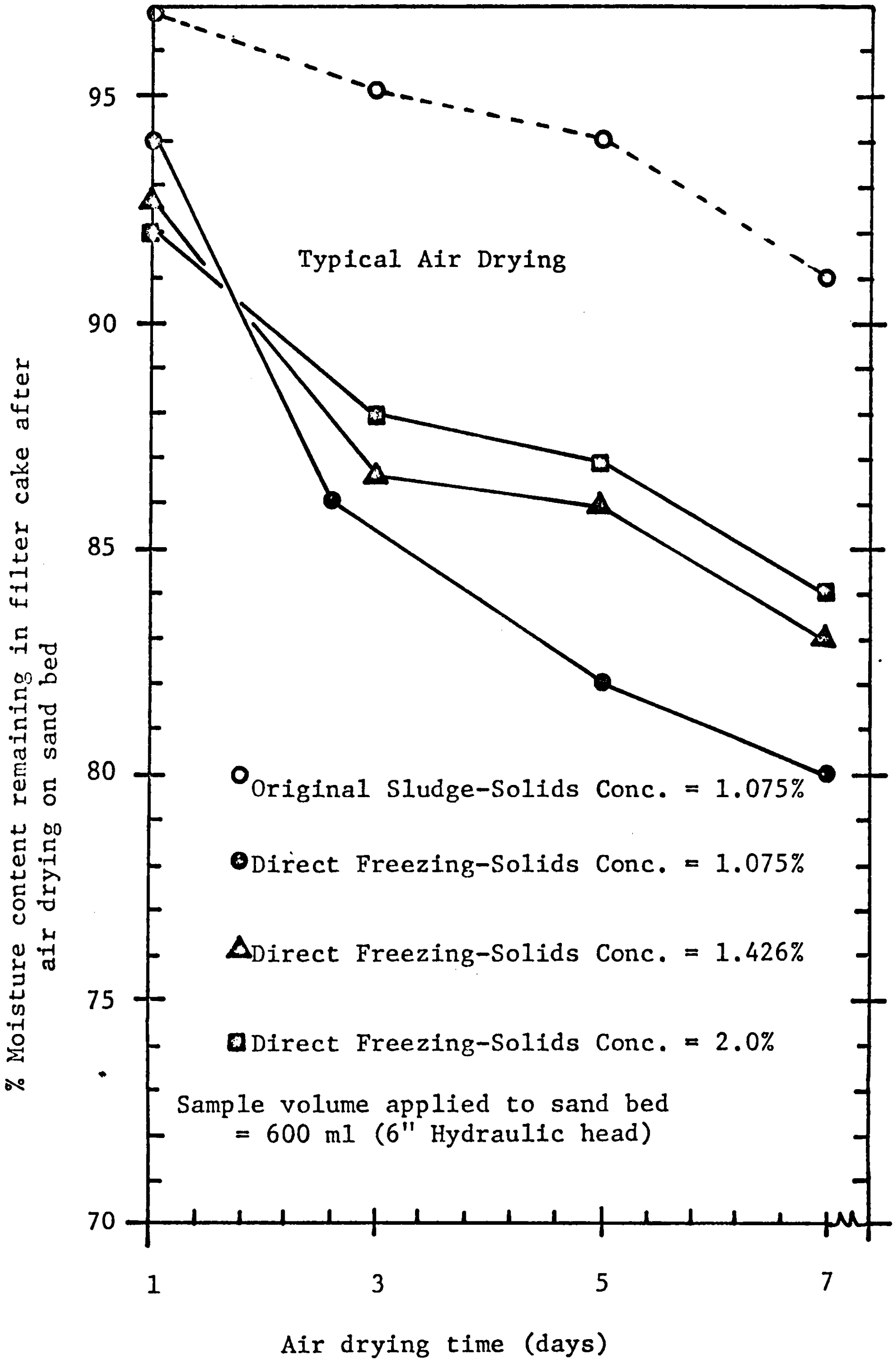


Figure 48. Bench scale sand bed studies--dewatering due to air drying (Sludge "B").

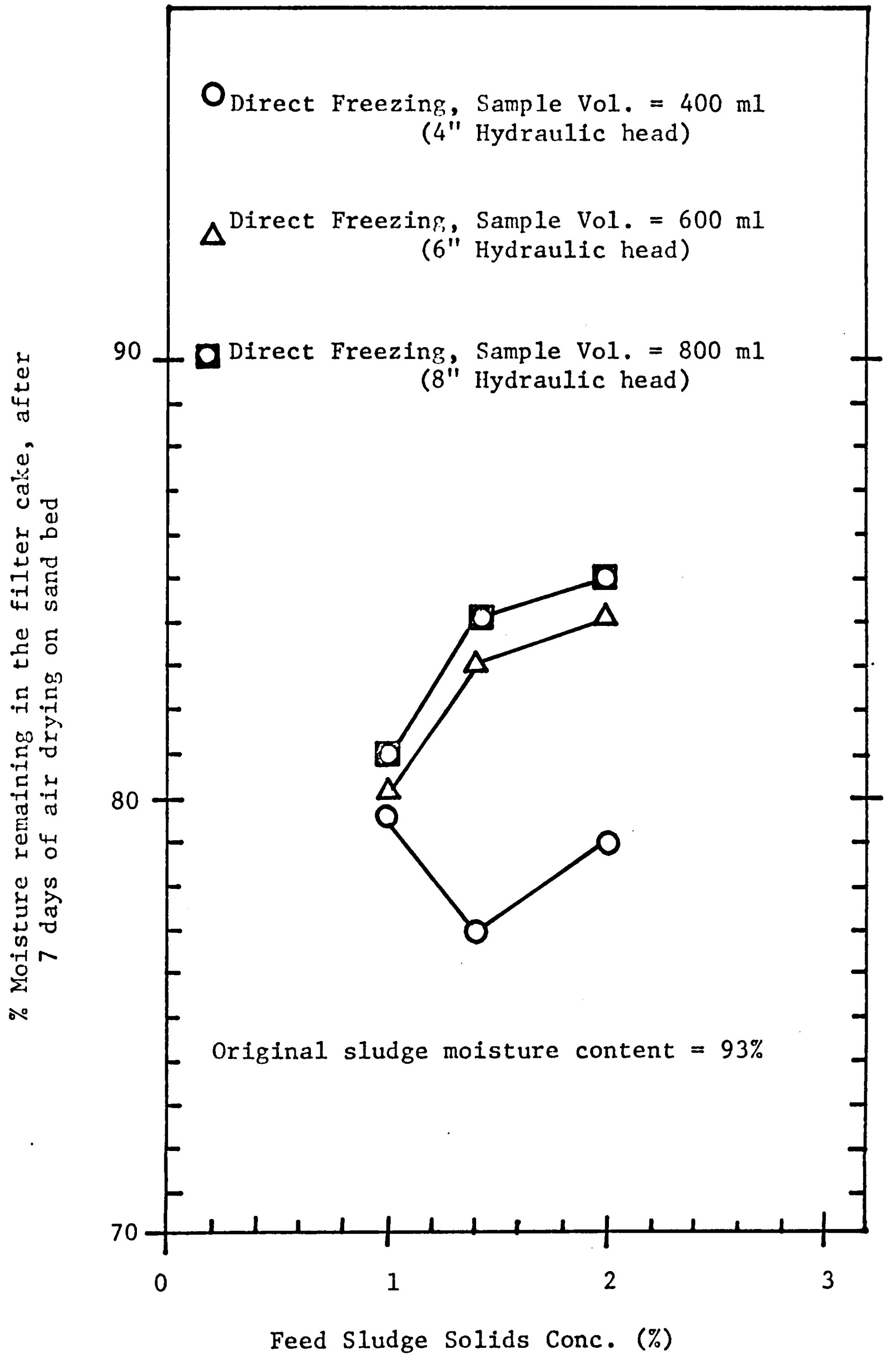


Figure 49. Effect of feed sludge solids concentration on the cake quality (Sludge "B").

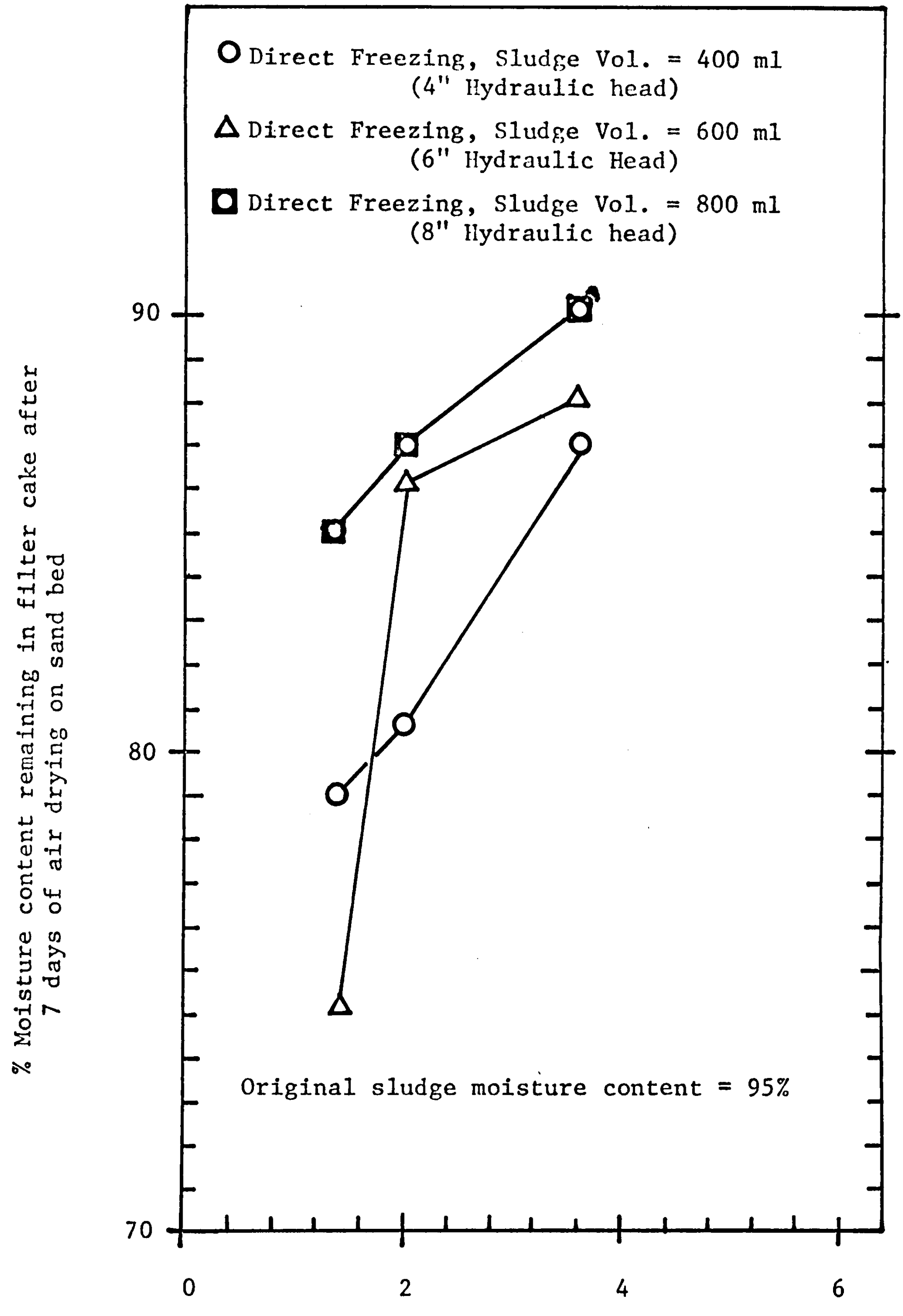


Figure 50. Effect of feed sludge solids concentration on the cake quality (Sludge "A").

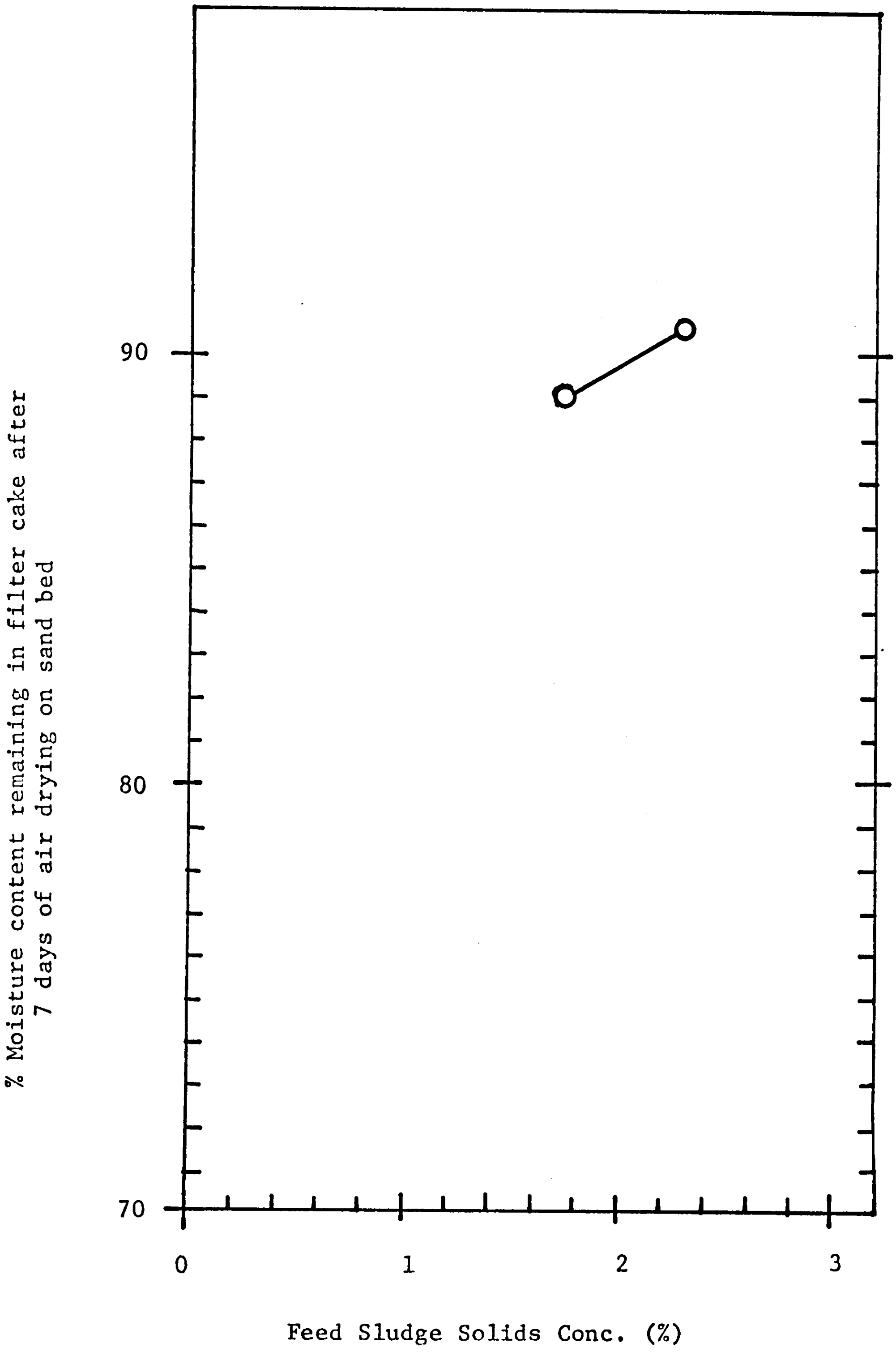


Figure 51. Effect of feed sludge solids concentration on cake quality (Sludge "C").

from 80% to 85.5% due to the solids concentration change from 1.075% to 2.0%. For Sludge "A" (Figure 50), cake moisture content varied from 75% to 90%, when the solids concentration varied from 1.43% to 3.6%. The lower cake moistures were observed when smaller sample volumes were applied, i.e., 400 ml, while higher cake moistures occurred with higher applied volumes, i.e., 800 ml. Sludge "C" (Figure 51) had the worst cake quality, and it retained the maximum moisture of all the sludges. At a solids concentration of 1.43% the cake moisture was 88%, while it rose to 90.5% at a solids concentration of 2.3%. The unconditioned sludges in the above cases had moisture contents from 93 to 98%. The effects of larger volumes, or higher hydraulic heads, were faster initial gravity drainage rates (Appendix III), but poorer cake qualities after 7 days of air drying.

As the solids loading (lbs/ft^2) increased from 1.5 to 4.5, the cake moisture content increased from 79% to 85% (Figure 52). The lower moisture contents were observed at lower solids concentrations, while higher solids concentrations resulted in poor cake quality. The unconditioned sludge contained 88% to 92% moisture content.

Physical Changes in Directly Frozen Sludge

It was observed microscopically that the unconditioned sludge floc was quite disperse and microorganisms such as protozoa, rotifers, sludge worms, bacteria could be seen.

