A COMPARATIVE STUDY OF FREEZE-THAW PROCESSES FOR CONDITIONING WASTEWATER AND WATER TREATMENT SLUDGES

by

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(ABSTRACT)

This research effort involved the application of indirect- and direct-contact, freeze-thaw conditioning techniques for improving the dewatering characteristics of both wastewater and water treatment sludges. Sludges tested included waste activated sludge, primary sewage sludge, waste activated/primary sewage sludge mixtures and alum sludge. The direct-freeze methods examined were the use of a secondary refrigerant (butane) evaporated in the sludge and the use of gas hydrate or clathrate formation by addition of Freon 12 under appropriate temperature and pressure conditions. Sludges were also frozen solid using indirect freezing methods, thawed and tested for comparative purposes. Particle size distribution and floc density measurements were used to determine changes in particle characteristics; specific resistance values and dewatered dry solids concentration were used to assess dewatering characteristics. Results of direct- and indirect-contact, freeze-thaw conditioning were compared to the effects of polymer conditioning. The results indicated that direct-freeze methods do not appear technically or economically competitive with currently accepted conditioning methods. The superior results obtained with the indirect-contact, freeze-thaw process when compared to the direct-contact processes suggested that the extent and rate of freezing may greatly influence the particle characteristics of the conditioned sludge, and thus its dewatering characteristics.

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I. INTRODUCTION

Sludge production is an inevitable result of many wastewater and certain water treatment processes. These solids must be stabilized, sometimes thickened and conditioned, and then dewatered before ultimate disposal. For most sludge generators, disposal methods are limited to landfilling, incineration, and other processes, the costs of which depend upon the volume of the sludge to be disposed. The drier the sludge, the more efficient and less expensive the process usually is.

Sludge conditioning is selectively undertaken for one of two purposes: (1) to improve the dewatering rate of a sludge (i.e., to decrease the amount of time required to remove a given amount of water from the sludge); and (2) to improve the extent of dewatering or thickening (i.e., to increase the amount of water removed from the sludge.) In addition, conditioning is frequently necessary to obtain an easily handled product.

Conditioning can decrease the resistance of sludge to dewatering to one percent or less of the original resistance of the unconditioned sludge. It typically reduces moisture content from about 95 to 98 percent to about 60 to 75 percent for the final dewatered product[1].

Freeze-thaw conditioning occurs when sludge is allowed to come into contact with air, water vapor, a secondary refrigerant, or other freezing agent under temperature and pressure conditions conducive to freezing. Freezing may occur naturally (for example, when lagooned water sludges freeze during extended periods of cold weather) or may be artifically induced by indirect or direct contact between sludge and a refrigerant.

Freeze-thaw conditioning can produce an extremely dry, grainy, odorless product composed of up to 60 to 70 percent solids[2]. Such conditioning often increases the solids handling capacity (e.g., filter yield) of mechanical dewatering equipment. In fact, certain sludges drain so easily following freeze-thaw conditioning that there is no need for thickening or filtration after conditioning if sufficient land is available for gravity dewatering[3]. Freeze-thaw processing has been used to condition a wide variety of sludges, including water treatment sludges as well as domestic and industrial wastewater sludges.

With the exception of natural freezing, processes used to freeze sludge are often technically complex, expensive, and energy intensive. Natural freezing requires large areas of land for proper lagooning and storage. Nevertheless, these disadvantages may be offset by the unusually high solids concentrations made possible by freeze-thaw conditioning, and the tractable nature of the product sludge.

The results obtained from freeze-thaw conditioning must be evaluated against the standards set by chemical conditioning. The addition of inorganic metal salts (e.g., ferric chloride, aluminum hydroxide, ferrous sulfate, and lime) as conditioning agents has a long history of successful employment in water and wastewater treatment practice. Likewise, polymer conditioning has become increasingly popular.

The purposes of this investigation were:

1. to develop methods for direct-contact, freeze-thaw conditioning processes;

2. to use these methods to condition a variety of sludges;

3. to compare the results of direct-contact, freeze-thaw conditioning to indirect-contact, freeze-thaw conditioning and polymer conditioning.

4. to develop a model of the freeze-thaw process.

II. LITERATURE REVIEW

A review of the literature was conducted to develop a technical and historical context for the current investigation. This review addresses the following specific goals:

- to evaluate methods of evaluating conditioning effectiveness, i.e., improvements in the rate and extent of dewatering of conditioned sludges, and to determine which methods were appropriate to the current investigation;

- to research process descriptions and histories for freeze-thaw processes as background for selection of freeze-thaw methods and agents;

- to assess the impact of process and handling variables on the effectiveness of freeze-thaw conditioning in past studies as background for development of freeze-thaw techniques; and

- to present proposed mechanisms of freeze-thaw conditioning.

EVALUATING CONDITIONING EFFECTIVENESS

The parameters of interest in evaluating the effectiveness of conditioning methods and agents are the rate and the extent of sludge dewatering. For most sludges, these dewatering characteristics are dependent upon factors such as particle size distribution, floc water content, and other properties. Common measures of dewatering characteristics---specific resistance and compressibility---are calculated using equations predicated on these variables. These parameters and their derivations are introduced in this section. The physical phenomenon of blinding and its mathematical relationship to specific resistance are also presented. Finally, the relationships of particle size and other sludge particle characteristics to specific resistance are reviewed.

Specific Resistance

The specific resistance of a sludge is a measure of the relative ease (or difficulty) with which filtrate flows through the cake formed as sludge drains under an applied vacuum. The lower the specific resistance, the easier the sludge is to dewater. This parameter is defined as the resistance per unit weight of dry cake solids per unit volume of filtrate collected and is expressed in units of length per mass (m/kg).

Specific resistance is calculated from the data obtained from a laboratory procedure known as the Buchner funnel test. The test is conducted using an apparatus consisting of a Buchner funnel secured atop a graduated cylinder. The desired vacuum (pressure differential) is applied and the amount of filtrate removed from the sample over the period of filtration is recorded at intervals. The time required for the filter cake to crack is noted, and the final cake solids concentration determined on a sample of the filter cake as well.

Although the Buchner funnel procedure bears a closer resemblance to vacuum filtration than to other methods of dewatering, its accuracy in predicting vacuum filter yields is arguable[4-6]. Its usefulness in differentiating among conditioning methods and doses for a given sludge is, however, generally accepted.

For a given sludge with a specific initial solids concentration, the time required to obtain a specified volume of filtrate, or the time required for the filter cake to crack, gives a rough estimate of dewatering rate. The usefulness of this estimate is limited, however, since these data do not predict sludge behavior over a range of solids concentrations. In addition, fibrous or poorly dewatering sludges may produce a cracked cake only after an inordinately long filtration period, or not at all.

A more useful calculation obtained from the data collected in the Buchner funnel test yields specific resistance. The concept and derivation of this parameter is based upon equations fundamental to filtration theory. The basic equation is Darcy's law, which states

$$\frac{dV}{dt} = \frac{(P)}{\mu}\frac{(AK)}{L} \qquad [1]$$

where

dV/dt = rate of flow (volume of filtrate collected per unit time);

P = pressure difference

A = area

μ = viscosity

K = permeability

L = thickness.

Stated simply, the change in filtrate volume with time, dV/dt, is proportional to three variables: (1) the area of filtration, A, (2) the pressure applied across the material filtered (medium and sludge cake), P, and (3) the permeability of the medium and the cake, K. The change is inversely proportional to the viscosity, μ, and to the thickness of the cake, L.

The resistance R is defined as the inverse of the permeability. Substitution of R for 1/K in Equation 1 yields:

$$\frac{dV}{dt} = \frac{P}{\mu}\frac{A}{LR} \qquad [2]$$

where R is the combined resistance offered by the filter paper (R_m) and the cake resistance (R_c). These two resistances are sometimes considered separately [6,7]. It is argued that the initial resistance offered by the filter before the cake begins to form is significant when compared to the resistance offered by the sludge. The two resistances can be considered, however, a single factor if filter media resistance is always negligible when compared to cake resistance[5]. Significant filter resistance is usually caused by filter clogging by sludge particles, in which case the resulting increase in resistance is due to the sludge itself.

This disagreement has led to differences in the method used to acquire the data used to determine specific resistance. Gale[7] recommended ignoring the first filtrate to pass through the filter and noting volume only when the filter resistance relative to the cake resistance is negligible. Notebaert[5] recommended recording filtrate volume as soon as the first filtrate is released. In this study the protocol suggested by Notebaert's argument was used, and the corresponding derivation is presented here.

The specific resistance r is defined as the resistance per unit weight of dry cake solids. It can be expressed as:

$$r = \frac{Rv}{w} \qquad [3]$$

where

R = combined resistance per unit volume of filtrate

v = volume of cake deposited per unit filtrate volume

w = filter cake deposited per unit volume of filtrate

The solids loading term w may be determined from a material balance:

$$w = \frac{C_k C_o}{\{100(C_k - C_o)\}} \quad [4]$$

where C_o and C_k are the initial and final cake solids concentrations, respectively.