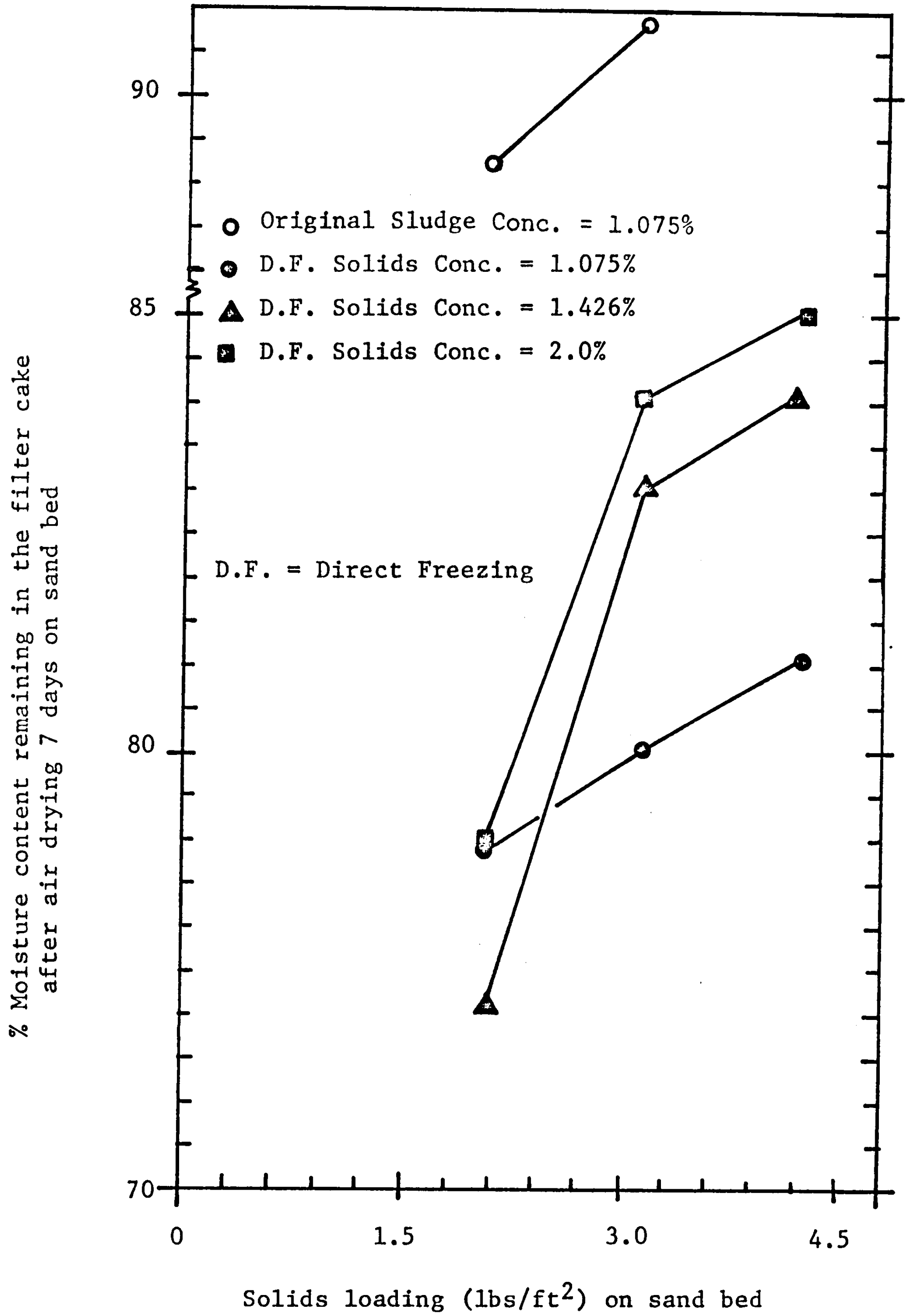


Figure 52. Effect of solids loading on the cake quality (Sludge "B").

After freezing, however, the above microorganisms could not be identified, but bigger clumps of flocs were observed surrounded by empty spaces, which indicated that direct freezing had enhanced the phenomenon of flocculation.

Wet Sieve Analysis

Sieve analysis of the sludge before and after freeze conditioning showed that increases in the butane contact time resulted in retainment of greater weights of samples on smaller screen sizes (Figure 53). The retainment of unconditioned sludge was only 20% as great as that of the conditioned sludge. This analysis also indicated that direct freezing promotes greater floc size, thus confirming the enhancement of the flocculation phenomenon.

Feasibility of Substituting Freon-114 for Butane

Substitution of Freon-114 for butane as the refrigerant resulted in flash freezing and the formation of a gas hydrate which, upon thawing, gave very poor settling and dewatering characteristics. Some of the data from these experiments are plotted in Figure 24.

Effect of Sludge Origin on Applicability of Direct Freezing

As a further evaluation of the system, two other types of sludges were conditioned during this investigation. These were waste activated sludges from a pulp and paper

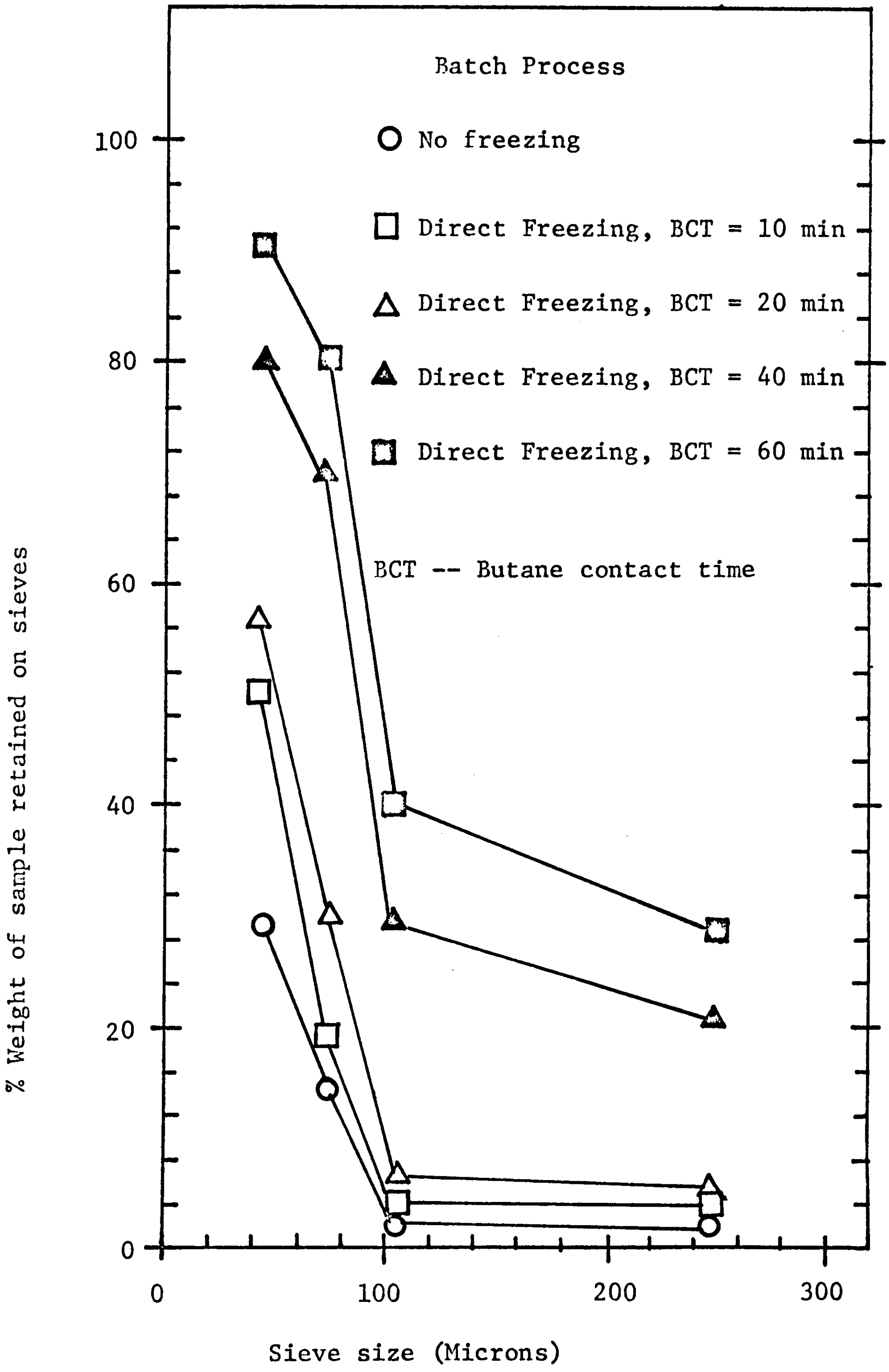


Figure 53. Effect of butane contact time on the flocculation (Sludge "C").

waste treatment plant, and an activated sludge that had been aerobically digested at various temperatures for eleven days.

Pulp and Paper Waste Sludge Results

It was observed that direct slurry (or solid) freezing, without any chemical addition, produced the same changes in sludge characteristics as an alum coagulant dosage of more than 500 p.p.m. Direct freezing with a coagulant dose as low as 200 p.p.m. resulted in reduction of specific resistance from 11 x 10^{13} m/kg (chemically conditioned with 200 p.p.m. dosage--no freezing) to 3 x 10^{13} m/kg. The pulp and paper sludge could be conditioned with coagulant alone, but it would require a much higher dosage and would still not achieve as great an improvement in dewatering characteristics as would direct freezing with very small dosages of coagulants. Supernatant and filtrate qualities were greatly improved from the color reduction point of view. After conditioning, the supernatant and filtrate color changed from orange to pale-yellow. For additional results, see Appendix VI.

Aerobically Digested Sludge Results

Sludge aerobically digested at temperatures ranging from 20° to 45°C responded very well to either direct slurry or solid freezing with or without chemical addition. From a specific resistance and quality of cake viewpoint, aerobic digestion temperatures of 20°C and 30°C were the most favorable with 30°C being the best of all.

Direct freezing without chemicals resulted in specific resistance and cake moisture content values of 3.5×10^{13} m/kg and from 60% to 80%, respectively (Figure 71). The lower values occurred at temperatures of 20°C and 30°C, while the higher values were observed for digestion temperatures equal to or greater than 35°C. When chemical addition and direct freezing were used, the specific resistance and cake moisture content values varied from 0.2×10^{13} to 5.5×10^{13} m/kg and from 20% to 62%, respectively, a considerable improvement. The unconditioned sludge had specific resistance and cake moisture values of 43×10^{13} m/kg and 98%. Additional supporting data are in Appendix VI.

Direct Freezing Process Economics

One of the most important factors contributing towards the economic success of the direct freezing process was how much butane could be stripped and recovered for reuse. It was observed that 40% to 60% of the butane vapors from the freezer could be compressed for reuse when a single compressor was used, while some of the butane which was trapped or dissolved in the supernatant could be stripped by slight vacuums (Figure 54) in the butane-stripping tank. When the stripping temperature was 0 to 1°C, lower flows of supernatant, e.g. 30 ml/min, were more favorable to the stripping

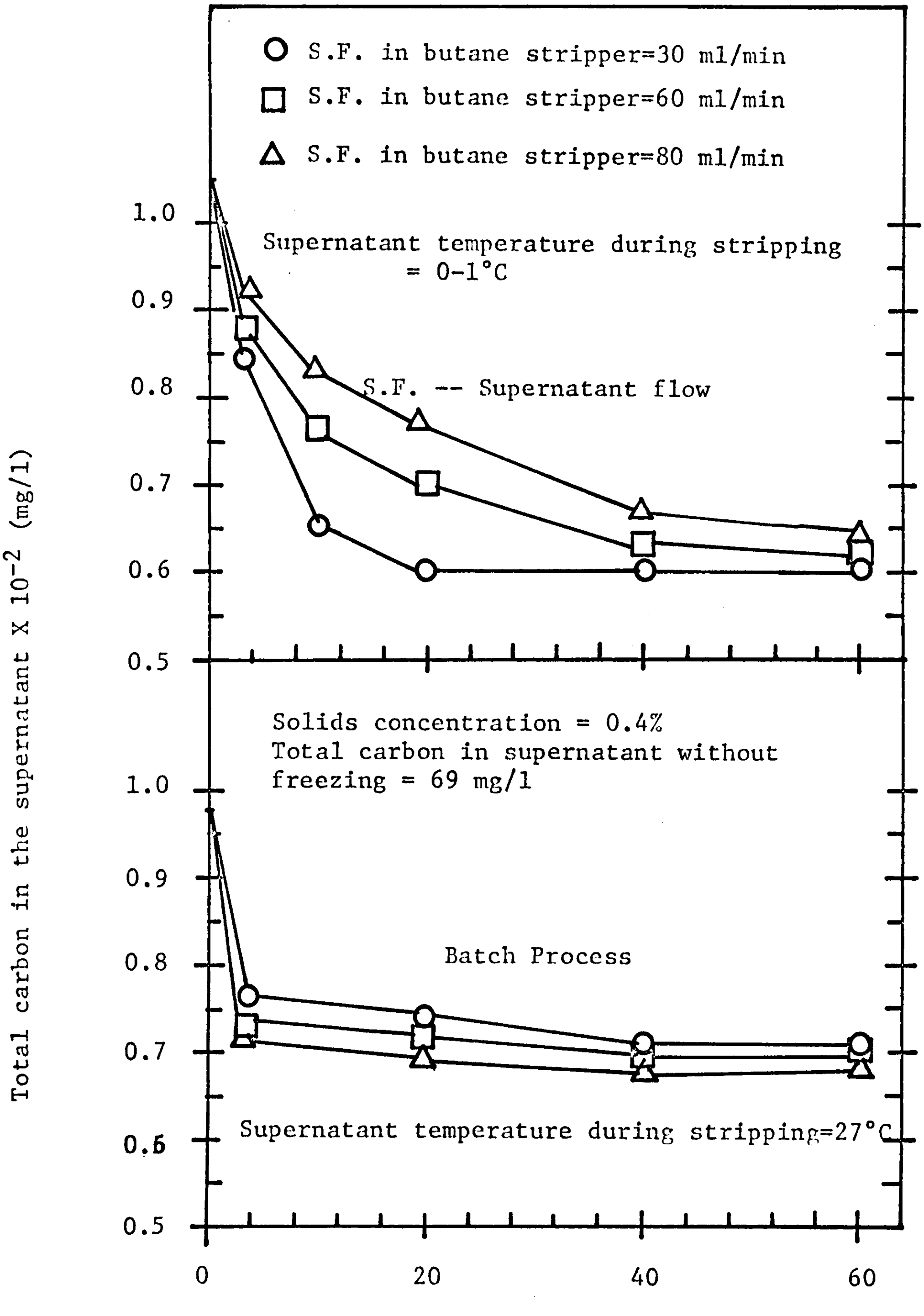


Figure 54. Effect of applied vacuum on butane stripping from supernatant (Sludge "C").

phenomenon, whereas higher flows, e.g. 84 ml/min, gave better results when the supernatant temperature was 27°C. Most of the butane could be stripped at vacuums of 5 to 10 cm.

To determine the energy requirements of direct freezing by butane, an activated sludge sewage treatment plant that produced 50,000 lbs/day of waste activated sludge with a solids concentration of 1.5 percent was assumed for the calculations. It was then calculated that 9.5×10^6 BTU's of heat would have to be extracted from the sludge to freeze it. To do so would require 6.75×10^4 lbs. of butane. The vaporized butane would then lose 7.45×10^6 BTU's thawing the frozen sludge, thereby leaving the vapors with 2.05×10^6 BTU. Additional refrigeration, at the rate of 288,000 BTU's per ton of refrigeration, required to extract the rest of the heat, would be 7 tons, or 14 H.P. of ammonia refrigeration system including all auxiliaries. To condense the vapors by compression would require an additional H.P. of 19 for a total H.P. requirement of 33 for a complete butane freezing cycle. By comparison, simple direct freezing would require 66 H.P., assuming an ammmonia refrigeration system, and an additional 9 H.P. would be required to thaw the sludge for a total of 75 H.P. per cycle.

A particularly attractive aspect of the butane freezing process is the low percent moisture left in the sludge after filtration. From the experimental results, this value was found to be in the range of 30 to 70 percent, a value considerably lower than that attained by other procedures. For example, chemically conditioned and vacuum filtered waste activated sludge usually contains 90 percent moisture or more. If incinerated, the sludge from the butane freezing process would sustain combustion by itself and would generate a considerable amount of excess energy that might be converted and used for refrigeration purposes. Most sludge incineration processes are not self-supporting.

The cost of conditioning by the butane freezing process would vary according to the sludge solids concentration, the size of the treatment plant, the cost of liquid butane, the cost of power, the cost of money, and the type of labor available. This cost would also be a function of the amount of butane recovered, which depends upon whether a primary compression or a secondary compression cycle is used. Considering these variables, it is estimated that the cost would range from $6 to $20 per ton of dry solids handled. This does not include dewatering equipment or capital, maintenance, and operating costs of the equipment. However, comparison with other processes that have been evaluated the same way indicates that the butane process would be cheaper (Table A-7). The economic advantage of the process is further enhanced by the fact that it produces a supernatant and a filtrate of such high quality that it would not exert a significant load on the biological process if returned to the plant. Supporting data are in Appendix V.

CHAPTER V

DISCUSSION OF RESULTS

The purpose of this chapter is to interpret the results of the previous chapter and provide some insight to assist a design engineer in designing a slurry freezing process for sludge conditioning. For simplification, butane contact time was used as the chief parameter for expressing degree of conditioning; however, it should be recognized that conditioning is also a function of the rate of heat transfer and differential temperatures, i.e. the difference in the freezing temperature of the sludge and that of the top layer of the sludge column. The latter two parameters may have a strong effect on the required contact times of the batch and the continuous freezing units. The important point is, the long contact times required with the continuous unit were peculiar to the equipment configuration used and should not be considered as descriptive of the slurry freezing process.

Sludge Characterization

The most important point revealed by sludge characterization was that after conditioning all of the three sludges had a high percent total volatile solids content, but the percentages of volatile suspended solids were somewhat less than those of the unconditioned sludges. Thus, a higher dissolved organic solids content was produced during freezing.

The higher dissolved solids can be explained by two factors, the presence of butane trapped and/or dissolved in sludge particles and, sludge destruction or cellular rupture, which would reduce the volatile suspended solids, thereby releasing internal water rich in dissolved organics. Of the two, the major contribution is most likely from the osmotic dehydration of the cells, thus forcing the internal cellular water which is rich in dissolved organics into solution. The butane gets stripped off during vacuum filtration without interfering much in the results. Since the increase in dissolved organics was not considerable, it was indicative of the fact that the destruction or cellular rupture by dehydration was small. There were no significant changes in the pH and C.O.D. values of the filtrate.

The contribution of cellular osmotic dehydration became very significant during indirect freezing conducted by Katz (29) because the total dissolved solids content and the C.O.D. values of the filtrate were many times higher than that of the unconditioned sludge. The high dissolved solids content, after solid, indirect freezing, was attributed to the tremendous ice pressure exerted on the sludge particles. Such pressure was estimated as being equivalent to 12 atmospheres by Clements (27). In direct slurry freezing, the exertion of pressure was a small fraction of that amount.

Direct Freeze Conditioning

Experimental results show that one of the most important factors contributing to the optimization, success and efficiency of the direct freezing process was butane contact time with the sludge. The effectiveness of the butane contact time depended on many factors, a few of which follow:

1) Configuration of freezer and mode of freezing.
2) Solids concentration present in the freezer sludge.
3) Maintenance of proper operating conditions in the freezer.
4) Storage of sludge samples before freezing.
5) Reuse of recovered butane.

It was observed that the conditioning results obtained with the batch freezing were much superior to the continuous operation for the following reasons: a) In the batch freezer the applied sample volumes were 1500 ml, which gave a sludge thickness of 1/4" to 3/8". Smaller thicknesses gave higher surface area for heat transfer and the coefficient of heat transfer significantly increased. A similar result has been previously reported by Clements (27), Sewage Commission, Milwaukee (38), and Cheng (30) for indirect freezing systems. On the other hand, in the continuous flow apparatus, for higher contact times, the sludge depth (thickness) in the freezer ranged from 6" to 12", thus reducing heat transfer efficiency and resulting in higher and higher required contact times to obtain a certain process efficiency. Greater sludge depths also exerted pressure on the liquid butane bubble at the diffuser which raised the boiling point of butane, thus reducing the effective driving force (temperature differential) between liquid butane and sludge.

The presence of just one diffuser located in the center of the continuous freezer was not enough for equal and similar heat transfer between the sludge particles and the butane. The modes of freezing in batch and continuous were different. In batch systems each cell was exposed to the same butane contact time and remained in the freezer whereas in the continuous system, some short circuiting most likely occurred, which reduced the process efficiency.

Butane contact time was also very sensitive to changes in the feed sludge solids concentration. A contact time determined at a particular solids concentration did not give the same improvement when used for a sludge at higher solids concentration. This effect was similar to that obtained by Major *et al*. (87), who, while working with *E. coli* suspensions in freezing medium, found that the percentage of the number of cells surviving increased as the concentration of suspension cells changed if the same freezing medium, time and temperature were maintained. It was also postulated by Major *et al*. (88) that greater cell survivals occurred at higher cell concentrations because solutes escaping from some injured cells acted as protective agents thus preventing cellular dehydration or biochemical changes, which otherwise might have led to cell lysis and release of cellular water.

It was also observed that there were quick improvements in sludge characteristics (Figures 20, 21, 22) up to a certain contact time; improvements then slowed down for a "lag time," after which further improvement occurred. This could be explained by postulating that after a certain threshold degree of contact, during which capsular water froze applying mechanical stress on the cell, a lag phase occurred during which the internal water slowly moved out. The greatest improvement occurred, however, when most of the internal water had flowed out and frozen as an ice crystal, and the internal proteins, due to expulsion of water, came in contact with each other, resulting in covalent S-S bond. This latter action made the above phenomenon irreversible and resulted in cellular precipitation and flocculation. If at higher solids concentrations, the threshold contact time the cell was maintained in a frozen condition for a long time after threshold contact time, there was an effect which was equivalent to the "Storage time effect on cells in the frozen condition." The effect and concept of storage time in the frozen state was previously mentioned by Clements (27), Sewage Commission, Milwaukee (38) and many others. By keeping the cell in that state greater stresses were exerted on the cell, which promoted flocculation and resulted in faster solids-liquid separation upon thawing.

Of equal importance was the maintenance of proper operational driving forces; i.e., temperature and pressure.

Deviation from optimum conditions resulted in higher butane contact times and poorer settling and dewatering characteristics of the conditioned sludge.

Sludge samples used in the batch studies were applied to the freezer without any prior storage and the results were much better when compared to the continuous process. The solids concentration process used to obtain the desired concentrations involved 3-7 days of operation, during which time the sludge changed its color from brown to black. The C.O.D. values of the supernatant did not change, however. During the process of concentration, although samples were being aerated, it was often observed by smell that the sludge was anaerobic. The effect of anaerobiosis resulted in higher required contact times to achieve the same results without sample storage.

In the continuous process recovered butane was used. With this experimental system recovered butane was contaminated by air and oil from the vacuum pump and therefore was not as pure as the original butane. These impurities reduced the butane heat exchange capacity, thus resulting in higher required butane contact times.

Proper control of the process of thawing was also important for the promotion of better settling characteristics. It was observed that optimum settling occurred when the temperature in the settling cylinder was between 10° - 15°C. The reason for this range was that below 10°C, complete solid-liquid separation did not take place, whereas at temperatures higher than 15°C, the butane vapor pressure (trapped between sludge particles) was high enough to keep the sludge particles floating or suspended, resulting in two thick layers of sludge at the top and bottom of the cylinder with clear liquid in between. This temperature sensitivity range became more and more important as freezing was carried out to solid state and higher contact times were used. In this type of freezing, the percentage of butane trapped was more than during slurry freezing, but if the temperature range during settling was kept between 10°-15°C, direct solid freezing gave slightly better settling results.

The rate of settling was also a function of the butane contact time and the feed sludge solids concentration. For an increase in solids concentration from 1% to 2% (Sludge "B" contact time 12 hrs), the sludge settling efficiency decreased by a factor of 30. However, the rate of settling accelerated three times as the contact time was increased from 12 hrs to 40 hrs, in the case of Sludge "A." The interfacial settling velocities of 4 to 12 ft/hr are much higher than values reported in the literature.

Another important factor contributing to conditioning improvement was the rate of freezing as controlled by the flow rates of butane. Moderately high butane flow rates (15 - 30 m/min) resulted in "quick freezing," while at still higher flow rates ($\geq$ 35 ml/min) "flash freezing" occurred.

The feed sludge flow was 3-5 ml/min in both cases. Both of the above freezing rates resulted in fast rates of freezing that did not allow enough time for most of the internal water to flow out of the cell and freeze around it, which was necessary for significant improvements in the dewatering characteristics. On the other hand, slower flow rates (< 10 ml/min) resulted in a slow rate of freezing and the formation of an extracellular ice that produced mechanical stress, electrolytic changes and, finally, osmotic dehydration of cells. The above phenomena of slow and flash freezing were previously reported by Katz (29), Clements (27), and many others. They reported that "flash freezing" did not improve the dewatering characteristics very much, while slow freezing was very effective in enhancing flocculation phenomenon, thus resulting in better results.

Direct freezing (slurry or solid) without chemicals, when compared to other sludge conditioning processes such as indirect freezing as used by Clements (27), gave better settling characteristics. Indirect freezing without chemicals did not settle well, but after the addition of coagulants like Al+++, Fe+++, etc., gave comparable results. The difference could be due to the different characteristics of the two sludges. Heat treatment (16) gave comparatively slower settling rates in the beginning, followed by faster rates of settling, but at the expense of a very poor quality of supernatant and filtrate. The direct freeze conditioning of sludges "A," "B" and "C" gave different settling characteristics. Thus the effectiveness of a sludge conditioning process is directly related to the sludge characteristics. Even the sludge from the same source could respond differently if handled in a different way before freezing or any other conditioning procedure.

Specific Resistance, Coefficient of Compressibility and Filter Cake Quality

The results indicated that the specific resistance progressively increased as the solids concentrations were increased. For each 1% increase in solids (using a sample volume of 50 ml and applied vacuum 12" Hg), the increase in specific resistance was observed to be 1 x 10^{13} m/kg. This relationship held good until the solids concentration was 3.6%, after which further increases in solids concentration decreased the specific resistance. At lower solids concentration the sludges were very compressible when subjected to vacuum, thus choking and clogging of the filtering media occurred and the resistance to water flow increased. At higher solids concentration, however, the thickness of filter cake increased which acted as a filtering aid when subjected to vacuum and the filtering media did not clog. Volumetric loadings on the Buchner funnel also had an adverse effect on the testing procedure. For every 50 ml increase in applied sample volume, the specific resistance increased on the order of 1 x 10^{13} m/kg for sludge "A," but higher volumetric loadings of Sludge "B" reduced the specific resistance only when the solids concentration was $\leq$ 3.6%. When the solids concentration was increased above that level, the higher volumetric loadings had adverse effects on specific resistance.

Higher volumetric loadings result in greater hydraulic loads, and when the vacuum was applied it gave the effect of higher applied vacuum, thus resulting in faster cake compression and giving rise to greater specific resistance values.

An increase in applied vacuum (12" Hg to 24" Hg) resulted in higher specific resistance and coefficient of compressibility values for sludge "A" and "C," but for Sludge "B" these values decreased up to 18" Hg vacuums, after which they increased. For each increment of 1" Hg in applied vacuum, the corresponding increase in specific resistance was approximately 0.1 x 10^{13} m/kg, assuming that the solids concentration and applied sample volume remained constant.

Specific resistance and coefficient of compressibility are good tools for comparative studies of sludges from different sources from a filterability point of view, but for determining the suitability and performance of filters for a particular sludge, the "leaf-filter test" is more reliable. High specific resistance of a sludge is indicative of the fact that the sludge is very compressible which, in turn, means a poorer quality of filter cake, while higher coefficients of compressibility would mean less filter yield and vice versa.

Specific resistance values after direct freeze conditioning were of the order of 10^{13} m/kg while for unconditioned sludges they were closer to 10^{14} m/kg. The coefficient of compressibility values were closer to one at higher solids concentrations. The above values are comparable to or better than most of the other conditioning processes. Out of the three sludges, Sludge "C" had the highest specific resistance, but the compressibility coefficient was comparable to those of the other sludges.

Filter cake quality was affected by the feed sludge solids concentration. For each 1% increase in solids concentration the cake moisture increased by 5 to 15% for all sludges up to solids concentrations of 3.6%, but at higher concentrations the cake moisture decreased. This is because at high solids concentration the filter cake was less compressible and therefore, greater filtrate volumes were collected. Also, the initial moisture content of the cake was less to start with.

High applied sample volumes and vacuums resulted in poor quality of cake. For each additional 50 ml of volume applied, the cake moisture content increased from 12 to 20%, while each 1" Hg increment of applied vacuum resulted in an increase in the cake moisture content of 1%. Filter cake moisture varied from 60 to 80%, the lower values for Sludge "A" and "B" and the higher values for Sludge "C."

An optimum rate of solids production value of 7 lbs/ft^2/hr was observed at a screen solids loading of 0.2 lbs/ft^2/hr for conditioned sludge without chemicals, but chemical addition increased the production rate to 18 at a screen solids loading to 0.3 lbs/ft^2. The higher solids production rate for sludge conditioned with chemicals was due to the fact that Al+++ enhanced the colloidal destabilization, resulting in greater flocculation and greater cake strength. The cake production rate for unconditioned sludge was negligible. The reason of higher cake production in conditioned sludge without chemicals as compared to unconditioned sludge was the fact that freezing results in flocculation phenomenon as was evidenced by microscopic examination and wet sieve analysis. Coakley (17) reported that coarser particles, resulting from flocculation filter or dewater well when subjected to gravity or vacuum dewatering. Higher solids loadings resulted in poorer cake quality in conditioned sludge both with and without chemical addition.

Dewatering Characteristics on Sand Beds

Dewatering on sand beds consists mainly of two phenomena: 1) drainage and 2) air drying.

In the case of drainage, the initial faster rates were due to the filtration of free water, after which there was a lag time during which the sludge particles compacted together and then released the water held in between them resulting in a secondary increase in drainage but at rates somewhat slower than the initial rate. After one day of gravity drainage, further dewatering was almost entirely due to evaporation. Again the initial rate of moisture reduction was relatively high, because the moisture could move to the surface for evaporation, but after seven days there was no further appreciable moisture reduction, indicating that the constant drying rate had ended and that the cake moisture content values at that point were the critical moisture values. However, the constant drying rate lines did not exactly follow a straight-line pattern, as previously reported by other researchers (189, 190). This difference was possibly due to the fact that part of the "constant drying rate" might have already been incorporated with drainage after one day.

Higher cake moisture values were observed in the continuous flow process samples after gravity drainage as compared to batch process samples. It is possible that entrained air in the filtering media caused the slower gravity drainage rates, whereas during evaluation of the batch process the filtering media were washed 4-6 hours, which evacuated the entrained air before the samples were applied.

Higher applied hydraulic heads on sample volumes resulted in poor cake quality after seven days of air drying because the moisture trapped in the lower portions of the cake could not move up to the top surfaces because of higher resistance offered by the solids. A similar effect was noticed due to increases in solids concentration for the same reason. For each increment of 1% solids concentration increase, the cake moisture content increased anywhere from 10 to 15%, and for every 200 ml increase in the volumetric loading the cake moisture increased from 2 to 6%. Greater cake moisture retentions were observed at higher solids concentration and volumetric (or hydraulic) loadings.

Each increment of solids loading of 1 lb/ft^2 of sand bed resulted in a 2% increase in the cake moisture content.

Butane Stripping from Supernatant

At lower supernatant temperatures, the residence time of the bubble in the stripping flask was important. Therefore, smaller flow rates were more favorable. However, for high temperatures the bubble residence time was not important because the vapor-pressure of the butane was high enough that it could be stripped by application of a slight vacuum. Also, at higher flows the bubble dispersion was greater, hence at higher supernatant temperatures higher flow rates were more favorable.

Application to Waste Sludges from Other Sources

The results show that direct freezing, either solid or slurry, can be successfully used as a conditioning process for waste activated sludges with or without chemical addition regardless of the type of waste treated or the activated sludge modification used.

CHAPTER VI

CONCLUSIONS

Based on the results of this investigation the following conclusions were made:

1) The direct slurry freezing process using liquid normal butane as the refrigerant is an excellent method for conditioning waste activated sludge to promote settling, concentration and dewatering.
2) The quality of subsequent filter cake and the rate and degree of settleability of the conditioned sludge is directly related to the "butane contact" or freezing time whereas specific resistance and the compressibility coefficient are inversely related.
3) Settled sludge concentrations after freezing and thawing ranged from 10 to 14%.
4) Filter cake moisture content from vacuum filtration after conditioning ranged from 40-80%.
5) Moisture in the cake from sand beds after seven days of air drying ranged from 30 to 90%.
6) The C.O.D. values of the supernatant and filtrate (from gravity drainage and vacuum filtration) after conditioning were ≤ 1.5 times the unconditioned values. But the values from the other conditioning

processes like heat treatment (16) were 10 to 15 times higher than the unconditioned values.