In order to introduce the specific resistance r into Equation 1, vV is substituted for AL:

$$\frac{dV}{dt} = \frac{P}{\mu} \frac{A^2}{vVR} \quad [5]$$

Substituting rw for Rv, Equation 3 becomes:

$$\frac{dV}{dt} = \frac{P}{\mu} \frac{A^2}{Vrw} \quad [6]$$

Equation 6 can then be rearranged to:

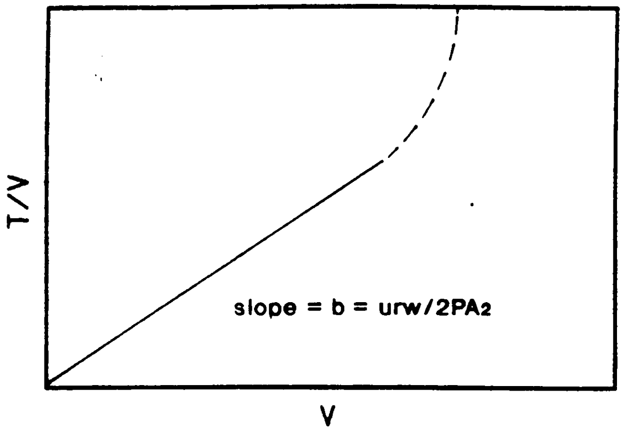
$$dt = \frac{(\mu Vrw)dV}{(PA^2)} \quad [7]$$

Assuming pressure changes during the test are negligible, Equation 7 can be integrated to obtain:

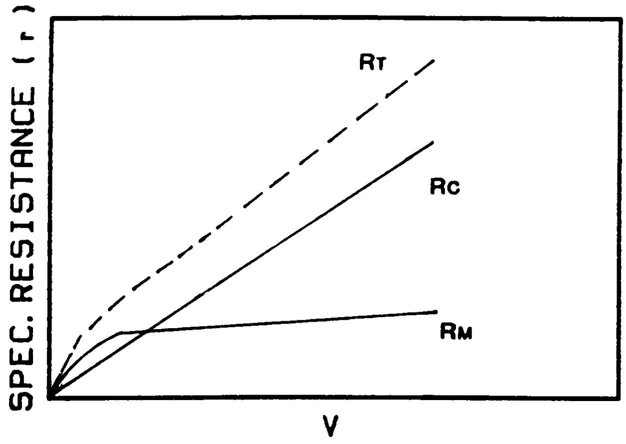
$$t = \frac{\mu rwV^2}{2PA^2} \quad [8]$$

Equation 8 can be rearranged in the form y = bx, as shown in Figure 1a:

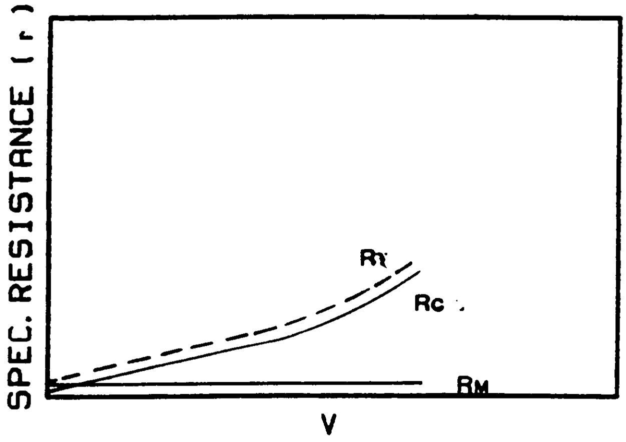
$$\frac{t}{V} = V \frac{\mu rw_2}{2PA^2} \quad [9]$$



1A. SCHEMATIC DIAGRAM OF TYPICAL BUCHNER FUNNEL FILTRATION DATA FOR SLUDGE EXHIBITING NO BLINDING PHENOMENA



1B. SCHEMATIC DIAGRAM OF r FOR A MEDIUM-BLINDED SLUDGE



1C. SCHEMATIC DIAGRAM OF r FOR A CAKE-BLINDED SLUDGE

FIGURE 1. CHARACTERISTIC DEWATERING RESPONSE FOR UNBLINDED AND BLINDED SLUDGE SAMPLES.

The slope of the line t/V vs V is:

$$b = \frac{\mu r w}{2PA^2} \qquad [10]$$

The specific resistance is then defined:

$$r = \frac{2PA^2 b}{\mu w} \qquad [11]$$

This resistance is an average value, being predicated upon an average cake solids content, a constant pressure drop across the cake, and the assumption that any filtrate squeezed from the cake itself is small in proportion to the amount flowing through it[7].

Although specific resistance is widely used as a shorthand method of describing how well a sludge will dewater, Karr and Keinath[8] noted that this test does not predict other characteristics essential to good dewatering, such as pick-up and release characteristics, shear resistance, and scrolling properties. For example, an activated sludge with a very low specific resistance may in fact be intractable, whereas a highly resistant anaerobic sludge may handle very easily.

Compressibility

The compressibility of a sludge affects its response to vacuum or pressure filtration. By measuring the specific resistance at different pressures, the coefficient of compressibility can be determined. It is defined as the slope of the line obtained when the logarithm of the resistance is plotted against pressure:

$$\log r = S_0 \log P + \text{constant} \qquad [12]$$

An incompressible material has a coefficient of compressibility of zero. Increasingly compressible materials have higher coefficients of compressibility[6].

Blinding

The equations used to develop the concept of specific resistance presuppose a straight line relationship between t/V and V. When graphed according to this relationship, actual laboratory data often produce a curve rather than a straight line. Notebaert[5] suggested that this nonlinearity occurs when the combined resistance ($R_c + R_m$) of sludges with heterogeneous particle distributions changes during the course of filtration. Medium resistance changes when small particles (equal in diameter to the medium pore diameter) lodge in the pores of the medium, resulting in blinding. The rate of media clogging decreases as the cake builds up and small particles are retained in the cake itself (Figure 1b). Cake resistance changes when small particles lodge in the pores of deeper layers of the filter cake, causing blinding of the cake itself. If these small particles are larger than the pore size of the medium, specific resistance tends to increase with time of filtration (Figure 1c). The redistribution of particles results in deformation and compression of the cake.

In order to model the resultant curvilinearity, r is redefined as r':

$$r' = \frac{r\ (V)^{x}}{A} \qquad [13]$$

Substituting, Equation 6 becomes:

$$\frac{dV}{dt} = \frac{PA}{\mu rw(V/A)^{(1+x)}} \qquad [14]$$

Integrating Equation 14 yields:

$$T = \frac{\mu rw}{(2+x)A^{(2+x)}PV^{(2+x)}} \qquad [15]$$

Taking the logarithm of both sides, Equation 15 becomes:

$$\log T = \frac{\log\ (\mu rw)}{(2+x)A^{(2+x)}P} + (2+x)\log V \qquad [16]$$

which can be plotted as a line of the form

$$\log T = \log a + (2+x)\log V \qquad [17]$$

where a is the average specific resistance.

The value of (2+x) can be used to characterize the response of a given sludge to filtration. Notebaert[5] found that sludges with x greater than or approximately equal to zero were more compressible, with coefficients of compressibility of about 1. Sludges with values of x less than zero were less compressible, with coefficients of compressibility of about 0.3 to 0.5.

Huang[9] derived a similar concept from examination of specific resistance data. He replaced the "x" in Notebaert's equation with β (the blinding coefficient), where β is related to change in cake resistance which develops as cake deposition proceeds. Equation 15 can be transformed by replacing x with β and taking the logarithm of both sides:

$$\ln t = (\beta + 2)\ln V + \ln \frac{(2\mu w)}{(\beta+2)PA} \qquad [18]$$

Blinding sludges (more compressible) have values of β greater than zero. This corresponds to a slope of $(2 + x)$ greater than 2 in Notebaert's discussion. For perfectly incompressible sludges, β equals zero. For sludges which do not resist filtration, β equals -1[6].

Karr and Keinath[8] approached the problem of blinding sludges by comparing specific resistance values obtained at different solids concentrations for a given sludge. The Blinding Index (BI) was defined to range from zero (unblinded) to 100 percent (completely blinded). It is defined as:

$$BI = 100 \frac{(r_1-r_2)}{r_2} \frac{c_2}{(c_2-c_1)} \qquad [19]$$

where r_1 and r_2 equal the specific resistance values determined at initial solids concentrations c_1 and c_2, respectively.

For an unblinded sludge, the two specific resistances would be equal, and thus BI = 0. For a completely blinded sludge, the two terms are inversely equal. Their product is equal to 1, and thus BI = 100. The validity of the relationship hinges on the dependence of the specific resistance of a blinding sludge on solids concentration. The Blinding Index is cumbersome, requiring two specific resistances at differing solids concentrations.

The Relationship of Particle Size and Other Particle Characteristics to Specific Resistance

The relationship between specific resistance and the particulate structure of the sludge cake formed upon filtration was discussed by Gale in 1967[7]. He based his derivation upon the Kozeny equation:

$$r^* = \frac{KS_o^2(1-e)}{e^3 p_p} \qquad [20]$$

where

r^* = specific resistance

K = Kozeny constant, or parameter

S_o = specific surface area of the particles

e = fractional voidage of the bed

p_p = particle density.

The specific surface area, S_o, is inversely related to the equivalent diameter of the particles in the sludge cake. As the diameter of the particles increases, S_o decreases. As can be seen from Equation 20, as S_o increases (signifying a decrease in particle size), r* increases as well.

This is, of course, based on the premise that the voidage remains the same with changes in particle size. Gale noted that, in fact, flocculated sludges often produced filter cakes of lower solids content. The lower solids content resulted in a higher voidage and thus even lower specific resistance. On the other hand, particle compression during filtration would result in lower voidage and thus higher specific resistance.

According to Equation 20, increases in particle density would result in decreases in specific resistance. Gale noted that increases in particle density would correspond to decreases in the numbers of particles per unit weight of solids. This decrease would result in a decrease in the surface area across which filtrate must flow. An increase in the weight of aggregates of particles, i.e., floc density, might not correspond, however, to an increase in particle density. Aggregates might grow in size without increasing on a weight per mL basis. Thus, it is not surprising that Knocke and Wakeland[10] found that specific resistance did not vary consistently with floc density.

Gale speculated that the presence of fines in a sludge increased specific resistance by increasing the specific surface area and reducing cake voidage. Research by others suggested that dilution promoted release of fines. Roberts and Olsson[11] discovered that dilution of low solids activated sludge resulted in increased capillary suction times (CST's). Ademiliuyi[12] found that specific resistance increased with dilution of domestic sludge to about 2 percent and then decreased, while resistance of piggery and water treatment sludges decreased with dilution to 4 and 3 percent, respectively, and then increased.

Roberts and Olsson[11] found that the polymer dose for low solids activated sludge depended upon the concentration of colloidal particles. Similarly, Knocke and Wakeland[10], finding that changes in specific resistance with specific surface area were slight for poorly dewatering biological sludges, suggested that conditioning dose for these sludges was dependent upon the concentration of biopolymer in the sludge.

The results of research reported by Karr and Keinath[8] showed that changes in specific resistance with mixing, storage time, pH and conditioning could be attributed in large part to corresponding changes in particle size distribution. In these experiments, samples of raw, activated, and anaerobically digested sludges were reconstituted to approximately equal fractions of different size ranges of particles. Buchner funnel tests were then conducted on the samples.