7) Slow rates of freezing, i.e. lower butane flow rates, produce better dewatering characteristics in the waste sludges.
8) There is a direct relationship between the solids concentration and specific resistance and coefficient of compressibility values up to a concentration of 3.6% whereas settleability and cake quality are inversely proportional. However, higher solids concentrations, i.e. > 3.6%, result in a direct cake quality relationship.
9) Higher volumetric loadings resulted in a poorer quality of cake from both vacuum filtration and gravity sandbed dewatering.
10) Direct freezing causes cellular dehydration and enhances the flocculation phenomenon.
11) Using conditioned sludge from the slurry freezing process, the rate of solids production by a gravo-vacuum system is more efficient than ordinary vacuum filtration.
12) Storage of samples either before freezing or after thawing was detrimental to the subsequent dewatering characteristics.

13) Freon-114 was not found to be a suitable refrigerant for conditioning of waste activated sludge in a direct freezing system.

14) The direct slurry freezing process has a favorable economic comparison when compared to other processes such as heat treatment, presently used for waste activated sludge conditioning.

15) Direct slurry freezing is considerably more efficient than the indirect freezing. It would have a total power requirement of only 33 H.P. to condition 750 lbs (dry solids) of waste activated sludge per day where indirect ammonia refrigeration freezing would require 75 H.P.

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APPENDIX I

DESCRIPTION OF SOURCES OF SEWAGE SLUDGES

Source #1

Route 81 Sludge (Sludge "A"):--This is a small extended aeration waste treatment plant which treats approximately 6,000 gallons per day of domestic sewage from a motorist rest area located on Interstate 81 near a Radford, Virginia interchange. The plan has a comminutor, but no primary settling. Aeration is by means of a surface aerator and sludge is recycled to the aeration tank from the final settling basin by an air lift pump.

Source #2

Corning Glassworks Sludge (Sludge "B"):--This is a small extended aeration plant located at the Blacksburg Corning Glassworks Plant. This plant treats a domestic waste of approximately 24,000 gallons per day from the plant employees. This plant has a communitor but no primary settling. Aeration is by means of four diffused aerators and the sludge is recycled to the aeration tank from the final settling tank by air lift pumps.

Source #3

Roanoke Sludge (Sludge "C"):--This is a conventional activated sludge treatment plant serving the City of Roanoke, Virginia. This plant has a designed flow of about 24 million gallons per day, originating from both domestic and industrial sources. The sewage flow to the treatment plant is usually much higher than the above flow, and hence this plant is always overloaded. As a consequence, the sludge is nearly always of poor quality and has very poor dewatering and settleability characteristics.

APPENDIX II

C.O.D. AND SOLIDS MASS BALANCE

Table A-1. Solids Mass Balance (Sludge "A")

					Orig.sludge	Fr.sludge
Supernatant	Total solids (mg/l)				530	590
	Total volatile solids (mg/l)				200	205
Sludge	Total solids (mg/l)				15,590	12,450
	Total volatile solids (mg/l)				11,970	9,760
	M.L.S.S. (mg/l)				14,300	12,270
	V.S.S. (mg/l)				11,700	9,370
Filtrate (vacuum)	Total solids (mg/l)	Sample Vol. (ml)	50	12" Hg Vac.	380	460
				18" Hg Vac.	310	370
				24" Hg Vac.	380	510
			100	12" Hg Vac.	460	400
			150	12" Hg Vac.	260	470
	Total volatile solids (mg/l)	Sample Vol. (ml)	50	12" Hg Vac.	140	175
				18" Hg Vac	110	70
				24" Hg Vac	120	119
			100	12" Hg Vac.	120	120
			150	12" Hg Vac.	---	150
Filtrate (Gravity)	Total solids (mg/l)	Sample Vol. (ml)	400	---	660	800
			600	---	1,020	1,490
			800	---	1,200	1,600
	Total volatile solids (mg/l)	Sample Vol. (ml)	400	---	200	140
			600	---	500	540
			800	---	700	600

Table A-2. C.O.D. Mass Balance (Sludge "A")

	C.O.D. of M.L.S.S. (mg/l)	C.O.D. of Supernatant (mg/l)	C.O.D. of vacuum filtrate (mg/l)						C.O.D. Of Gravity filtrate(mg/l)		
			*50 ml Sample vol.				12" Hg Vac		*400 ml sample vol	*600 ml Sample	*800 ml Sample
			12" Hg	18" Hg	20" Hg	24"Hg	*100 ml	*150 ml			
Orig. Sludge (14,300 mg/l)	15,680	200	120	80	40	40	200	80	160	200	250
*Frozen sludge (12,270 mg/l)	14,240	300	120	40	160	40	400		280	360	400

*Air or vacuum stripped samples

Table A-3. Effects of Solids Concentration on the Supernatant and Filtrate Quality (Sludge "A")

M.L.S.S. (mg/l)		Original		Frozen sludge			
		Super.	Filt. (vacuum)	Supernatant		Filt. (vac)	
				Strip.	Unstrip.	Strip.	Unstrip.
14,300	Total Solids (mg/l)	530	380	450	720	460	--
	Total Volatile solids (mg/l)	200	140	80	420	175	--
	C.O.D. (mg/l)	200	120	200	---	120	--
20,000	Tot. Solids (mg/l)	400	315	675	790	360	440
	Tot. Volatile Solids (mg/l)	120	110	295	385	80	170
	C.O.D. (mg/l)	400	---	640	1120	2320	2560
*100,000	Tot. Solids	---	---	---	---	---	---
	Tot. Vol. Solids	---	---	---	---	---	---
	C.O.D.	---	---	---	---	2360	---

*Concentrated from the 2.0% sludge, after freezing and thawing.

Table A-4. Solids Mass Balance (Sludge "B")

					Orig. sludge	Fr. sludge
Supernatant	Total solids (mg/l)				430	853
	Total volatile solids (mg/l)				150	400
Sludge	Total solids (mg/l)				14,690	8,700
	Total volatile solids (mg/l)				11,470	7,670
	M.L.S.S. (mg/l)				14,260	8,070
	V.S.S. (mg/l)				11,000	6,700
Filtrate (vacuum)	Total solids (mg/l)	Sample Vol. (ml)	50	12" Hg Vac.	625	820
				18" Hg Vac.	580	920
				24" Hg Vac.	560	1,120
			100	12" Hg Vac.	575	870
			150	12" Hg Vac.	650	920
	Total Volatile Solids (mg/l)	Sample Vol. (ml)	50	12" Hg Vac.	210	495
				18" Hg Vac.	200	550
				24" Hg Vac	180	550
			100	12" Hg Vac.	200	450
			150	12" Hg Vac.	270	550
Filtrate (Gravity)	Total solids (mg/l)	Sample vol. (ml)	400	---	710	1,110
			600	---	760	835
			800	---	900	---
	Total volatile solids (mg/l)	Sample vol. (ml)	400	---	260	290
			600	---	285	350
			800	---	400	---

Table A-5. C.O.D. Mass Balance (Sludge "B")

	C.O.D. M.L.S.S (mg/l)	C.O.D. Super. (mg/l)	C.O.D. of vacuum filtrate (mg/l)						C.O.D. of Gravity filtrate (mg/l)		
			50 ml. sample vol.				12" Hg Vac		400 ml	600 ml	800 ml
			12" Hg	18" Hg	20"Hg	24"Hg	100 ml	150 ml			
Original sludge (14,260 mg/l)	20,000	200	320	200	---	200	280	280	320	160	---
Frozen sludge (8,070 mg/l)	10,400	120	240	240	---	300	560	700	320	240	---

Table A-6. Solids Analysis Sludge "C"
(Batch Process)

					Original	Frozen
Supernatant	Total Solids (mg/l)				430	650
	Total Volatile Solids (mg/l)				125	400
Sludge	Total Solids (mg/l)				14,500	8,700
	Total Volatile Solids (mg/l)				10,150	7,040
	M.L.S.S. (mg/l)				13,500	8,500
	V.S.S. (mg/l)				9,500	6,500
Filtrate	Total Solids (mg/l)	Sample volume (ml)	50	12 Hg. v.	1,100	200
			--			
			--			
	Total Volatile Solids (mg/l)	Sample volume (ml)	50	12 Hg. v.	400	100
			--			
			--			
Gravity	Total Solids (mg/l)	Sample volume (ml)	50		4,800	2,000
			--			
			--			
	Total Volatile Solids (mg/l)	Sample volume (ml)	50		600	400
			--			
			--			

APPENDIX III

GRAVITY DRAINAGE AND AIR DRYING ON SAND BEDS

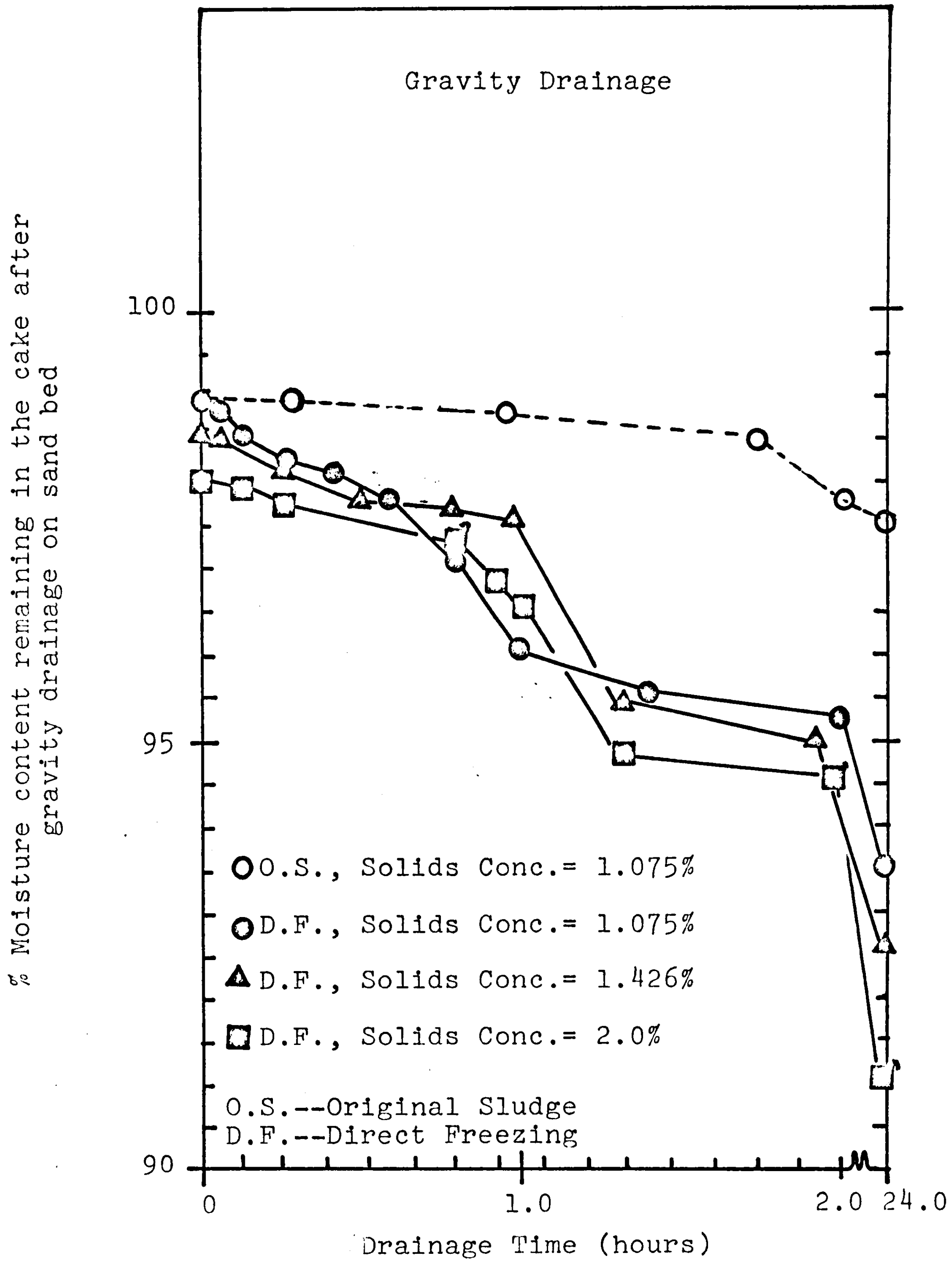

Figure 55. Bench Scale sand bed studies dewatering due to gravity drainage (Sludge "B").

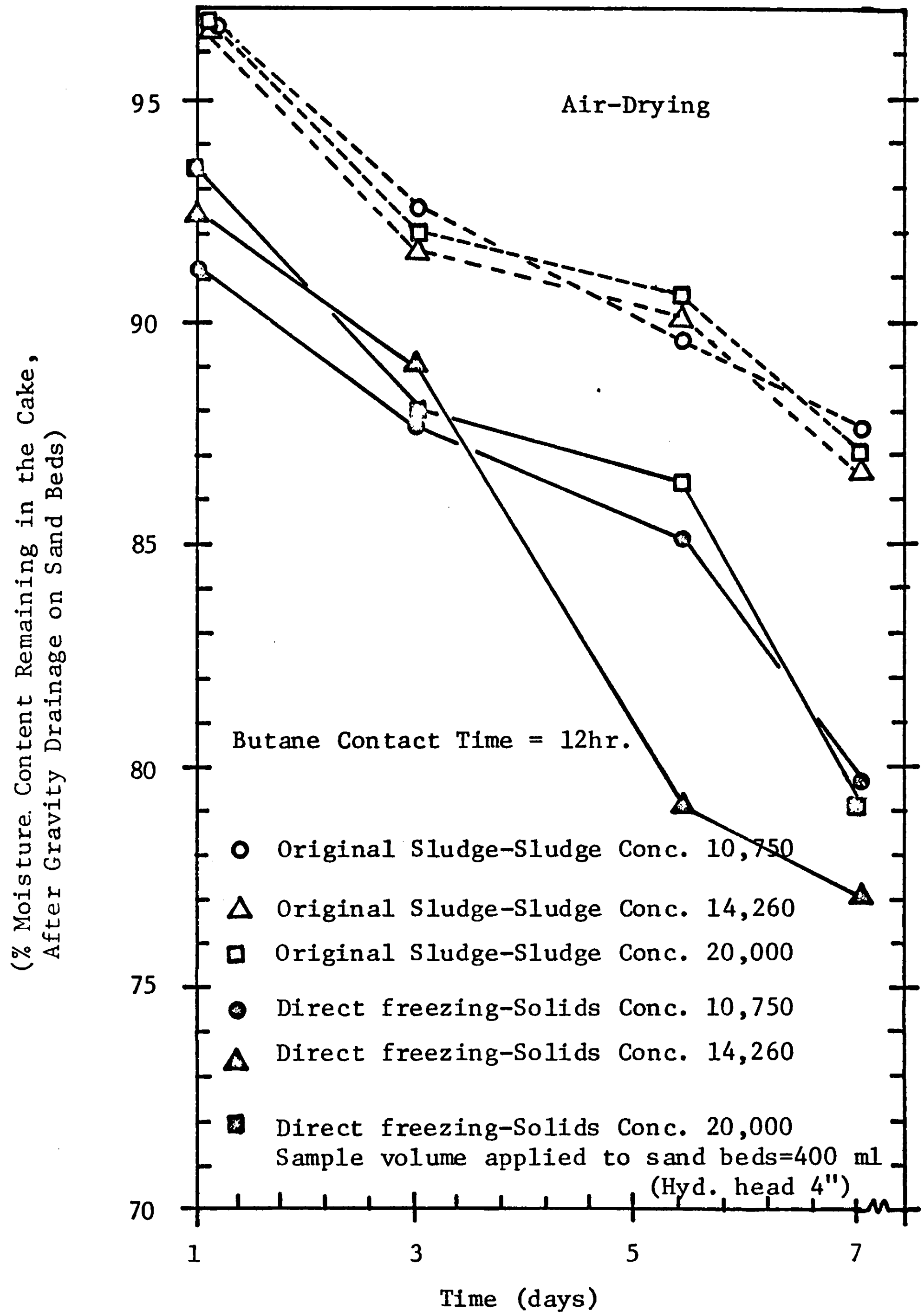

Figure 56: Bench Scale Sand-Bed Studies, Dewatering due to Air-Drying (Corning Glassworks Sludge)

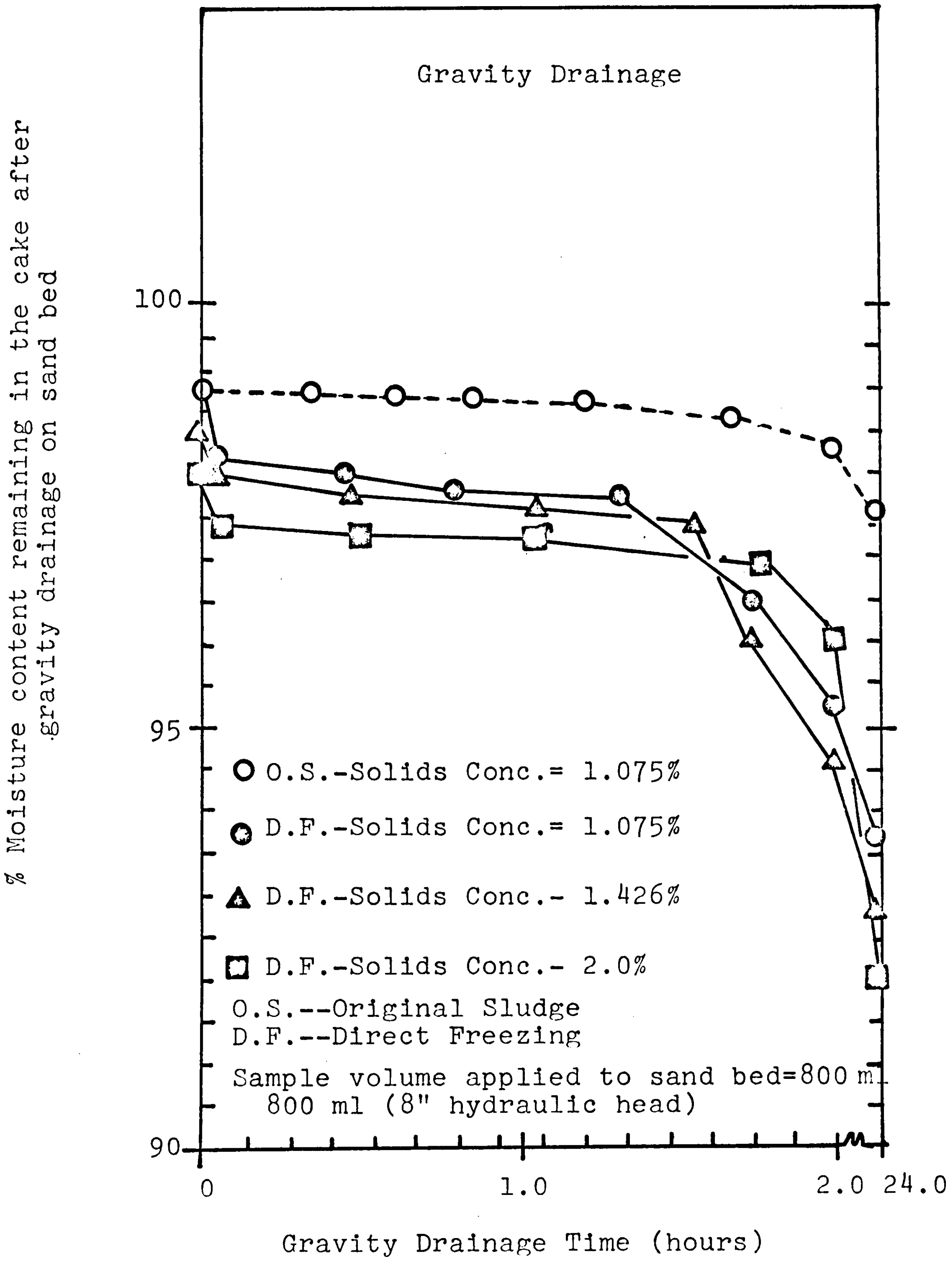

Figure 57. Bench scale sand bed studies-dewatering due to gravity drainage (Sludge "B").

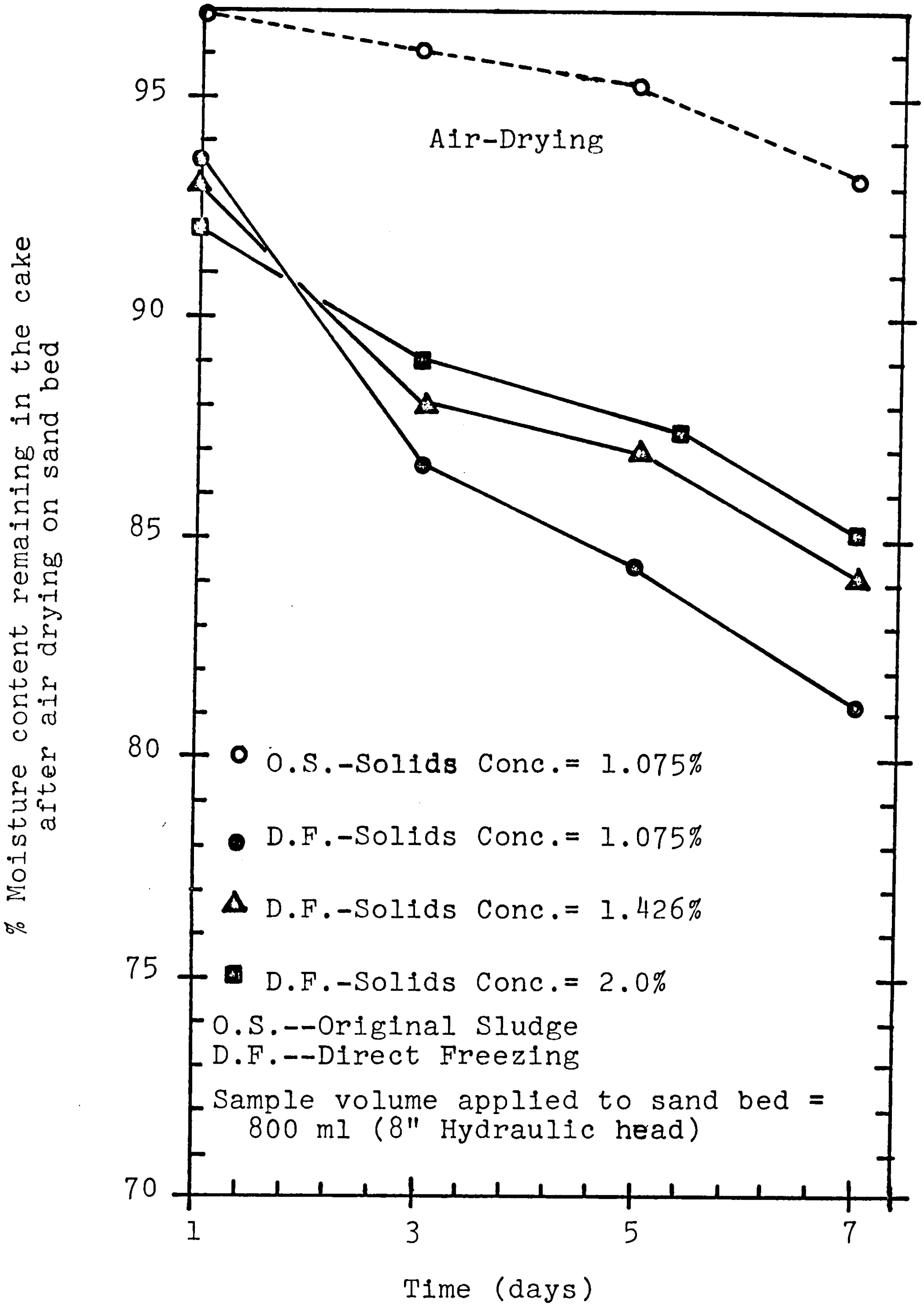

Figure 58. Bench scale sand bed studies-dewatering due to air-drying (Sludge "B")

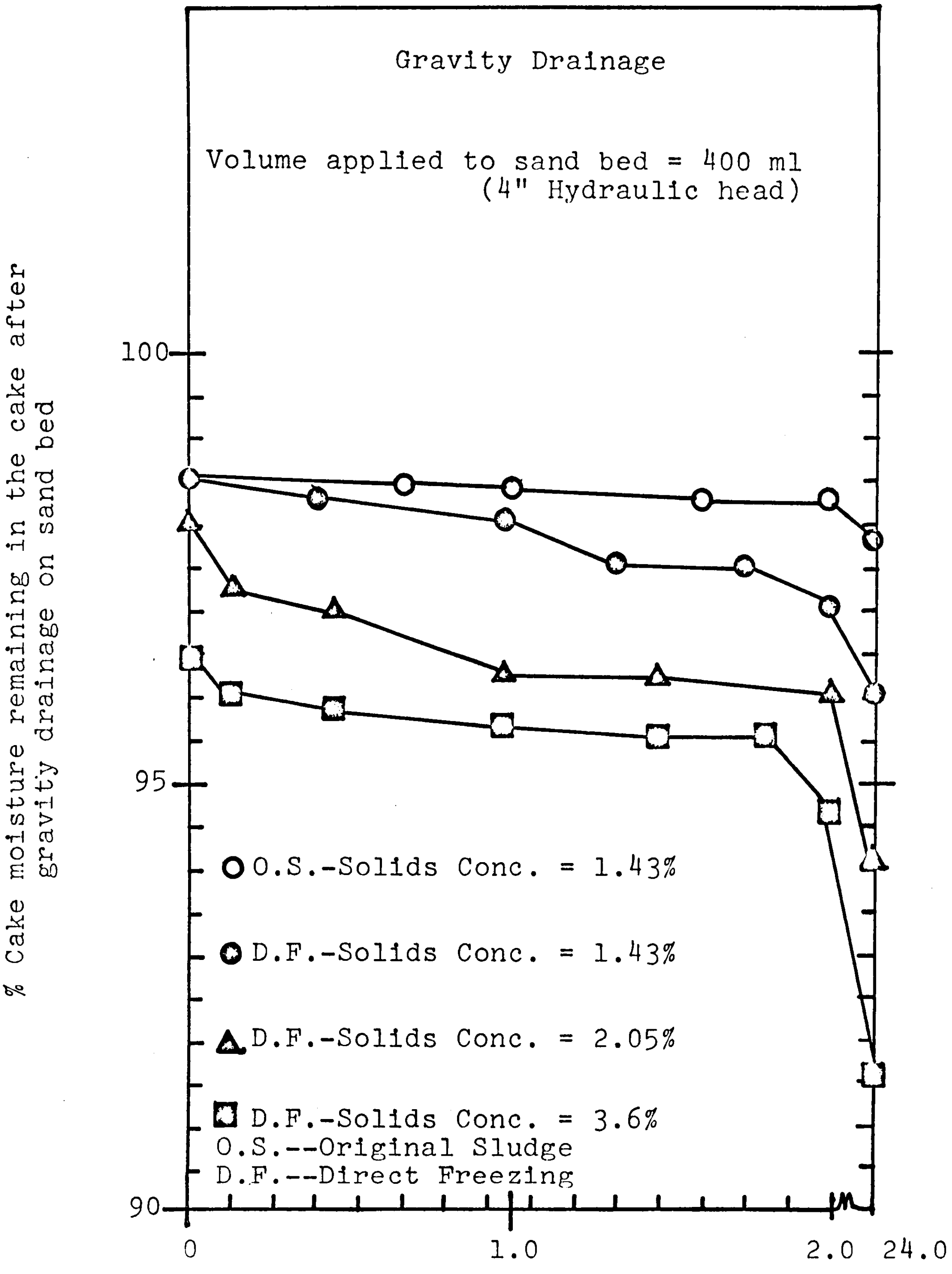

Figure 59. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "A")

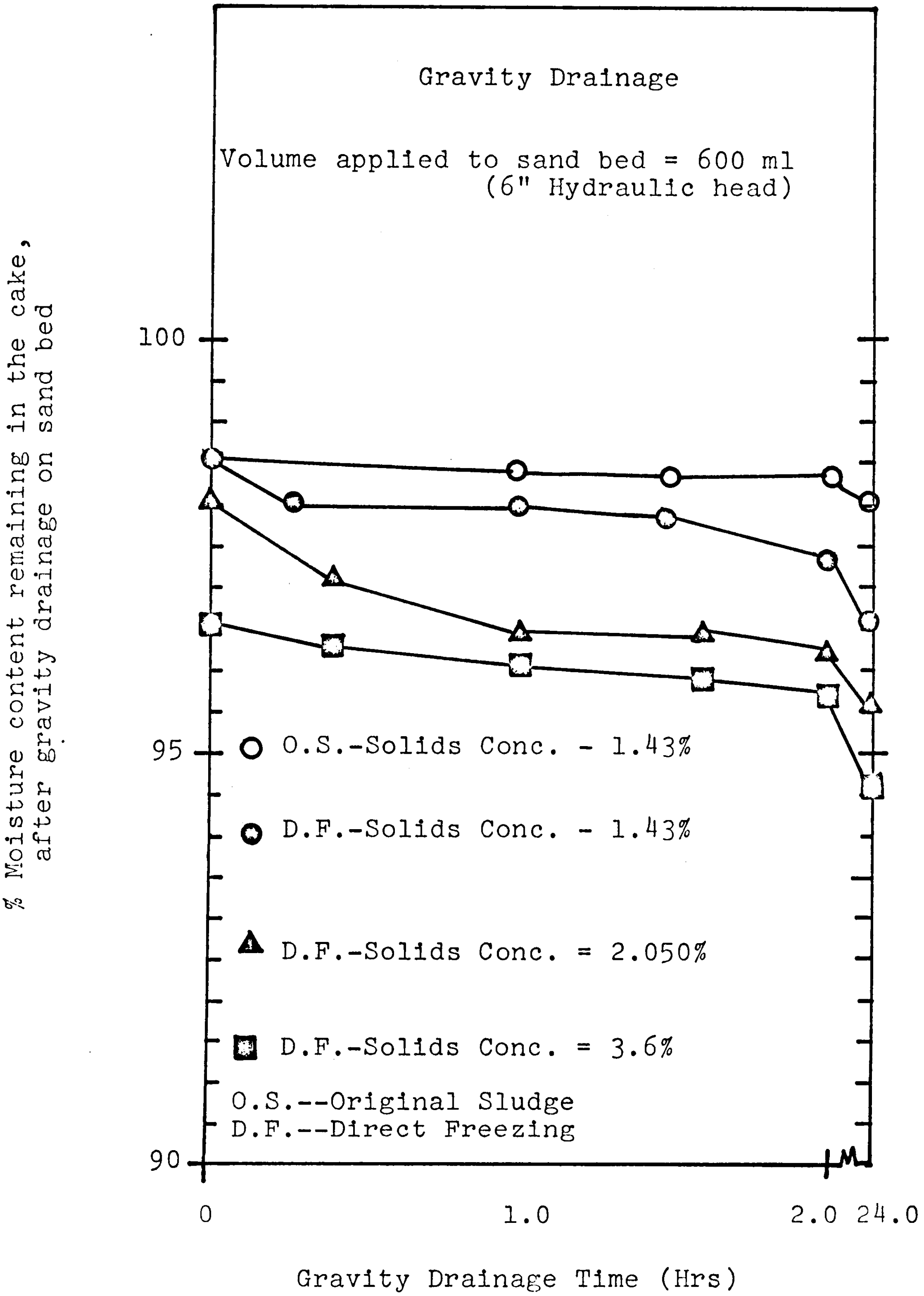

Figure 60. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "A")

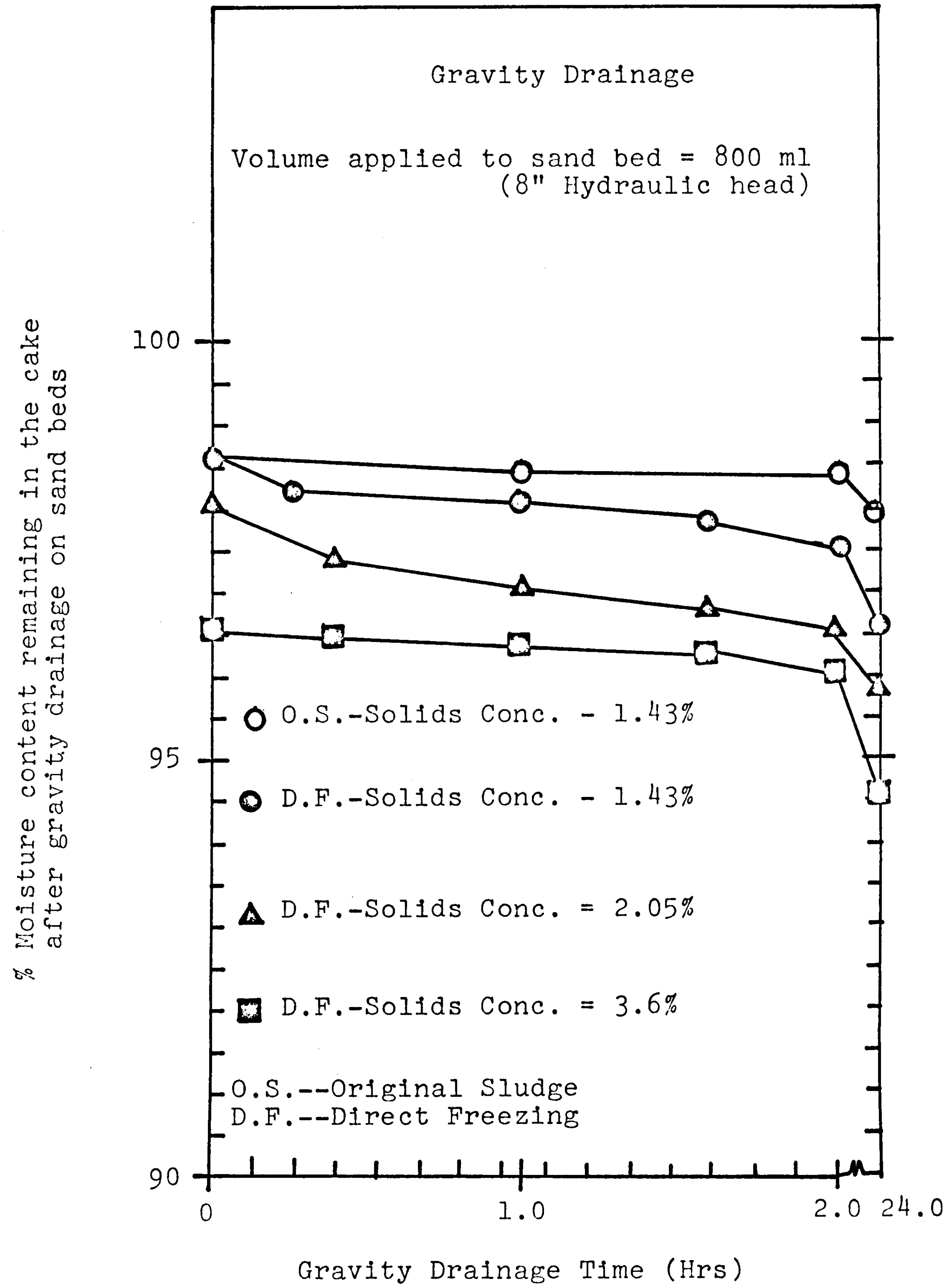

Figure 61. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "A")