In general, Karr and Keinath found specific resistance values were closely related to particle size distribution. The relative size of the supracolloid fraction (composed of particles of diameters between 1 and 100 microns) determined how well a sludge would dewater. The lower this fraction, the lower the characteristic sludge specific resistance. Exceptions were attributed to different distributions within particle size fractions, changes due to storage durng testing, measurement errors, and other factors.

These results point out a main defect with utilizing Equation 20 for characterizing the filtration response of heterogeneous sludges: that is, that the effective diameter, or other measures of mean particle or floc size, can represent distributions of widely varying shapes and physico-chemical characteristics. Representative measures of floc or particle size (such as mean diameter) may not suffice in predicting changes in specific resistance.

FREEZE-THAW PROCESSES

There are three main types of freeze-thaw processes used to condition sludges: natural, indirect-contact, and direct-contact. Natural processes depend upon extended periods of cold weather to freeze sludge exposed in beds or lagoons. Indirect-contact processes rely upon contact between sludge and a refrigerant across a heat transfer surface. Direct-contact processes promote unmediated contact between sludge and refrigerant. Direct-contact processes include those in which water freezes in intimate contact with an evaporating refrigerant as well as those in which solid gas hydrates are formed.

Direct-contact processes are limited by certain authors[13,14] to those in which freezing occurs as the result of water evaporation at reduced pressures. These sources may refer to those processes using an immiscible refrigerant as "indirect" freezing. In the current study, processes which involve intimate contact between sludge and any refrigerant, water vapor or secondary refrigerant, are classed as direct-contact processes. Indirect-contact processes are those which do not involve intimate contact between sludge and freezing agent.

Natural Freeze-Thaw Conditioning

In climates where freezing temperatures predominate for prolonged periods, sludges exposed in beds or lagoons freeze slowly and completely. Upon thawing, these sludges show much improved dewatering characteristics.

Canfield and Sutphin[15] described the results of natural freeze-thaw conditioning of alum sludge from a high-rate direct filtration plant in Onondaga County, New York. The sludge was lagooned at 18-inch depths, and the supernatant drained off regularly. After freezing and thawing, the solids content of the decanted sludge increased from 8 to 25 percent. The product texture varied from powdery to granular.

Bishop and Fulton[16] reported the results of natural freeze-thaw conditioning of alum sludge from a treatment plant near Rochester, New York. Solids content increased from approximately 6 percent for unfrozen lagooned sludges to 17 percent for frozen and thawed sludges. The product sludge dewatered quickly when placed on a sand filter.

In a study reported by Penman and Van Es[17], anaerobic sludge in

Winnipeg, Manitoba, was settled throughout summer and fall in lagoons to depths of 2 feet. The supernatant was drained off regularly. During winter, sludge was pumped into the lagoons to depths of 8 feet. Throughout the following spring, summer and fall, the thawed supernatant was returned to the plant and the beds allowed to lie dormant. They were allowed to freeze again the following winter. Subsequent thawing produced a sludge with a solids concentration of about 20 percent, suitable for land application.

Tilsworth et al.[18] reported the results of natural freeze-thaw conditioning of extended aeration sludge in College, Alaska, where freezing conditions prevail three to four months a year. Sludge placed at 6-inch depths froze in about 30 to 50 days. Once the sludge thawed, solids content increased by 225 to 920 percent. The product was granular, had little odor, and was easy to transport and place.

In experiments in Ely, Minnesota, and Cincinnati, Ohio, Farrell et al.[19] found that complete freezing of alum wastewater sludge increased initial dry solids content and improved specific resistance (from 2.1 to 9.5 percent, and from 104 to 3.43 x 10^{11} m/kg).

Reed et al.[20] developed a sludge-specific equation for predicting the total depth of sludge which could be conditioned by exposure to subfreezing temperatures, based on application of sludge in 8-cm layers. The method was verified by field applications in Hanover, New Hampshire, and from comparison with historical data from Duluth, Minnesota.

Indirect-Contact, Freeze-Thaw Conditioning

Indirect-contact, freeze-thaw conditioning processes rely on an intermediate surface to transfer heat between the sludge to be conditioned and a circulating refrigerant. The refrigerant either has a large heat capacity, enabling it to absorb heat from the sludge at high rates with no phase change (e.g., glycol or brine) or it vaporizes during the process, absorbing the heat of vaporization from the sludge.

Full- and pilot-scale indirect-contact processes for conditioning alum water sludges at two plants in England (at Stocks and at Fishmoor) were the subject of a number of articles in the 1960's[21-23]. The process at the Stocks water treatment facility consisted of slowly freezing sludge at 15^{0}F in 150-gallon tanks. Compressed ammonia was pumped through 480 3/4-inch-diameter vertical pipes immersed in the sludge. The liquid ammonia flowing through the pipes vaporized as it was warmed by the sludge. The heat required to warm and vaporize the ammonia was drawn from the sludge, causing the sludge to freeze. In order to make the process economical, sludge and ammonia were cooled prior to the freezing step by heat exchange with the frozen product. Latent heat recovery minimized condensing requirements and also thawed the frozen sludge. The operation was performed in batch, with approximately 90 minutes required for freezing and 45 minutes for thawing. The plant at Stocks processed 33,000 gpd of sludge. Prethickened sludge drained to 60 to 70 percent solids after freezing.

Although the process resulted in a more easily handled product and a large increase in solids concentration, the system suffered certain drawbacks. The main problem was the high cost of construction and maintenance. Also, the repeated cycles of freezing and thawing placed great strain on the tanks, which required frequent repair or replacement.

Indirect freezing of alum water treatment sludge was investigated in the laboratory for the Milwaukee Sewerage Commission[24,25]. In a bench-scale study, alum sludge was poured into tall, thin rectangular pans, to depths of 1/2 to 2 inches. Contact with circulating glycol or brine at operating temperatures of between 5 and 25^{0}F froze the sludge in batch operations lasting from 20 to 60 minutes. Vacuum filtration produced a sludge cake of 67 to 75 percent solids from prethickened sludge. The same sludges without treatment produced sludge cakes of 18 to 21 percent solids. The encouraging results obtained in the laboratory led to a feasibility study for a pilot plant for the Milwaukee Sewerage Commission[24]. Activated sludge was to be frozen at 1/2-inch depths in pans on a conveyer, in contact with chilled brine for 100 minutes. However, cost analyses showed that the estimated expense of the system was too great, and the pilot study was never implemented.

Direct-Contact, Freeze-Thaw Conditioning

Much of the research and development of direct-contact, freeze-thaw technology was conducted in the 1950's and 1960's under the sponsorship of the Office of Saline Water Research. Brian[13] and Barduhn[26] published excellent reviews on the status of this technology in 1968 and 1975, respectively. General process descriptions were presented by Fraser and Gibson[27], Fraser and Johnson[28], and Weiss[29]. The flow of information declined sharply upon the demise of the Office of Saline Water Research, which was abolished in 1974 after several years of federal budget cuts[26].

Research directed towards application of direct-contact, freeze-thaw processes to wastewater treatment and sludge conditioning has been limited. The AVCO Corporation[26,28] developed a commercial direct-contact process utilizing Freon 114 to recover recyclabe constituents from plating wastewater. Kahn and other researchers at Virginia Polytechic Institute and State University[30-32] conducted experiments to investigate the feasibility of conditioning wastewater sludges primarily with butane (some experiments were conducted with Freon 114 as well) in direct-contact processes. Molayem and Bardaki[53] used Freon 11 in a gas hydrate process to dewater wastewater sludges.

Direct-contact, freeze-thaw processes were developed as comparatively efficient alternatives to evaporative techniques of desalination. The advantages of direct-contact freeze-thaw processes include:

- absence of a metallic heat transfer surface;
- minimal scaling, corrosion, and fouling; and

- minimal pretreatment requirements.

Energy savings are due mainly to the absence of a heat transfer surface. Although the latent heat of evaporation is about seven times the latent heat of fusion, this potential energy savings is compensated for by the fact that the freezing point depression caused by dissolved salts in seawater (and dissolved solids in wastewater) is about seven times the boiling point elevation[28].

Because of practical limitations of equipment efficiency and control, however, processes usually operate at temperature differences greater than the theoretical minima set by freezing point depression (for freezing) or boiling point elevation (for distillation)[34]. Energy requirements for freezing processes are relatively low when compared to evaporative processes because of the small temperature differentials which drive the reaction between feed and refrigerant. For each degree that the minima are exceeded, distillation processes suffer a sevenfold loss in efficiency compared to freezing processes. The closeness of the temperature differential used in freezing processes to theoretical temperature differences is a direct result of the absence of a heat transfer surface[26].

Because the processes are carried out at low temperatures, scaling and corrosion are rare. The lack of a heat transfer surface results in fouling being confined to reactor walls. In turn, the absence of the potential for scaling, corrosion, and fouling precludes the need for pretreatment.

These advantages are offset by two disadvantages. First, refrigerants are expensive and removal to acceptable levels can be difficult to achieve. Second, scale-up of desalination processes is limited by the availability of efficient compression equipment required to recover spent refrigerant[13].

There are three types of direct-contact, freeze-thaw processes:

- vacuum freezing, vapor compression processes;
- secondary refrigerant processes; and
- gas hydrate processes.

In the discussion that follows, feed and solution are used as general terms to include seawater, wastewater, and sludge.

Vacuum Flash, Vapor Compression Processes - In vacuum flash, vapor compression (VFVC) processes, precooled solution is fed into a vacuum chamber where conditions are maintained slightly below the triple point of water. At this point, water evaporates and forms ice simultaneously. The heat of vaporization is about seven times the heat of fusion; thus, under ideal conditions, seven pounds of ice are formed for every pound of vapor released.

The process has certain serious disadvantages. It requires large mechanical compressors to condense the water vapor produced, and a great deal of space. High volumes of low pressure water vapor must be handled, with a pound of water vapor occupying 4600 cubic feet at the operating pressure. To overcome some of these difficulties, a variation of this process---the vacuum freezing ejector process---was developed. In it, ejectors replace some of the compressors. The process is complex and both the original and the variation suffer from large size and low efficiency[28].