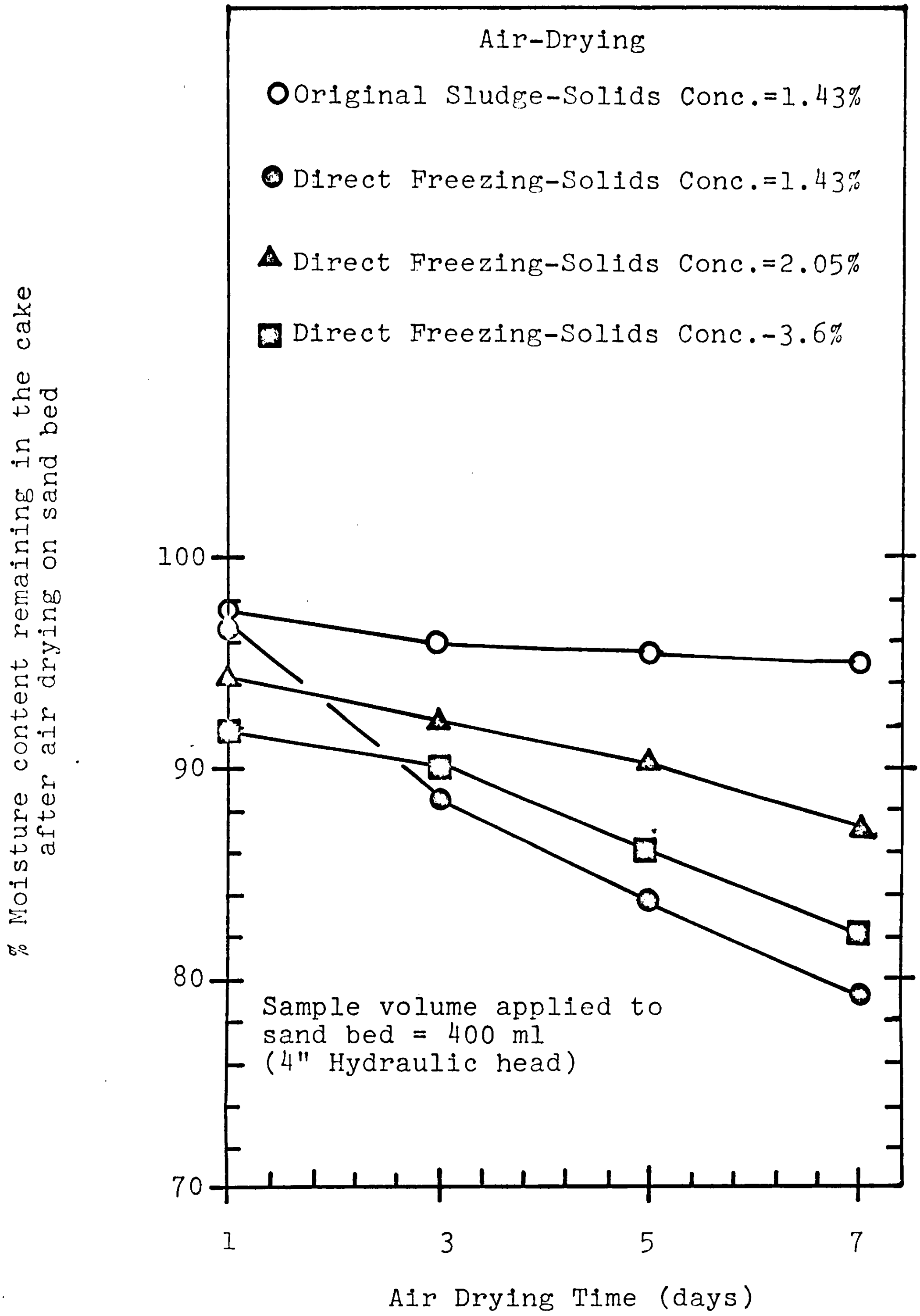

Figure 62. Bench scale sand bed studies, dewatering due to air drying (Sludge "A")

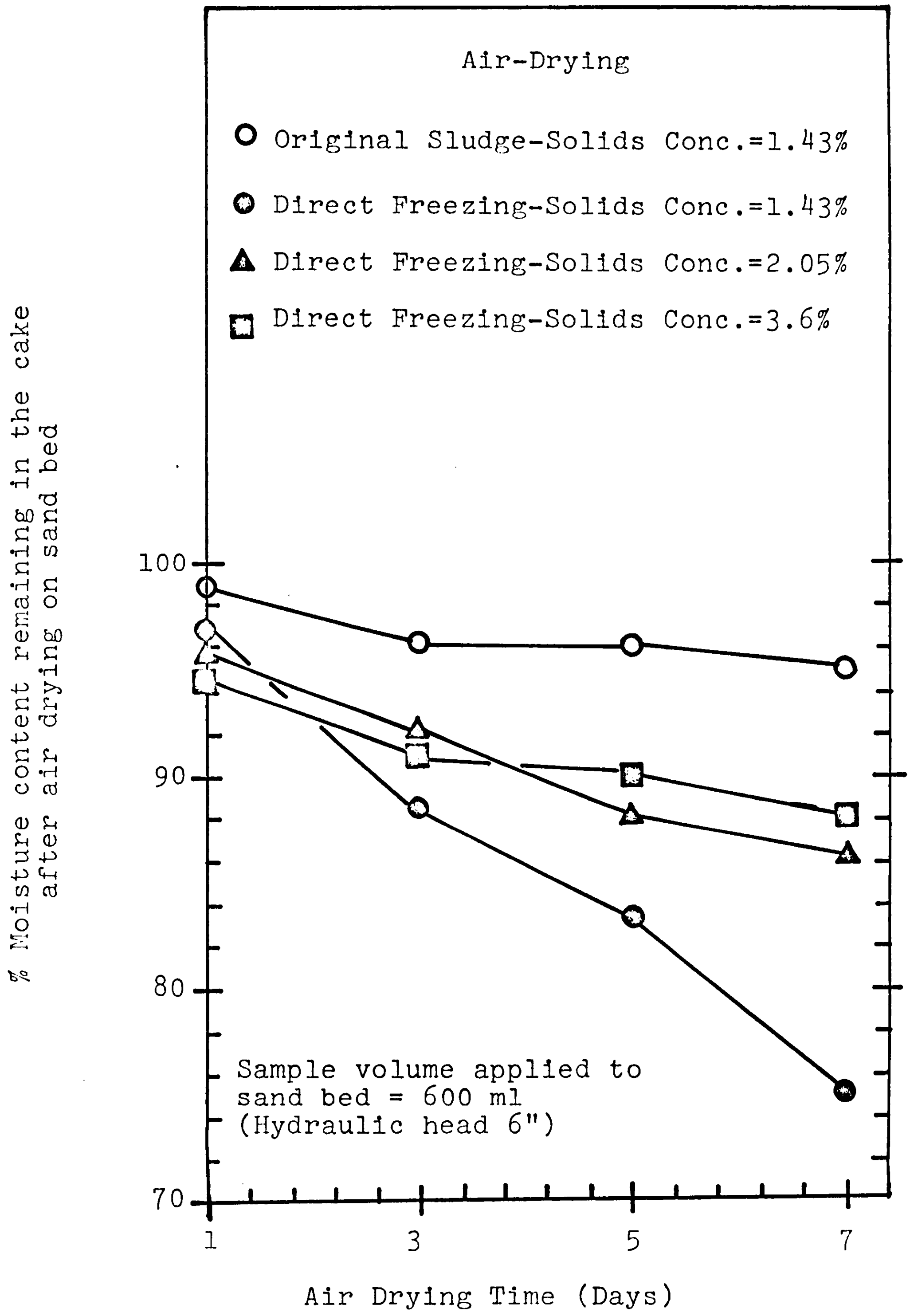

Figure 63. Bench scale sand bed studies, dewatering due to air drying (Sludge "A")

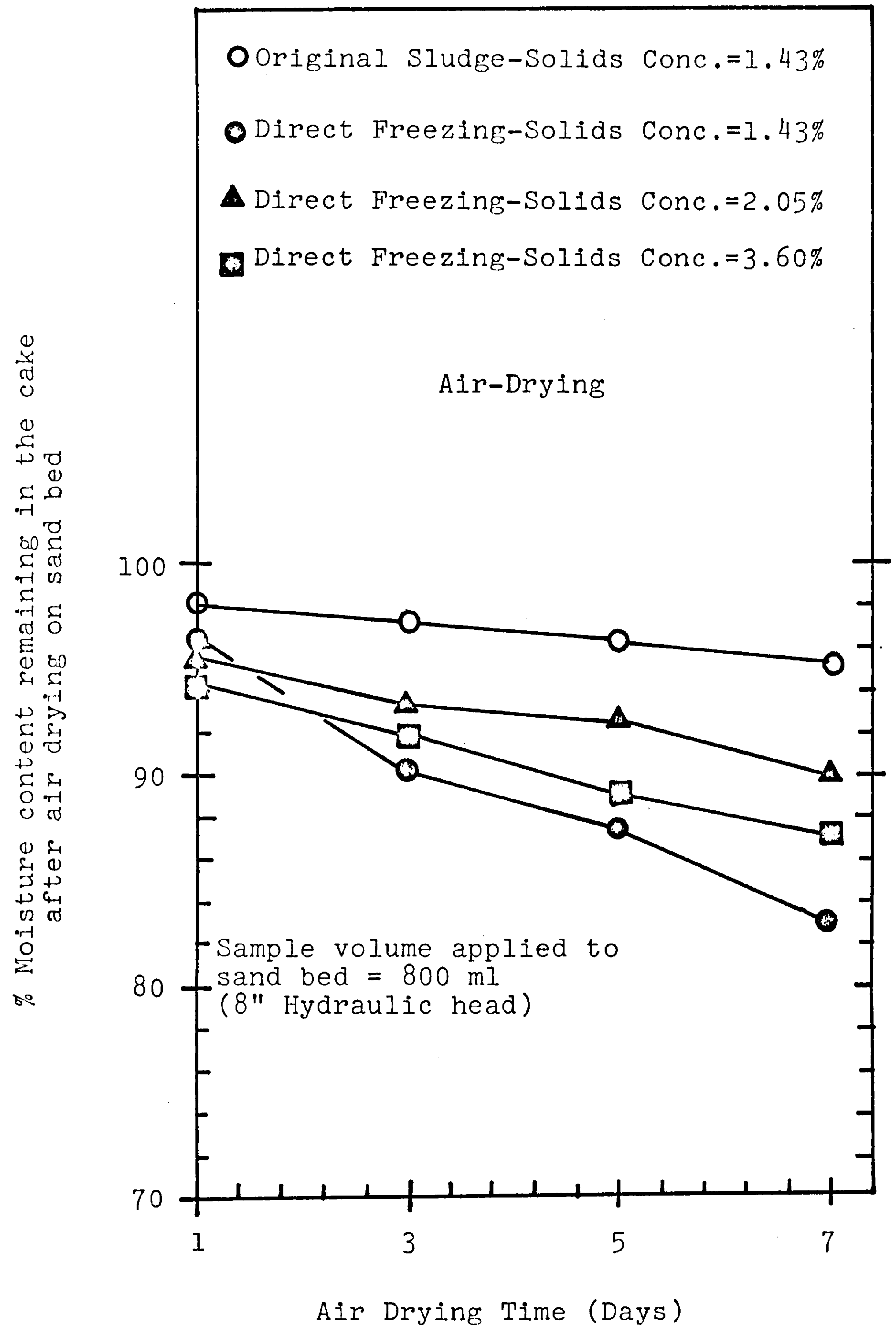

Figure 64 . Bench scale sand bed studies, dewatering due to air drying (Sludge "A")

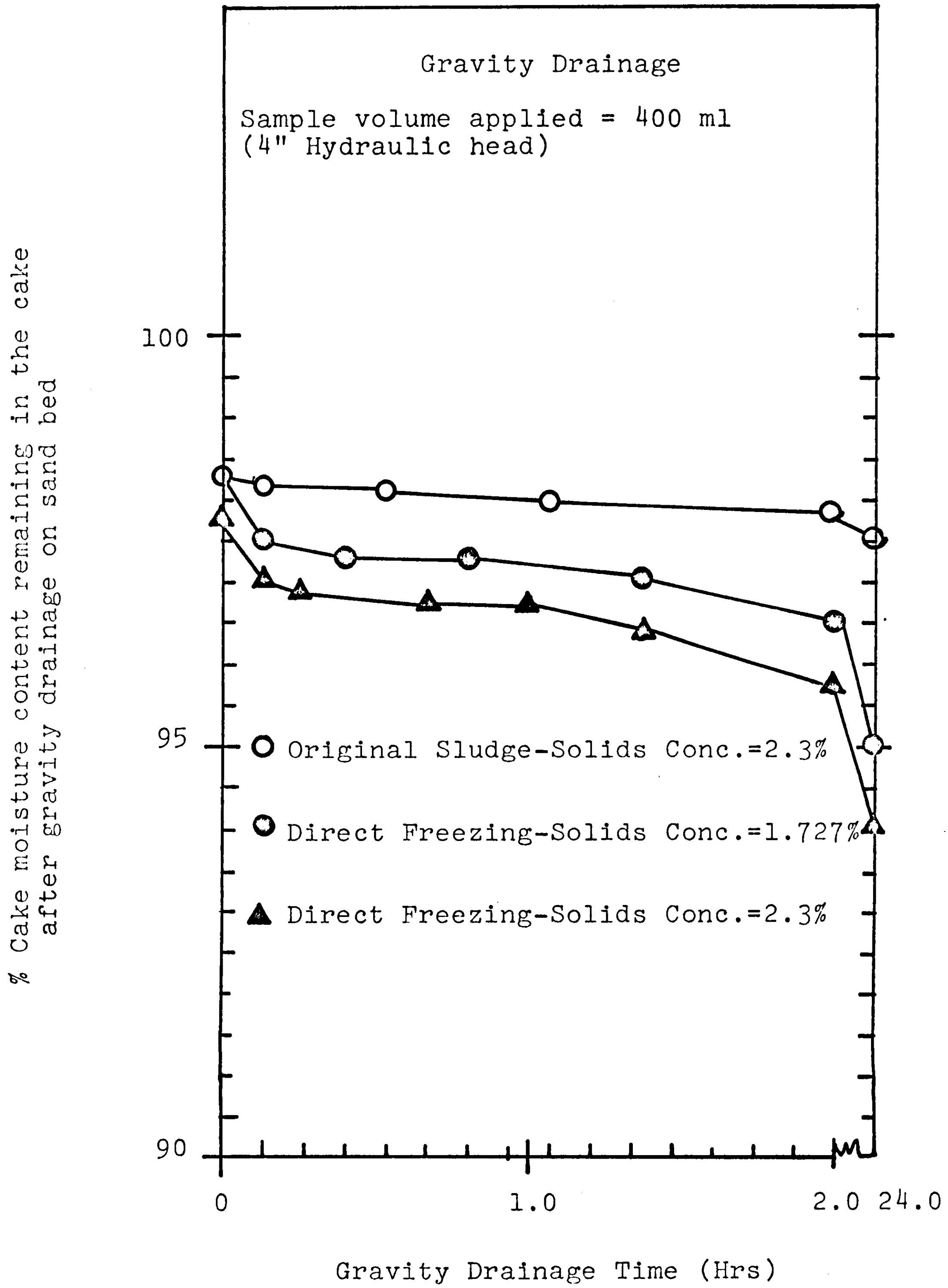

Figure 65. Bench scale sand bed studies, dewatering due to gravity drainage (Sludge "C")