Several commercial VFVC desalination pilot plants were constructed and installed in the United States and Israel during the 1960's, by Colt Industries and the Carrier Corporation. These plants produced up to 240,000 gallons of fresh water from sea water daily. By 1975, however, none of the U.S. plants were operating due to various process and mechanical deficiences[13,26,35].

Application of the VFVC process to treatment of paper pulp mill effluent for dissolved solids and biochemical oxygen demand (BOD) reduction was suggested by Johnson in 1969[35]. However, a review of the literature uncovered no reports of utilization of this process either for treating wastewater or conditioning sludge.

Secondary Refrigerant Processes - Secondary refrigerant freezing processes rely on intimate contact between the solution to be treated---the "primary" solution---and an agent with a low boiling point at ambient or near ambient pressure---the "secondary" refrigerant, introduced specifically for the purpose of heat transfer. Initially developed as desalination technology, secondary refrigerant processes have been applied in commercial ventures for wastewater recovery. In addition, several research studies on the effectiveness of secondary refrigerant processes have been documented.

Process Description - In secondary refrigerant freezing, precooled solution is fed into a reactor where it is intimately mixed with an immiscible refrigerant. Conditions in the reactor are maintained such that the refrigerant boils at a temperature lower than the freezing point of water. As the refrigerant evaporates, it absorbs the heat necessary for vaporization from the solution, freezing the water.

A typical process diagram for secondary refrigerant desalination is presented in Figure 2[27]. The process comprises four unit operations:

- heat exchange,
- freezing/crystallization,
- washing, and
- melting/condensing.

These are discussed in further detail below.

Heat exchange - Feed is precooled prior to freezing by contact with the ice slurry and waste concentrate produced during desalination. Precooling avoids the use of excessive amounts of refrigerant to lower temperature of feed to process freezing levels.

Freezing/Crystallization - Precooled feed and liquid

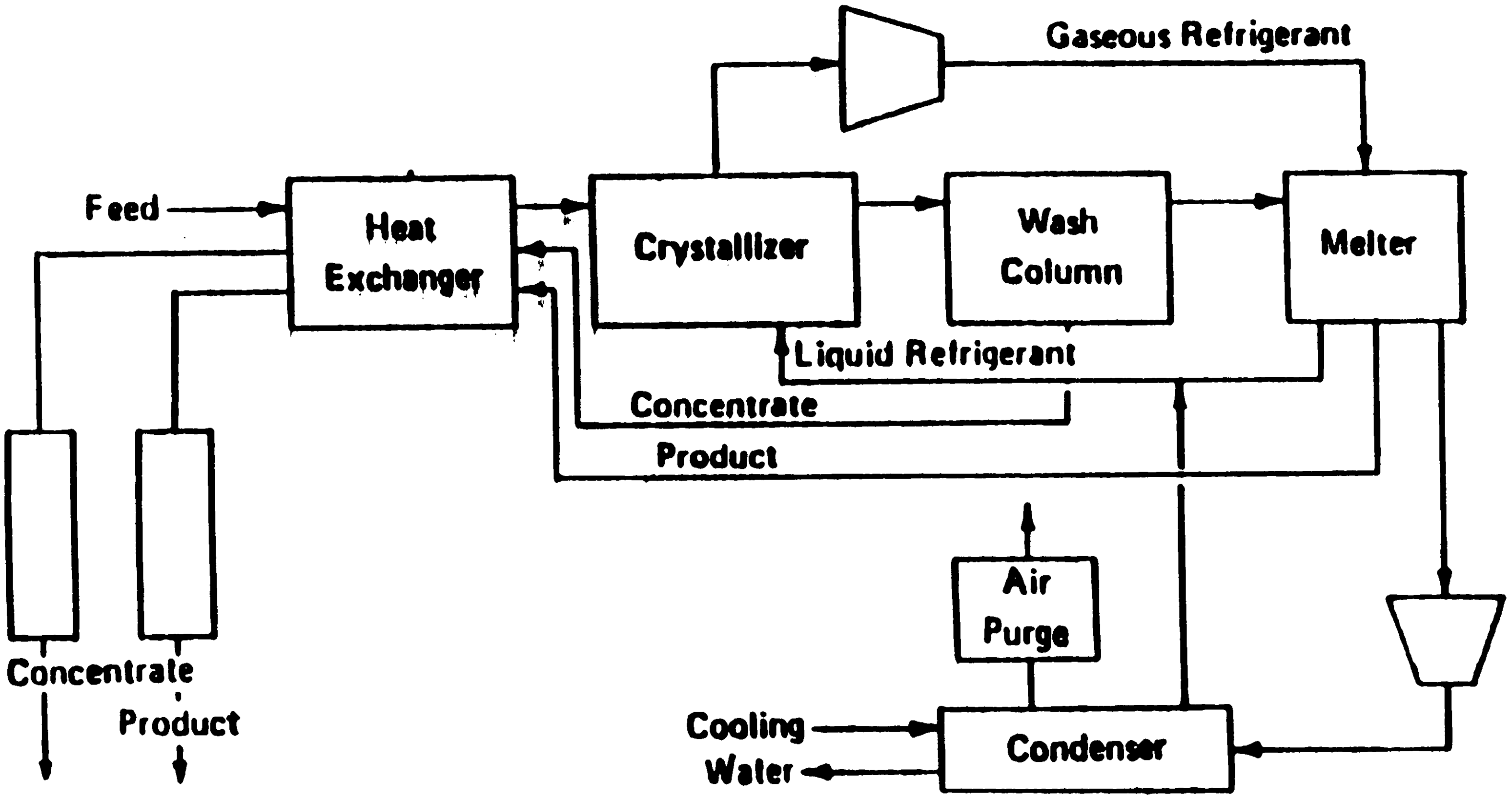


FIGURE 2. TYPICAL PROCESS FLOW SCHEMATIC FOR SECONDARY REFRIGERANT DESALINATION (FROM FRASER. JH. AND GIBSON. WE. (27))

refrigerant are pumped into a reactor (crystallizer) under pressure conditions such that the evaporating temperature of the refrigerant is lower than the freezing temperature of the feed[13]. The refrigerant evaporates when it comes into contact with the feed, lowering the water temperature below its freezing point. Pure ice crystals (approximately 200 microns in diameter) form, excluding all other material, including solute and particles[26]. The reactor contents may be mixed by the turbulence created by evaporating refrigerant; additional agitation may also be provided.

Washing - The slurry from the reactor containing a mixture of pure ice crystals and concentrate is washed, removing the concentrate from the ice.

Melting/Condensing - Spent refrigerant vapors undergo two compression stages[13]. Primary compression raises the temperature of the vaporized refrigerant to the melting point of ice. The vapor is pumped to the melter/condenser, where it condenses in contact with the product slurry. However, not all of the vapor can be condensed on the product, due to incomplete heat exchange, heat leaks into the system, and the work input of compressors, pumps, and agitators. Some of the vapor is thus compressed to a higher pressure to be condensed at a higher temperature with cooling water.

In adapting the secondary refrigerant process for sludge conditioning, the washing step is usually omitted as the object of conditioning is not to produce pure water, nor to recover concentrate, but to take advantage of the irreversible changes which occur during freezing.

Thermodynamics and Kinetics of the Process - Discussions of the thermodynamic principles involved in freezing processes have been presented by Dodge and Eshaya[36], Gilliland[37], and Wiegandt[38].

The minimum amount of theoretical reversible work necessary to separate fresh water from seawater (or other solution) depends upon the temperature of the process and the percent conversion attained[36]. For example, the minimum amount of work required to separate 1000 gallons of fresh water from 2000 gallons of a 3.5 percent saline solution at 25°C, (a 50 percent conversion or recovery rate), is variously calculated to be from 2.89 kW-hr to 4.15 kW-hr[36,37,39]. In analyzing a continuous system in which the product water is in equilibrium with the final concentrate alone, the minimum work rises to 5.8 kW-hr/1000 gallons.

Although the work of separation is minimized at low recovery rates, the work of pumping the feed through the process approaches infinity as the yield of fresh water approaches zero. For example, to recover 1000 gallons of fresh water at a 50 percent recovery rate requires pumping 2000 gallons of solution. To recover 1000 gallons of freshwater at a 0.5 percent recovery rate requires pumping 200,000 gallons of solution. At about a 50 percent recovery rate, the pumping work becomes minimal with respect to the work required to separate the fresh water from the solution, and this is the reason the recovery rate is typically selected as 50 percent.

Although the amount of heat required to freeze and thaw an equal amount of seawater are approximately the same, additional energy is required for freezing because the freezing point of seawater is depressed by salts below the melting point of the pure ice formed. The minimum reversible work required by freezing processes depends upon the freezing point depression, the process and ambient temperatures, and the latent heat of fusion. It can be calculated from the following equation:

$$W = Q \frac{(T_1 - T_2)}{T_2} \frac{T_o}{T_1} \qquad [21]$$

where

Q = heat of fusion

T_1,T_2 = freezing temperature of pure water and seawater, respectively

T_o = ambient temperature.

Work is required to pump the heat of fusion from the depressed freezing temperature of the solution to the freezing point of water and to discharge the heat from the work of pumping to ambient temperature. The amount of minimum theoretical work required for 50 percent recovery from a 3.5-percent saline solution is approximately 6.3 kW-hr/1000 gallons of fresh water produced. However, irreversible effects in actual processes raise the theoretical work requirement to 40 kW-hr/1000 gallons, or more. These effects include pressure drops from fluid friction and from throttling, heat leaks into the system, and finite temperature and concentration gradients, among others[36].

Optimum temperature and pressure conditions for secondary refrigerant processes depend upon the vapor saturation curve of the refrigerant and the liquid-solid curve of the solution to be frozen. A pressure is selected at which the temperature of the point on the vapor saturation curve is below the freezing temperature of the solution. The difference between these two temperatures is the driving force of the reaction.

The heat of vaporization of butane (165 Btu/lb) is slightly greater than the heat of fusion of water (144 Btu/lb). Theoretically, 1.15 lb of ice should form when water is contacted with 1 lb of butane. In practice, refrigerant requirements are increased by insufficient precooling of feed, incomplete mixing, and other factors.

Process History - Several types of refrigerants have been used in secondary refrigerant freeze-thaw processes, including butane and certain halogenated halocarbons. The attractiveness of butane as a secondary refrigerant is that its boiling point at ambient pressure is just below the freezing point of water. It also has a low solubility in water, varying from 70 mg/L at 25^{0} to 150 mg/L at 0^{o}C. At the temperatures maintained in secondary refrigerant processes, it does not form gas or liquid hydrates. Finally, butane is relatively inexpensive when compared to other refrigerants.

The major disadvantage of butane processes is poor refrigerant recovery. Although relatively insoluble in water, liquid butane tends to emulsify in impure solutions. Carryover of liquid butane in slurry processes has been reported to vary from 1 to 10 g/L, and it is estimated that freeze-thaw products may contain emulsified butane concentrations up to 10 times the concentration of dissolved butane in freeze-thaw products[26]. Loss of butane associated with the product is not only expensive, but may prevent reuse or complicate disposal of the contaminated product.

Various separation techniques which have been used to remove butane from freeze-thaw products include stripping under vacuum and at atmospheric pressure; stripping using vacuum sprays and packed columns[26] and charcoal filtration following vacuum stripping[13]. Application of any such separation method obviously increases the overall cost of the process.

A secondary disadvantage of butane is its potential for explosion at ambient temperature in the presence of oxygen. This explosion hazard requires special consideration in the design of the mechanical systems used for secondary refrigerant freezing and also increases process cost.

Halogenated derivatives of hydrocarbons (which are also used extensively in gas hydrate processes) are more familiar as Freons and Arctons, the trade names under which they are manufactured. (An explanation of numerical designations based on formula is included in Appendix A.) They are generally nonflammable and nontoxic, with low solubilities in water. Their densities, which are considerably greater than water (e.g., Freon 114 has a specific gravity of 1.54) make them easily separable.

As a group, the halogenated hydrocarbons have several disadvantages. Their main drawback is that they are relatively expensive in comparison with other secondary refrigerants. Also, in gaseous form, they are heavier than air and can create a suffocating environment if large amounts are released in confined spaces without proper ventilation. Certain members of this group have been the subject of controversy in the past decade, regarding potentially destructive impacts on the atmospheric ozone layer.

Secondary refrigerant desalination projects have been developed and installed worldwide. Various desalination projects utilizing secondary refrigerant processes were undertaken by commercial concerns in the United States in the 1960's[13]. Among them, Blaw-Knox Co. and Struthers Scientific and International Corporation installed and operated 55,000 gpd and 15,000 gpd desalination plants, respectively.

The Japanese desalination industry has a long history of research and development in secondary refrigerant processes as evidenced by the large number of patents issued since the 1950's. Unfortunately, little of the research associated with these efforts has been reported in the English scientific literature. Articles by Nagashima and Maeda[40] in 1979 and Nagashima et al.[41] in 1981 reported on the development of pilot- and full-scale direct contact desalination plants using horizontal reactors and butane as the secondary refrigerant in a standard process. The pilot plant treated 45 m^3/day (12,000 gpd) seawater and the full-scale plant had a capacity of 1000 m^3/day (264,000 gpd).

The British also have investigated the potential of butane processes for desalination. In his report on the status of desalination technology, Barduhn[26] presented brief descriptions of two bench-scale processes developed in England. The first, developed and tested by the British Atomic Energy Authority at Harwell in the years 1966 to 1972, produced as much as 200 lb ice/hr/ft^3. The second, operated between 1965 and 1970, by the British firm Simon Engineering, used a shell-and-draft tube reactor to produce ice at the rate of 150 lb ice/hr/ft^3.

Sludge Conditioning - Interest in secondary refrigerant processes as alternatives to conventional methods of wastewater treatment and sludge conditioning followed their development as desalination technology, with most references appearing in the 1970's. Research conducted by Kahn on direct freeze-thaw conditioning of wastewater sludges using butane was reported in several sources in the 1970's[30-32]. Experiments were conducted under both batch and continuous operating conditions. Batch experiments took place in a plexiglass reactor, with precooled butane (temperature = $-1.45^{o}C$) sparged into 1500 mL of sludge at a flowrate of 2.7×10^{-5} cfs (46 mL/min) under a 3 cm (1.2 in) Hg vacuum. Continuous experiments took place in a 6-inch-diameter cylindrical reactor, with a sludge depth of 6 to 12 inches. Sludge and butane were precooled in a heat exchange system through which chilled saline solution was circulated. Sludge and butane were fed to the reactor at rates of 3 to 5 mL/min and 5 to 7 mL/min, respectively, under a vacuum of 7 cm (2.8 in) Hg. The greater vacuum was necessary to ensure proper conditions for butane vaporization throughout the reactor. Butane vapors were collected and condensed by indirect contact with the product slurry. Two compressors in series achieved 70 to 80 percent butane recovery.

Sludges tested included waste activated sludges from one conventional and two extended aeration wastewater treatment plants. Selected results are presented in Table 1. Batch experiments reduced the specific resistance of the waste activated sludge from 4.7 to 1.8 $\times 10^{14}$ m/kg at a detention time of 60 minutes, and increased final solids concentration from gravity drainage from 18 percent for the unconditioned sludge to 77 percent for the conditioned sludge. It is interesting to note that substantial improvements in dewatering characteristics were achieved only at contact times of 40 minutes or more, when freezing was complete. Also, the resulting treated samples still indicated a poor dewatering sludge as evidenced by

TABLE 1

SELECTED RESULTS OF DIRECT-CONTACT, FREEZE-THAW CONDITIONING OF WASTE ACTIVATED SLUDGES WITH BUTANE[30]

BATCH CONDITIONING

Total Butane Dose, mL/L	Contact Time, min.	Specific Resistance, x 10^{11} m/kg	% Reduction in Specific Resistance
0	0	4,700	-
310	10	4,000	15
610	20	4,400	6
1,230	40	2,000	57
1,840	60	1,800	62

CONTINUOUS CONDITIONING

Total Butane Dose, mL/L	Contact Time, hr.	Specific Resistance, x 10^{11} m/kg	% Reduction in Specific Resistance
0	0	850	-
1,500	6	220	74
1,500	12	200	76
1,500	24	180	79
1,500	36	100	88

specific resistance values in excess of 1 x 10^{14} m/kg.

The continuous process resulted in a decrease in specific resistance for one of the extended aeration sludges from 8.5 to 2.2 x 10^{13} m/kg, with an increase in final solids concentration from one percent to 20 percent, after six hours contact time. Further improvements in specific resistance values and final solids concentration were noted as detention times were increased up to 36 hours.

The Crystallex process, developed and promoted extensively by AVCO Corporation in the early 1970's, was touted as a means of concentrating recoverable constituents in wastewater as well as desalinating seawater. The Crystallex process utilized Freon 114 as the refrigerant. In the process initially described by Fraser and Johnson[28], liquid Freon 114 and feed were introduced simultaneously as a spray over a mechanically agitated pool contained in a horizontal reactor. (The process was later modified such that the refrigerant was sparged into the pool from the floor of the reactor.) The ice slurry in the reactor was maintained in a fluid state by recirculating concentrate[26,42].

Slurry, concentrate, and any remaining liquid refrigerant were separated in a hydrocyclone. The slurry was then washed in a pressurized counter-current wash column, from whence it flowed to a shell-and-tube melter-condenser. Freon 114 was condensed along the outside of the melter-condenser tube. A refrigerated cold trap was used to separate non-condensable gases from the spent refrigerant after condensation. Vacuum stripping was used to remove traces of refrigerant from the product. Additional stripping, if required, was accomplished at atmospheric pressure[26,42,43].

The Crystallex process was used, in addition to desalinating seawater, in projects involving materials recovery from metal plating baths and concentration of pulp and paper wastes. Preliminary results from the treatment of a synthetic wastewater containing nickel, cadmium, chromium, and zinc, in a 2500-gpd pilot plant, showed that the process could reduce metal concentration in recovered water to less than 0.5 mg/L[26,28].

Kahn[30] also experimented with using Freon 114 to condition sludges; results were deemed unsatisfactory due to poor settling and dewatering characteristics of the conditioned sludge. Katz and Mason[34] and researchers working for the Sewerage Commission of Milwaukee[24] reported poor results from their attempts to condition sludge with liquid nitrogen, methyl chloride, butane, isobutane, and freon (type unspecified).

Gas Hydrate Processes - Extensive research was conducted in the 1960's on the use of gas hydrates in direct-contact freeze-thaw desalination processes. Basic studies were undertaken by Barduhn and coworkers at Syracuse University for the Office of Saline Water (OSW) of the United States Department of the Interior[44-53]. Their purpose was to isolate hydrate-forming agents that could be employed in economically competitive desalination processes; their efforts resulted in the development of several pilot plants. As for other freezing processes, however, research came to a halt and pilot plants disappeared when the OSW was abolished in 1974[26].

Similar in concept to secondary refrigerant processes, hydrate processes appear to have potential for use in wastewater treatment and, specifically, in sludge conditioning. The technology is virtually identical. Yet scant research has been conducted in this area. Research on utilization of gas hydrate processes for sludge conditioning has been limited; only one study by Molayem and Bardaki[33] could be found via traditional literature review methods.

Gas hydrates are nonstoichiometric compounds of gas and water characterized by a clathrate or cage structure. Molecules of gas or gas mixtures known as "guests" inhabit a "host" crystalline lattice of pure water[54]. The crystalline structure is maintained by hydrogen bonding between water molecules and by Van der Waals attraction between host and guest[55]. The physical interactions between the host and guest are relatively weak. Once the hydrate is formed, however, the molecules of gas are trapped and cannot escape until the host lattice breaks down[54].