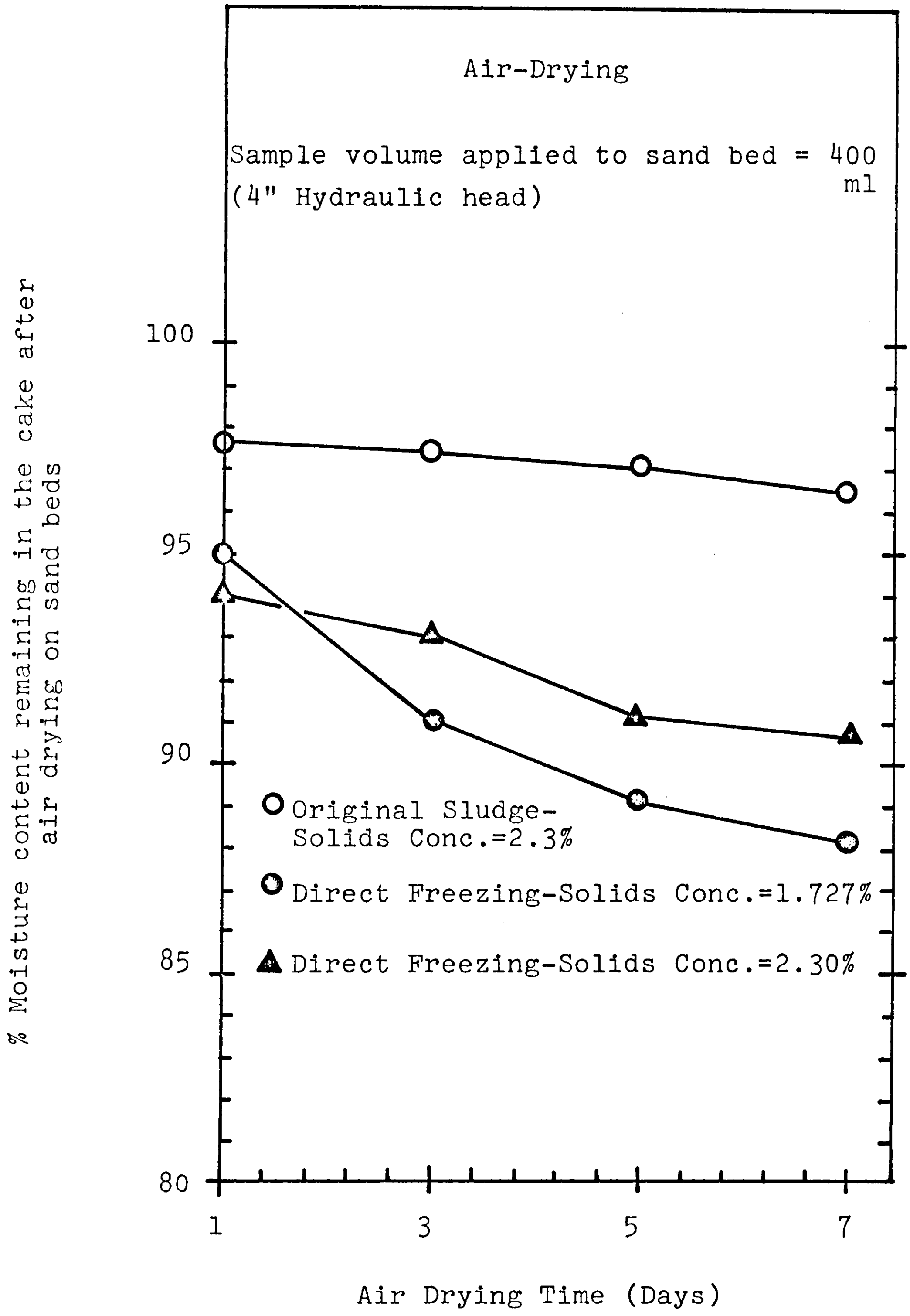

Figure 66 . Bench scale, sand bed studies, dewatering due to air drying (Sludge "C")

APPENDIX IV

BUTANE PROCESS ECONOMICS AND COMPARISON TO OTHER PROCESSES

I. Butane and Energy Requirements for Direct Freezing

Assume a waste activated sludge flow of 50,000 lbs/day with a solids concentration of 1.5% (typical of aerobic digestion) and at a temperature of 77°F.

Total dry solids = 750 lbs/day

A. Heat to be extracted from the sludge for freezing:

Weight of sludge to be frozen = 50,000 lbs/day

Temp. drop for freezing = (77-31) = 46°F

Latent heat of ice = 144 BTU

Heat extracted to freeze 50,000 lbs. of waste sludge = 50,000 x (46 + 144)

$$= 95 \times 10^5 \text{ BTU/day}$$

B. Butane (liquid) requirement for extraction of heat:

Latent heat of vaporization of butane at 30° to 31°F = 165 BTU/lb

Pounds of liquid butane required for extraction

$$95 \times 10^5 \text{ BTU} = \frac{95 \times 10^5}{165} = 6.75 \times 10^4 \text{ lbs/day}$$

Knowing the total butane, the rate of flow can be adjusted.

C. Heat required for thawing of sludge:

This heat would be supplied by the butane vapors from the freezer. The butane vapors, after compression and condensing, will thaw the sludge and become liquified for reuse.

Latent heat of frozen sludge plus a temperature rise of 5°F = (5 + 144)(50,000)

$$= 74.5 \times 10^5 \text{ BTU/day}$$

Heat contained in butane vapors = 95×10^5 BTU

Out of the total of 95×10^5, 74.5×10^5 will be used in cooling the sludge. The remaining heat that must be extracted before condensation back to the liquid state is 20.5×10^5 BTU/day.

D. Theoretical energy required for compressing vapors: (Primary cycle as used in the experiments)

$$W = \Delta H\left(\frac{T_1 - T_2}{T_1}\right)$$

T_1 = Temperature of butane for melting frozen sludge, in condenser, R°

T_2 = Temperature of butane leaving freezer, R°

ΔH = Latent heat of fusion, 144 BTU/lb

W = Work done in BTU/lb of sludge/hr

$$W = \frac{(144)(2)}{491} = 0.58 \text{ BTU/lb/hr}$$

To this the work required for mechanical and electrical inefficiency to remove heat of compression, etc., must be added.

Hence, W = 1 BTU/lb/hr

$$\text{Total horsepower} = \frac{1 \times 50{,}000}{2545} = 19 \text{ H.P. (1)}$$

Partially frozen sludge will be used to cool the compressor effluent to saturated liquid, but additional auxiliary refrigeration requirements for 20.5×10^5 BTU is as follows:

An ammonia refrigeration system, including all auxiliaries require per ton of refrigeration, = 2 H.P.

Refrigeration in tons, at the rate of 288,000 BTU per ton of refrigeration

$$= \frac{20.5 \times 10^5}{2.88 \times 10^5} = 7 \text{ tons}$$

Power required = 7 x 2 = 14 H.P. (2)

Total power required = (1) + (2) =

14 + 19 = 33 H.P.

II. Refrigeration and Power Requirement in Indirect Freezing

A. Freezing

Tons of ammonia refrigeration for

$$\text{sludge freezing} = \frac{95 \times 10^5}{2.88 \times 10^5} = 33 \text{ tons}$$

H.P. required = 33 x 2 = 66 H.P.

B. Thawing

Additional horsepower would be required for thawing the sludge (latent heat of fusion of ice is 1/7th of the latent heat of vaporization) = 1/7(66) = 9 H.P. Total horsepower required = 9 + 66 = 75 H.P.

III. Drying and Incineration of Dewatered Sludge

Assuming that the drying process was started immediately after dewatering (to avoid additional storage) the temperature of the dewatered sludge must be raised from 32 + 5 = 37°F to 212°F and then enough heat must be added to vaporize water.

From the data of percent moisture remaining in the sludge (as mentioned in the previous figures) a value of 30-40% is reasonable.

Sludge volume with 30-40% moisture and 750 lbs. of solids = 15,000 lbs.

BTU required to raise the temperature of 15,000 lbs. of water from 37°F to 212°F = 15,000 (212-37) = 26×10^5 BTU (1)

BTU required to evaporate this water into live steam = $(14{,}250)(970 \frac{\text{BTU}}{\text{lb}}) = 137 \times 10^5$ BTU (2)

BTU available from 750 lbs. of solids

= 750 x 5100 BTU/lb = 38×10^5 BTU (3)

Heat of combustion of butane at 60°F and at atmospheric pressure = 21,315 BTU/ft^3 of gas.

Assuming out of a total butane quantity of 6.75×10^4 lbs used for freezing, 10% will be stripped off from the sludge = $1/10\ (6.75 \times 10^4$ lbs) = 0.675×10^4 lbs

Specific volume of butane vapor at 37°F = 5.0 ft^3/lb

Hence, total volume of butane = $3.375 \times 10^4\ \text{ft}^3$

BTU's available from this volume of butane

$= 3.375 \times 10^4 \times 2.135 \times 10^4$

$= 8 \times 10^8$ BTU (4)

Total BTU required = (1) + (2) = 137 + 26

$\times 10^5 = 163 \times 10^5$ BTU (5)

Total BTU available = (3) + (4) (6)

From the above it can be seen that more BTU's are available than are needed and part of this could be converted into the H.P. requirement for the refrigeration unit and still have some excess power available.

Now 750 lbs of the dry solids contain about 50% ash

----- 375 lbs.

Thus, 50,000 lbs. of waste activated sludge have been reduced to 375 lbs. of ash in one continuous process. Hence the system is thermally self-sustaining.

Table A-7. Comparison of Butane-Freezing Process for Waste Activated Sludge Dewatering with the Other Processes (Part. 1)

Description		[1]Wet Air Oxidation (Zimpro Process)	[2]Heat Treatment (Proteous Process	Anaerobic Digestion	Aerobic Digestion
Sludge	COD	70-80% reduction	30-40% reduction	60-70% reduction	30-70% reduction
	pH	4-4.4	5.6	6-7	6-6.7
Supernatant	pH	4-4.8	5.9	6	4-7
	Quality	Very poor. High in nutrients & soluble organics	Very poor. High in nutrients	Poor. High in nutrients & soluble organics	Moderate. High in nutrients
Filtrate	pH	5.0	6	6	7-8.2
	Quality	Very poor	Very poor. High dissolved solids	Poor. High dissolved solids	Moderate. High dissolved solids
Energy requirements		Very high	Quite high	Moderate requirement	Low energy
Corrosion and sealing problem		Yes	Yes	Yes	Yes
Pretreatment requirement		No	No	No	Sometimes Essential
After-treatment		Extensive	Yes	Yes	Below average
Addition in vol. of sludge due to conditioning agent		No	No	No	No

Table A-7. (Part 1) - Continued

Description	[1]Wet Air Oxidation (Zimpro Process)	[2]Heat Treatment (Proteous Process)	Anaerobic Digestion	Aerobic Digestion
[3]Cost of conditioning per ton of dry solids with variable percent solids	$30-35	$8-20	$15-20	--

[1] Temp. of 450-600°F and pressure 1800 to 3000 p.s.i.

[2] Temp. 220°C (428°F) and pressure 250 p.s.i. maintained for 30 min.

[3] This cost does not include the cost of dewatering equipment after conditioning. These costs are from the literature.

Table A-7 . Comparison of Butane-Freezing Process for Waste Activated Sludge Dewatering with the Other Processes (Part 2)

Description		Chemical Conditioning	Direct Freezing	Butane Freezing
Sludge	COD	20-40% reduction	50-70% reduction	50% reduction
	pH	5.5-6	6-7	6.9-7
Supernatant	pH	6-6.5	7	6.9-7.25
	Quality	Moderate. Lesser in nutrients	Very poor. High nutrients and soluble organics	Much better.[4] Less soluble organics
Filtrate	pH	6.5	7-7.5	8-8.2
	Quality	Moderate. Less dissolved solids	Moderate. High dissolved solids	Good. Low[4] dissolved solids
Energy requirements		Low energy	Very high energy	Low energy
Corrosion and sealing problem		Yes	Yes	No
Pretreatment requirement		No	Normally required	No
After-treatment		Not much	Yes	Not much
Addition in vol. of sludge due to conditioning agent		Yes	Yes, if chemicals are used as preconditioners	No

Table A-7 . (Part 2) - Continued

Description	Chemical Conditioning	Direct Freezing	Butane Freezing
[3]Cost of conditioning per ton of dry solids with variable percent solids	$8-25	$10-30	$6-20

[3] This cost does not include the cost of dewatering equipment after conditioning. These costs are from the literature.

[4] No nitrate or phosphate analysis conducted.

APPENDIX V

APPLICATION OF DIRECT FREEZING TO WASTE SLUDGES FROM OTHER ACTIVATED SLUDGE PROCESSES

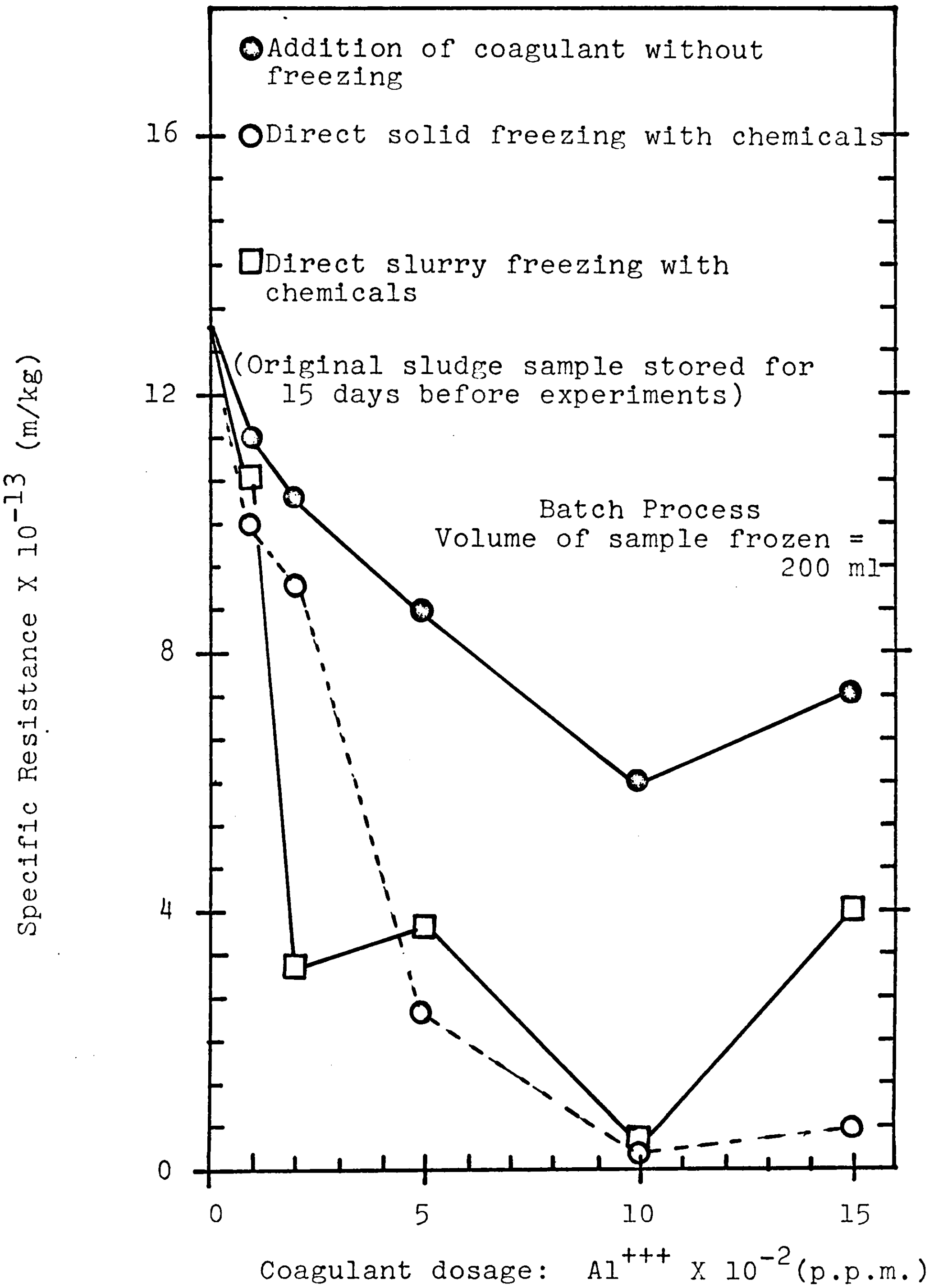

Figure 67. Effect of coagulant dosage on the specific resistance (Pulp and Paper waste sludge)