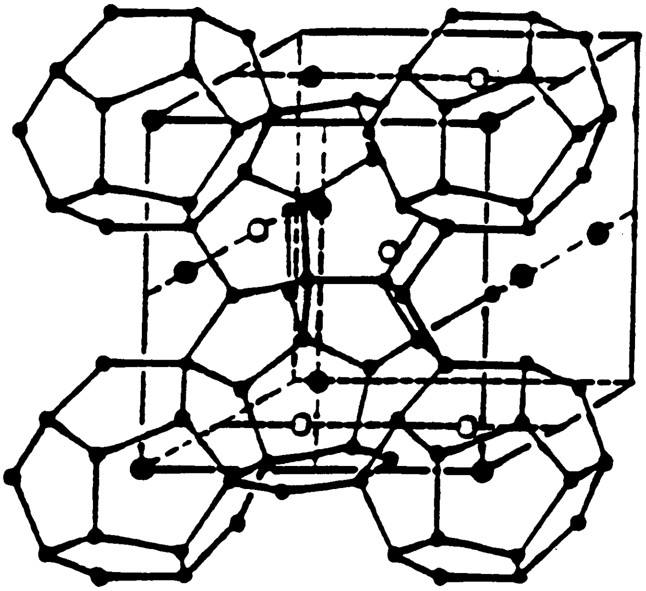
In desalination hydrate processes, salt-free hydrate crystals are induced to form from seawater, then separated and decomposed to form pure water and hydrating agent. The hydrating agent is then stripped from the product water.

Hydrate Structure - The composition of gas hydrates has been studied since the early 1800's. According to Cady[55], the models generally accepted today were elucidated in the 1950's by

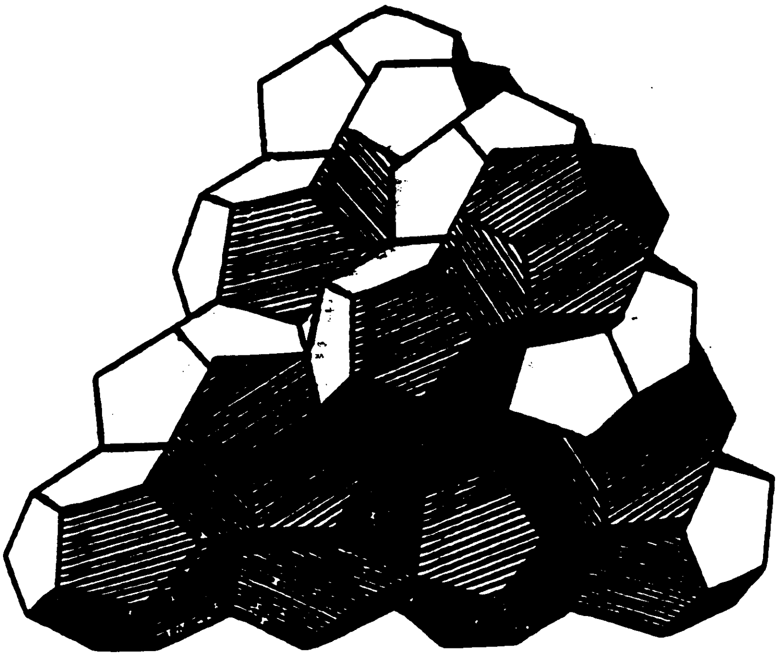
M. von Stackelberg, W. F. Claussen, and L. Pauling and R. E. Marsh.

There are two structural types of gas hydrates (denoted as Type I and Type II) consisting of 46 and 136 water molecules, respectively. The Type I structure (Figure 3a) consists of two pentagonal-dodecahedral cavities and six tetrakaidecahedral cavities, with radii of 0.29 and 0.46 nanometers (nm), respectively. Corners of the cavities are formed by hydrogen bonding of one corner oxygen atom to an outside oxygen atom and three other corner atoms[54]. A Type I hydrate (composed of 46 water molecules), can theoretically encompass eight molecules of a hydrate-forming agent "X" with diameter less than or equal to 0.58 nm. Thus, its theoretical composition can be expressed as $X_8(H_2O)_{46}$, or $X(H_2O)_{7.6}$. Experimental data show that molecules filling the small cavities rarely exceed 0.5 nm in diameter, whereas the large cavities are filled by molecules with diameters between 0.5 and 0.56 nm[55].

The Type II structure (Figure 3b) consists of sixteen pentagonal-dodecahedral cavities and eight hexkaidecahedral cavities, with radii of 0.24 and 0.345 nm, respectively. The small cavities are identical to the small cavities in the Type I structure. The larger cavities accommodate molecules of 0.56 to 0.66 nm diameter. If all twenty-four cavities of the 136-water-molecule framework are occupied, the composition of the hydrate is $X_{24}(H_2O)_{136}$, or $X(H_2O)_{5.66}$. If only the larger cavities are occupied, the composition is $X_8(H_2O)_{136}$, or $X(H_2O)_{17}$.



TYPE I HYDRATE



TYPE II HYDRATE

FIGURE 3. TYPE I AND TYPE II GAS HYDRATE STRUCTURES
(FROM BERECZ. E. AND BALLA-ACHS. M. (54))

Experimental data on hydration numbers (the number of water molecules per gas molecule) for both Type I and Type II structures show considerable variation from these ideal compositions[56]. In fact, it is normal for approximately ten to twenty percent of the cavities to be unoccupied, thereby raising the water-to-hydrating agent molecular ratio[54]. The fractional occupancy of a hydrate is also affected by temperature, pressure, and the size of the guest molecule.

The bond angles and bond distances between water molecules in both Type I and Type II hydrate structures are similar to those between water molecules in liquid water. The hydrogen bonds are approximately one percent longer, and the bond angles differ from tetrahedral ice angles by 3.7 degrees in Type I, and 3.0 degrees in Type II[57].

Approximately thirty-five gases form hydrates with Type I structure; there are about sixty-five gases which form Type II structure hydrates[57]. Although there is a wide diversity in the gases which form hydrates, they share certain common characteristics. The shape and size of the molecules conform to the cavities in the hydrate framework. The compounds are also typically homopolar, with low solubility and high volatility. They experience moderate Van der Waals forces[54].

Thermodyamics and Kinetics of the Process - The initial conditions of hydrate formation (which occurs only if a hydrating agent is present) are determined by the nature of the hydrating gas, the state of the water, the pressure, and the temperature. These conditions are best described by heterogeneous phase plots of pressure vs. temperature, such as the generalized phase diagram from Berecz[54] shown in Figure 4. The curves depicted are:

I - the vapor pressure curve of the hydrating agent saturated with water;
II - the vapor pressure curve of the hydrate;
III - the melting point curve of the hydrate; and
IV - the depression of the freezing point of water due to solubilization of the hydrating agent in water.

The hydrating gas exists in hydrate form in the regions to the upper left of curve II and left of curve III.

Each gas hydrate is characterized by a quadruple point; that is, a temperature and pressure at which ice, gas hydrate, liquid (or solid) hydrating agent, and gaseous hydrating agent are in equilibrium. This temperature and pressure are known as the critical or decomposition values for the hydrate. This point ($p_{k,1}$) is also the pressure and temperature at which the vapor pressure of the hydrate and the hydrating agent are equal. If the hydrate is partially occupied, this point will occur at lower temperatures and pressures[54].

According to Davidson[57], the lattice stability of the hydrate

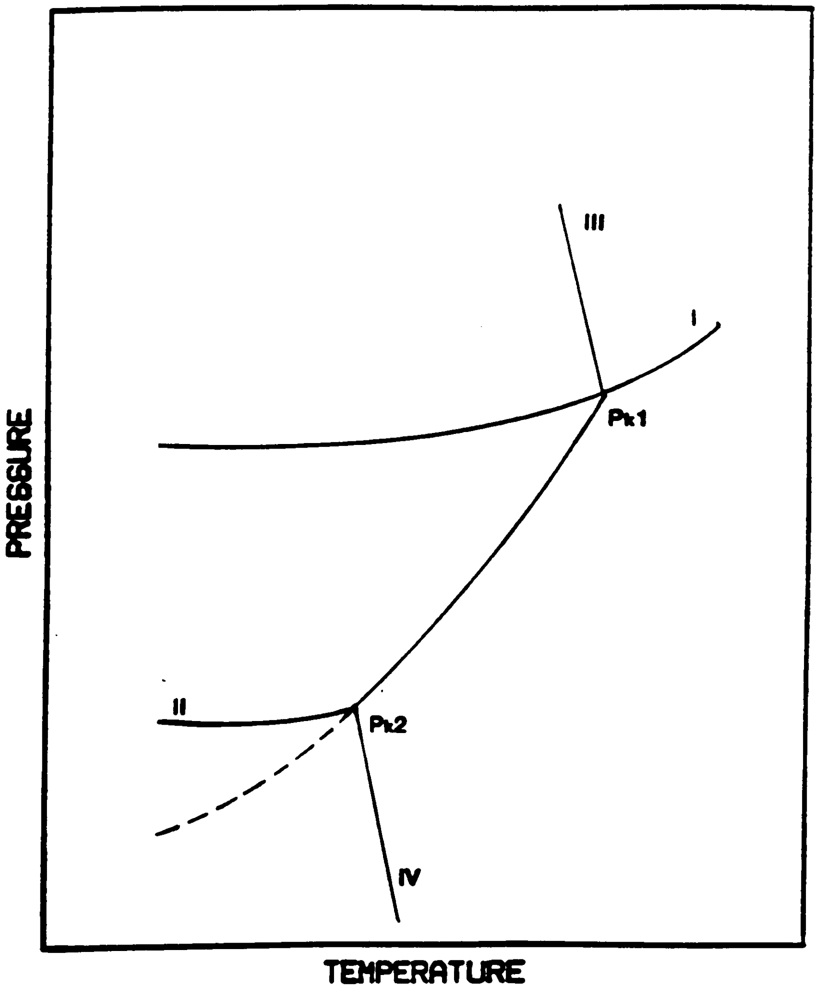


FIGURE 4. GENERALIZED GAS HYDRATE PHASE DIAGRAM
(FROM BERECZ (54))

structure depends upon the degree of cavity occupancy. Since the relative locations of guest and host molecules are known, the fractional occupancy of the hydrate structure can be modeled using a molecularly based, statistical theory of ideal localized adsorption[58]. Cady[55,56] has modeled the fractional occupancy of Type I hydrates using a Langmuir-type adsorption isotherm equation. Longer range interactions, asymmetry in gas-water interactions, and restrictions of rotation and vibration of gas molecules in hydrate cavities also must be considered, but are not usually specifically addressed in simplified models.