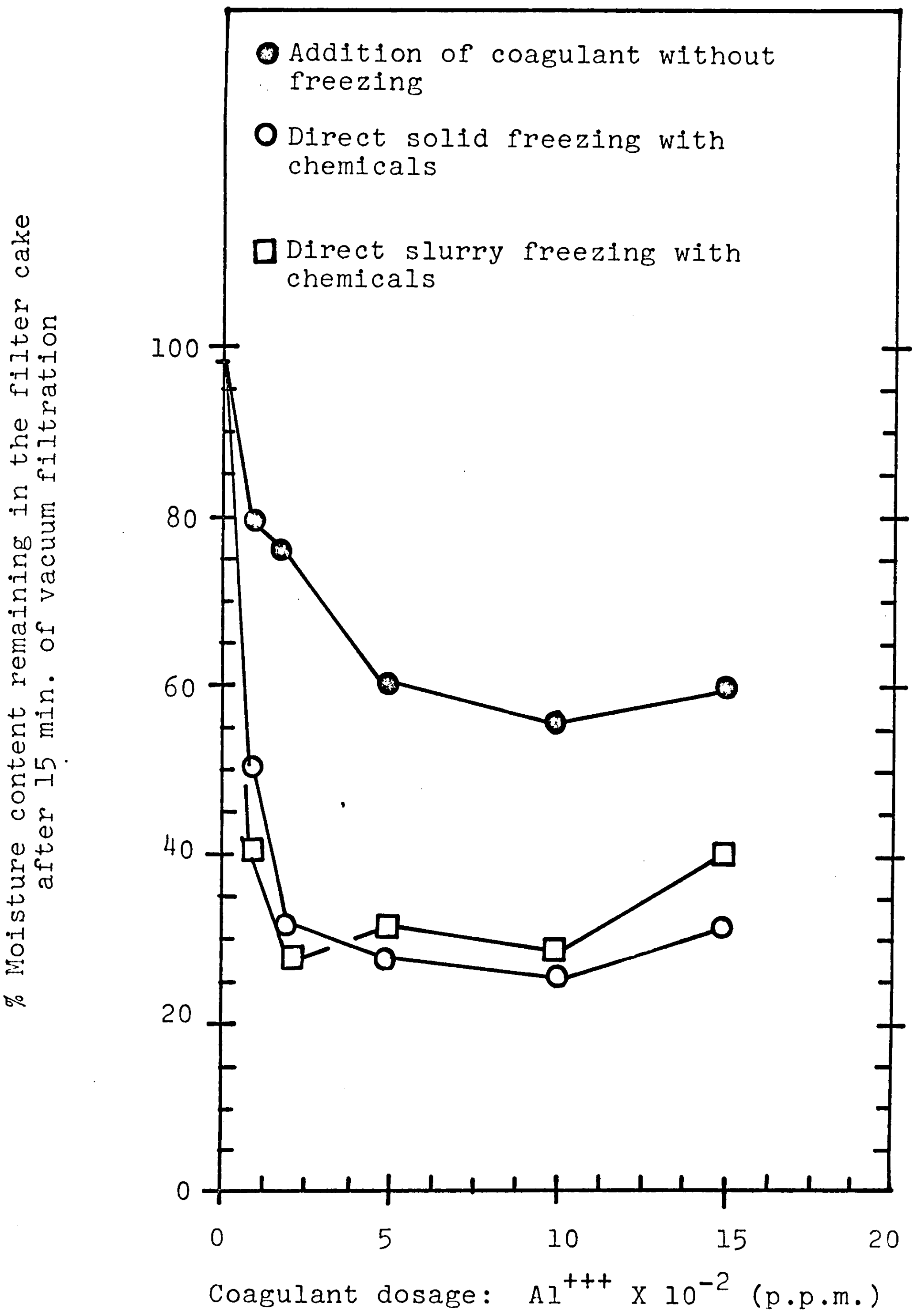

Figure 68. Effectof coagulant dosage on the filter cake quality (Pulp and Paper waste sludge)

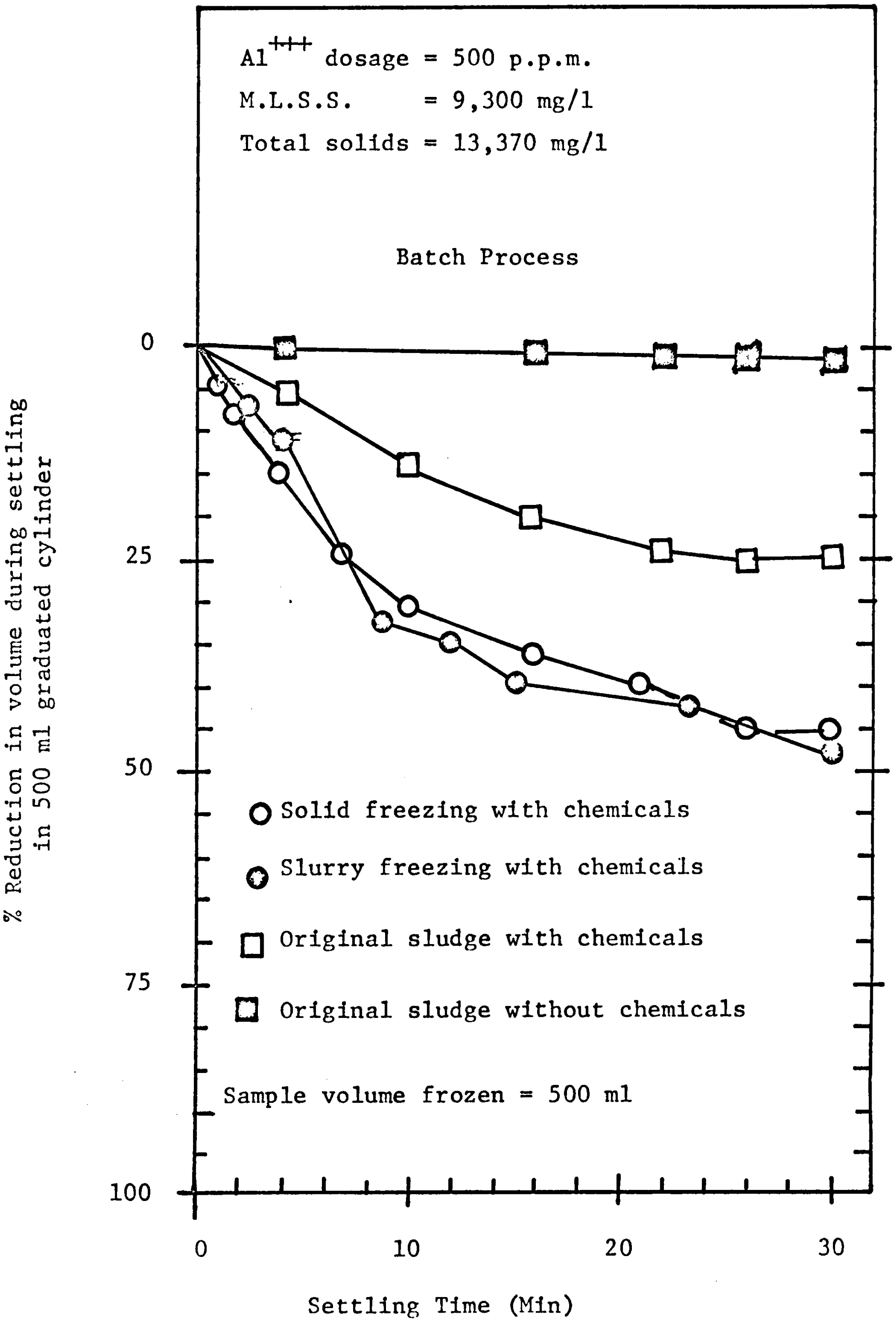

Figure 69. Settleability of Pulp and Paper waste sludge after direct freezing.

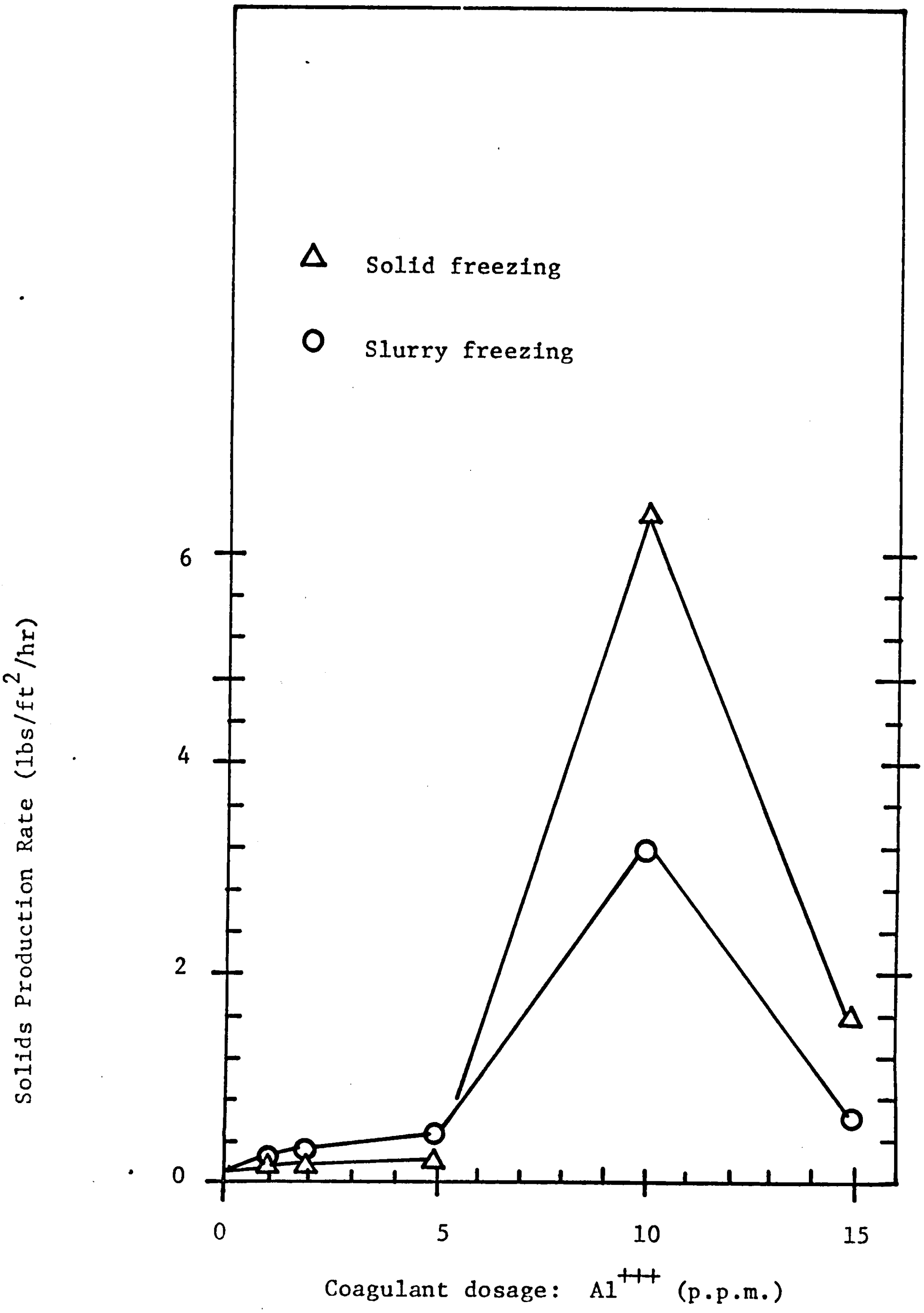

Figure 70. Variation of rate of solids production with 1000 p.p.m. Al^{+++} coagulant dosage using gravo-vacuum system (Pulp and Paper waste sludge)

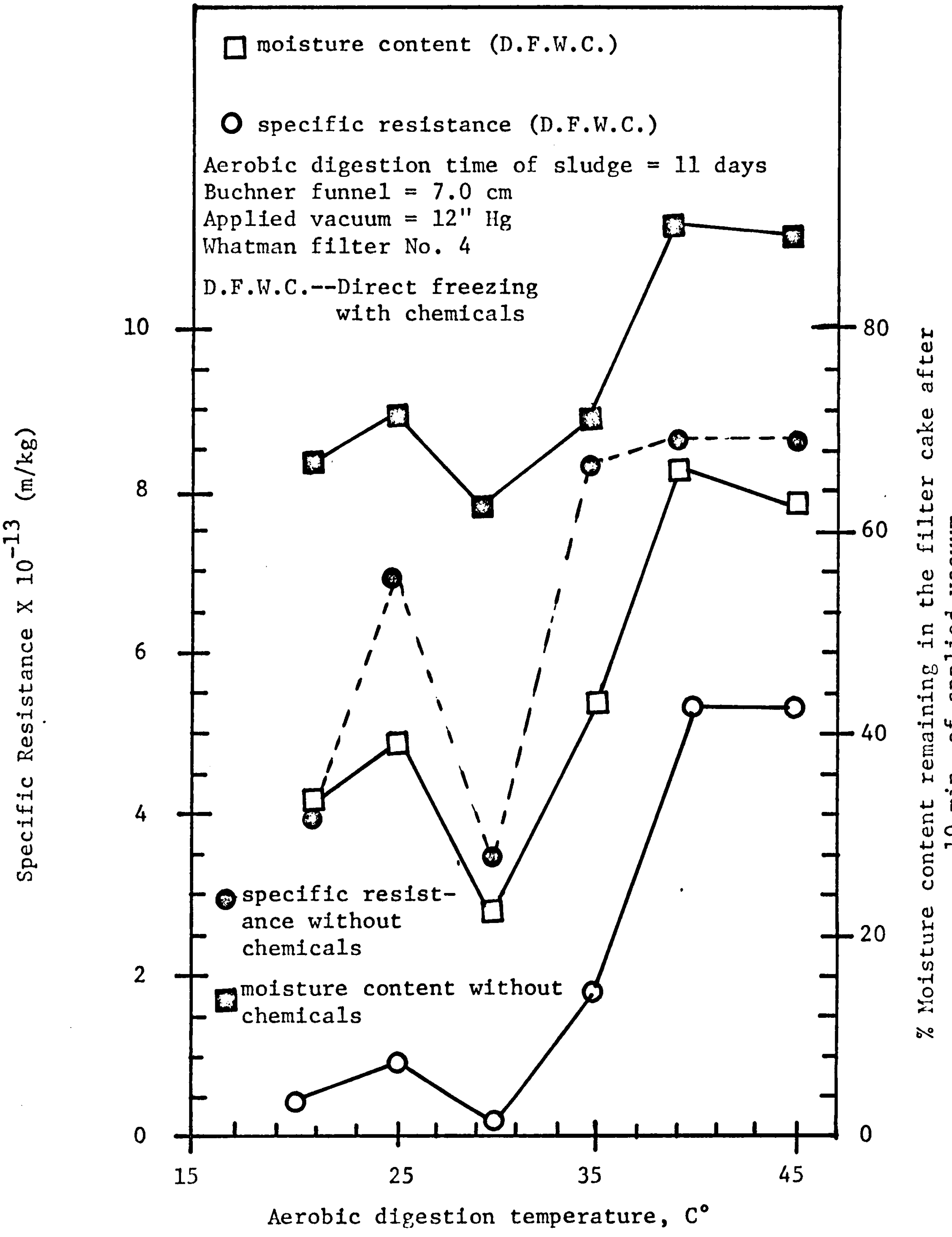

Figure 71. Effect of direct freezing on specific resistance and moisture content of aerobically digested sludge at different temperatures

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PRINCIPLES AND TECHNIQUES FOR THE CONDITIONING OF WASTE ACTIVATED SLUDGE BY DIRECT SLURRY FREEZING

by

M. Zulfiqar Ali Khan

(ABSTRACT)

Direct freezing has been extensively and successfully used for the desalination of saline waters, and for the concentration and recovery of by-products from industrial wastes. In this investigation the direct slurry freeze conditioning of waste-activated sludge was studied, and it was shown that it produces a considerable improvement in dewatering. Dewatering characteristics were adequately defined by the specific resistance and coefficient of compressibility values, by settling, and by filter cake quality when vacuum filtration and gravity drainage on sand beds were utilized.

The sludge samples for the principal part of the investigation were obtained from three different sources: two extended aeration plants treating domestic sewage and a conventional activated sludge plant treating combined industrial domestic wastes. During the latter part of the research, waste activated sludge samples from a plant treating pulp and paper waste and from aerobic digesters were also conditioned by the process.

Gravity settled sludge concentrations after freezing and thawing ranged from 10 to 14 percent. Filter cake moisture contents after vacuum filtration of the conditioned sludge ranged from 40 to 80 percent while cake moisture after gravity drainage on sand beds followed by seven days of air drying ranged from 30 to 90 percent. Very little change in supernatant quality occurred during direct slurry freeze conditioning. Direct microscopic and wet sieve analysis indicated that the principal mechanism of conditioning was the promotion of flocculation.

It was found that the degree of conditioning is a function of the "butane contact" or freezing time with better conditioning occurring with longer detention times. Variables affecting conditioning such as the feed solids concentration and the butane flow rate were evaluated as were various factors that affect the dewatering of the conditioned sludge.

An economic evaluation indicated that the direct slurry freezing process has an economic advantage when compared to other sludge conditioning processes such as indirect freezing and heat treatment. A cost estimate of \$6 to \$20 per ton of dry solids processed was projected.