John et al.[59] addressed second neighbor effects and smoothing of cavities due to asphericity of guest molecules. According to John and his coworkers, stability depends upon the strength of the physical interaction between host and guest. Thus, it follows that the stability of a hydrate is related to the molecular size of the hydrating agent, as attractive forces increase with increasing size. The relationship between stability and size is proportional[54].

The stability of a hydrate also depends upon the location of its vapor pressure curve. The higher the temperature at which the vapor pressure of the hydrate reaches 10.13 x 10^5Pa (145 psia), or conversely, the lower the dissociation pressure at 0^oC, the greater the hydrate stability[54].

The thermal dissociation of hydrates is a four-step process[54]. When the temperature drops sufficiently, the host lattice begins to sublimate. As it does, its clathrate structure starts to disintegrate. Guest molecules diffuse through the collapsing structure, and finally desorb from its surface.

The rate of formation of a hydrate is difficult to model as the system is complex, having two components and four phases[54]. It is affected by nucleation rates, crystal growth rates, heat transfer from the crystal to the aqueous liquid (or, in some cases, the vaporizing hydrating agent), and mass transfer of salt or other impurities away from the solid-liquid interface[50].

Hydrates are formed primarily at the phase boundary between liquid water and the gaseous hydrating agent[54]. There are two modes of nucleation which occur: (1) homogeneous nucleation on the surface of dispersed liquid agent droplets, and (2) heterogeneous nucleation initiated by crystal fracturing[60]. While hydrates can form inside the liquid on dissolved gas particles, this requires greater activation energy to reorient the surrounding water molecules. The high molar ratio of gas to water in the vapor phase makes hydrate formation in the vapor region unlikely as well[61].

Factors which have been found in laboratory studies to significantly affect the rate of formation of gas hydrates include

- δT, the magnitude of the process driving force; that is, the temperature differential between the equilibrium temperature of the hydrate at the bulk salt concentration and the actual bulk aqueous temperature;

- the degree of agitation or power input; and
- the salt concentration[50].

The driving force δT is expended primarily for (1) processes taking place between hydrate crystals and the aqueous phase and for (2) heat transfer from the aqueous phase to agent droplets, especially for vaporization of the hydrating agent[61]. Although Barduhn[61] suggested that the nature of the agent molecule may have little effect on the kinetics of hydrate formation, the relative demand of these two processes seems to vary with the hydrating agent used. Working with Freon 31, Barduhn estimated that two-thirds of the total driving force was consumed by agent evaporation, and one-third by crystal growth. In contrast, the Office of Saline Water Research reported results of earlier work with methyl bromide[51] which assigned ten to twenty percent of the driving force to the former, and eighty to ninety percent to the latter. In the formation of hydrates from refrigerants, the relative amount of liquid agent present surely affects the rate of formation as its presence enhances heat transfer through evaporation.

Agitation of the hydrate-containing aqueous solution promotes both homogeneous and heterogeneous nucleation by renewing contact surfaces constantly and by breaking crystals apart. Barduhn's group[60,61] developed empirical equations relating rates of formation of certain hydrates to the power input and to the driving force, δT.

Further research confirmed the importance of power input. Barduhn[61] noted a tenfold decrease in rate of production of Freon 31 and Freon 142a crystals brought to a steady state in a continuously stirred vessel when agitation ceased.

Mass transfer of salt and dissolved agent has been determined to be relatively unimportant in affecting formation rate, although increasing salt concentration does tend to cause a decrease in reaction rate[51].

Process History - In its annual report for 1960, the Office of Saline Water published a list of hydrate-forming agents for potential use in desalination processes, including several Freons, cyclopropane, methyl bromide and vinyl chloride[44]. A number of agents screened did not form simple hydrates. Others were considered impractical because of their relatively high decomposition pressures. In 1961, the OSW published a revised list of the most promising agents for use in desalination[45]. Chlorine, methyl chloride, Freon 12, and propane had been added to the list, while cyclopropane, Freon 12B2 and vinyl chloride had been dropped.

This initial research on hydrating agents specifically suited for desalination was carried out by Barduhn and coworkers[44,45]. Over the next twenty years, they produced a considerable body of thermodynamic and kinetic data for many of these agents, including Freons 12, 21, 31 and 142b[46,48,51-53,61]. Their criteria for the evaluation of a compound as a suitable hydrating agent included

- moderate decomposition temperature and pressure;
- high rate of hydrate formation;
- low losses due to solubilization or hydrolysis; and
- reasonable cost.

Secondary considerations included crystal separability and refrigerating capacity. More recent work by Kubota[58] produced thermodynamic data on Freon 13, Freon 23, and Freon 152a.

Hydrating agents of particular interest are discussed in more detail below. Their decomposition pressures and temperatures, as well as their hydration numbers, are given in Table 2.

Freon 12 (CCl_2F_2) forms a Type II hydrate, with an approximate composition of Freon $12(H_2O)_{17}$. It has a decomposition temperature of 12.1°C and a decomposition pressure of 4.58×10^5Pa (64.5 psia).

Freon 12 was used to start up the Koppers Co. propane hydrate pilot desalination plant, built for the OSW at Wrightsville Beach Test Facility, South Carolina, in 1966[50-52]. Freon 12 was also tested at the same location from March, 1967, to July, 1968, in a pilot program conducted by the Mason-Rust Co. Efforts concentrated on optimizing wash-separation processes rather than hydrate formation, as Freon 12 hydrate crystals proved difficult to separate. Production rates were low and failed to offset the high capital and operating expenses, and the plant finally closed down for economic reasons, although technically it worked well.

Freon 31 (CH_2ClF), a Type I hydrate, has a high decomposition

TABLE 2

DECOMPOSITION TEMPERATURES AND PRESSURES OF HYDRATING AGENTS

Agent	Decompos. Temp., °C	Decompos. Pressure, $\times 10^{-5}$ Pa	Hydration Number	Ref.
Carbon Dioxide	31.1	73.73	6	54
Chlorine	28.7	6.09	7.27	45
Cyclopropane	17.1	5.96	-	44
Freon 12	12.1	4.58	17	45
Freon 12B1	10.0	1.70	17	44
Freon 12B2	9.9	2.68	17	44
Freon 13	8.5	24.2	19.3	58
Freon 21	8.7	1.01	16.6	44
Freon 22B1	9.9	2.68	17	44
Freon 23	19.9	40.4	7.9	58
Freon 31	17.9	2.86	8.0	44
Freon 142B	13.1	2.32	7.2	45
Freon 152A	15.3	4.51	17	44
Methyl Bromide	14.7	1.53	7.9	44
Methyl Chloride	21	5.07	7.2	45
Propane	5.5	5.67	18.4	58
Vinyl Chloride	1.2	1.82	-	44

temperature (17.9°C) and a moderate decomposition pressure (2.86 x 10^5 Pa, or 41.5 psia). It has an extremely low hydrolysis rate and a high rate of formation. Results of kinetic studies showed that the Freon 31 hydrate formed six to ten times faster than hydrates of propane, methyl bromide, or Freon 12[52]. Crystals were granular and easy to wash[53]. Unfortunately, Freon 31 is no longer commercially available.

Freon 142b (CH_3CClF_2) produces a Type II hydrate which decomposes at 13.1°C and 2.32 x 10^5 Pa. Freon 142b was used in Barduhn's kinetic studies on the rate of formation of hydrates as function of temperature differential[44].

Propane (C_3H_8) forms a Type II hydrate with a relatively low decomposition temperature (5.7°C) and a high decomposition pressure (5.67 x 10^5 Pa, or 82.2 psia). Despite these unfavorable characteristics, it has been the subject of continued laboratory and pilot studies because of its ready availability[44,45,48-51].

In 1960 and 1961, the results of laboratory research conducted by Koppers Co. on a bench-scale propane hydrate desalination process were reported[44,45,48-51]. Hydrate yield varied from 3 to 21 weight percent of feed. Agitation proved critical; problems with crystal separation were also noted.

The laboratory bench-scale work undertaken by Koppers resulted in the design and construction of a 10,000-gpd pilot plant at the Wrightsville Beach Test Facility, which was completed in 1966[48-51]. The seawater was first pretreated by filtering suspended materials, chlorinating, and deaerating, and then prechilled. The seawater was introduced into a reactor where propane was added and hydrates were formed. Following hydrate formation, the hydrate crystals were washed, liquid propane was decanted from the waste brine and the product water, and the hydrate slurry was decomposed. Gaseous propane was stripped from the waste brine and product water streams. The ultimate failure of the pilot operation was attributed to the poor washing characteristics of the propane hydrate crystals.

In the early 1960's, the Sweet Water Development Company also tested a propane hydrate desalination process[46-48]. Pilot tests were conducted at a small scale on a 700-gpd pilot plant in St. Louis, Missouri. The encouraging results obtained from this plant led to the design and construction of a 20,000-gpd pilot unit at the OSW's Wrightsville Beach Test Facility. The process resembled that developed by Koppers. However, the washing operation relied on a cocurrent displacement system which employed a cyclone to separate propane, water, and hydrate crystals based on differences in densities. The cyclone did not provide satisfactory performance and was eventually replaced with a pressurized wash column.

Chlorine (Cl_2) produces a Type I hydrate that has one of the highest decomposition temperatures (28.7^oC) of the group of hydrates actively considered for use in desalination processes. Unfortunately, it also has a high decomposition pressure (6.09×10^5 Pa or 88.3 psia), is extremely corrosive, and is highly toxic. Because of its wide availability, however, it is still considered a potential desalination agent[62]. No references to its use in bench-scale, pilot or full-scale projects were found.

Carbon dioxide (CO_2) has a very high decomposition temperature ($31.1^{o}C$) and a very high decomposition pressure (73.73×10^{5}Pa or 1069 psia). Despite its high decomposition temperature and pressure, it is attractive as a desalination agent because it is nontoxic, nonflammable, and readily available at reasonable cost.

In 1964, it was reported that the Jacobs Engineering Company investigated the use of carbon dioxide as a hydrating agent for desalination[48]. The process used multiple stages of hydrate formation, applying the carbon dioxide step-wise to avoid flash hydrate formation, which apparently can have the same deleterious effects as flash freezing in freezing processes. Neither direct or indirect use of carbon dioxide as a refrigerant was practical, and ammonia was used for all heat transfer processes instead. Carbon dioxide recovery was accomplished by vacuum stripping. Crystal separation took place in a continuous classifier.

Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) have both been seriously considered as hydrating agents[55,58]. Methyl bromide is a Type I hydrate with a high decomposition temperature ($14.7^{o}C$) and low decomposition pressure (1.53×10^{5} Pa or 22.2 psia).

Kinetic studies on rate of formation of methyl bromide hydrate were conducted in a continuously fed, stirred vessel, and compared favorably with other agents. Methyl bromide was eliminated from consideration as a desalination agent, however, when it was discovered that its relative cost, due to a high rate of hydrolysis, made it economically unattractive[51].

Methyl chloride, also a Type I hydrate, has a high decomposition temperature (21.0°C) and an acceptably low rate of hydrolysis. Its high decomposition pressure (5.07×10^5 Pa or 73.5 psia) has discouraged researchers from pursuing further kinetic studies.

Sludge Conditioning - The literature search for this study found only one reference regarding the application of the gas hydrate process to sludge conditioning. Molayem and Bardaki[33] dewatered samples of primary and activated sludge as well as mixtures of the two sludges with excess quantites of Freon 11. 500-mL doses of Freon 11 were applied to 20 mL samples in 10-minute stages. Sludge solids were physically separated from Freon 11 hydrate crystals during the course of the experiments. As can be seen from the selected results presented in Table 3, high concentrations of final solids were obtained in certain instances.

The practical significance of this study is questionable for the following reasons:

1. Results were extremely variable. Percentage increases in final solids concentration varied from 13 to 94 percent for primary sludge; from 43 to 98 percent for activated sludge, and from 55 to 91 percent for mixtures.

2. Estimated values were used in calculating final solids.

TABLE 3

SELECTED RESULTS OF DIRECT-CONTACT, FREEZE-THAW CONDITIONING OF WASTEWATER SLUDGES WITH FREON 11[33]

ONE-STAGE CONDITIONING

Sludge	Initial Solids, %	Final Solids, %
Primary	7.0	54.0
Primary	7.0	14.7
Secondary	1.8	4.0
Secondary	1.8	52.6
Mixture	5.3	11.5
Mixture	5.7	40.5

TWO-STAGE CONDITIONING

Sludge	Initial Solids, %	Final Solids, %
Primary	7.4	20.3
Primary	9.3	10.6

Final solids concentrations were calculated from equations which required estimates of the amount of water remaining associated with the hydrates formed during the experiment.

3. Excessive amounts of Freon 11 were used in experiments. The applied Freon dose varied from 12.5 to 25 L Freon per L of sludge.

IMPACT OF PROCESS AND HANDLING VARIABLES ON CONDITIONING EFFECTIVENESS OF FREEZE-THAW CONDITIONING

Factors which affect the conditioning effectiveness of freeze-thaw conditioning processes include the rate and extent of freezing; type, amount, and point of chemical application; length and condition of storage; sludge solids content; and the amount and intensity of handling and mixing. These factors are discussed in the following subsections.

Rate and Extent of Freezing

It is generally accepted that effective freeze-thaw conditioning of sludges is only achieved by slow, complete freezing. Studies of natural and indirect freeze-thaw conditioning have, in general, borne out this belief[18,19,34,63]. Experiments conducted using secondary refrigerant processes have shown that slurry freezing could also be used to successfully condition sludges.

Katz and Mason[34] conducted indirect freezing experiments with waste activated sludge. They found that deep freezing caused the solids to separate from the liquid and form layers. Rejection of solids occurred at a critical freezing rate of 0.0005 mL/sec (0.03 mL/hr). At freezing rates greater than 0.001 mL/sec (0.06 mL/hr), sludge particles and unfrozen liquid were trapped in the advancing ice matrix. Rapidly frozen sludges did not dewater as well as sludges which had been frozen at a slower rate.

In experiments to determine the relationship between freezing speed and conditioning effects, Logsdon and Edgerly[64] progressively froze samples of barium sulfate sludge, iron and aluminum hydroxide sludges, and alum water treatment sludge. The 350-mL samples were placed in plastic bags and lowered into an antifreeze bath at a fixed rate. As freezing progressed, solids tended to migrate upwards and consolidate. The lower the freeze rate, the greater were the migration and consolidation. Critical velocity of the freezing isotherm was about 30 mm/hr, above which no migration occurred. Fast freezing of iron and alum sludges resulted in local segregation of particles. Although segregation patterns were different in frozen samples of the two different kinds of sludge, both sludges showed improved dewatering characteristics, as evidenced by decreases in the equivalent volume of settled solids in settled samples.

Ezekwo _et al._[62] subjected partially digested secondary sewage sludge to progressive freezing by lowering sludge-filled glass tubes through a chilled metal block. Freezing rate varied from 0.8 to 8.8

x 10^{-4} cm/sec (0.05 to 0.53 mm/hr). Although there were morphological differences observed in cross and longitudinal sections of sludge frozen at different rates, solids obtained upon gravity drainage did not vary appreciably with freezing rate.

In experiments in which biological sludges were frozen by contact with butane, Khan[30] and Randall, et al.,[32,65] found that slurry freezing improved dewatering characteristics. In both batch and continuous processes, increasing the contact time between sludge and butane improved conditioning. The improvement in the specific resistance of the activated sludge freeze-thaw conditioned in the batch process corresponded to a first-order reaction curve, approaching a maximum at 60 minutes. Contrary to results produced by solid freezing, filtrate quality improved with conditioning time, although supernatant quality decreased.

Chemical Addition

Several studies have reported that the addition of inorganic chemicals or polymers to freeze-thaw conditioning improved dewatering characteristics. The addition of ferric chloride to activated sludge prior to freezing improved dewatering rates[24]. Preaddition of alum to activated sludge increased solids production rate and resulted in more efficient solids capture[30], and improved dewatered solids concentration for a variety of wastewater treatment sludges[66]. Polymer addition prior to freezing also decreased sedimentation volumes of iron and alum sludges[63]; polymer addition to digested sewage sludge during the freezing process dramatically improved solids migration[67]. In contrast, chemical addition after conditioning has been found to hinder dewatering[24].

Baskerville[68] has suggested, that preconditioning with these agents strengthens the delicate flocs which constitute some biological and chemical sludges. The improved structure of the floc is more able to withstand the potentially destructive pressures of the freeze-thaw process.

Storage

Gale et al.[69], in their basic studies on the effects of handling variables on the dewatering characteristics of raw sewage sludge, found that storage of unconditioned and alum-conditioned sludges over a period of days resulted in large increases in specific resistance. Other researchers have confirmed that storage of sludge prior to and after freeze-thaw conditioning generally resulted in deterioration of dewatering characteristics. In a study for the Sewerage Commission of Milwaukee[24], samples of activated sludge stored for periods up to 24 hours, before and after indirect-contact, freeze-thaw conditioning, resulted in deterioration of dewatering characteristics. Khan[30] observed that storage of biological sludges both prior to and after direct-contact conditioning with butane hindered settling, filtration, and drainage.

Doe et al.[22] found that the dewatering characteristics of alum sludges deteriorated appreciably after 8 to 10 hours of thaw time following indirect-contact, freeze-thaw conditioning.

Thickening

The effect of initial solids concentration, and, thus, the usefulness of prethickening in freeze-thaw conditioning of sludges is disputed. Certain studies have shown that conditioning improves with increased initial solids concentration while others have shown the opposite effect. This is an important consideration as prethickening can decrease the volume of sludge freeze-thaw conditioning processes must handle, resulting in substantial cost savings.

Doe et al.[23] prethickened alum water treatment sludges to 2.4 and 4 percent prior to successful indirect-contact, freeze-thaw conditioning. In a study conducted for the Sewerage Commission of Milwaukee[24] activated sludge was prethickened to 4 percent with no adverse effect on the dewatering characteristics of the indirect-contact, freeze-thaw conditioned sludge.

Katz and Mason[34] found that the dewatering time of indirect-contact, freeze-thaw conditioned activated sludge decreased as feed solids concentration increased from about 1 to 1.5 percent to about 2 to 2.5 percent.

Ezekwo et al.[64] compared the solids concentration of progressively frozen, partially digested sewage sludge after thawing and gravity drainage. Undiluted sludge (4 percent) dewatered to a higher concentration than diluted sludge (2.2 percent).

In contrast to these studies, Tilsworth et al.[18] reported on natural freezing of extended aeration sludges, noting that the lower the solids content of the sludge, the more efficient the process.

Randall[32], in slurry freeze-thaw conditioning of biological sludges, also found that higher solids concentrations required longer detention times. The relationship could be modeled according to the equation:

$$Y_{CT} = a x_f^2 + b \qquad [24]$$

where

Y_{CT} = conditioning time
x_f = feed solids concentration
a,b = constants.

Handling and Mixing

Handling and mixing have been shown to have an adverse effect on the dewatering characteristics of certain sludges[22,23,69]. The effect depends upon the type of sludge and the intensity and duration of handling and mixing. Farrell[70] noted the negative effects of stirring on both sewage and alum hydroxide sludges which been freeze-thaw conditioned; the effect was more pronounced for sewage sludge. Khan[30], in his direct-contact, freeze-thaw conditioning experiments with biological sludges, found that mixing during the freezing process was necessary to maintain a pumpable slurry. Vigorous agitation resulted in a poorly settling sludge, but its effects could be partially allayed by subsequent slow stirring.

MECHANISMS OF FREEZE-THAW CONDITIONING

Freeze-thaw conditioning produces irreversible changes in the nature of some sludges, making them, in many cases, easier to dewater. Several mechanisms have been proposed to explain these changes. A discussion of the mechanisms involved in freeze-thaw conditioning of sludges is difficult to approach, as various theories put forth are based upon the extent and rate of freezing as well as the type of sludge conditioned. Mechanisms can be roughly divided into two categories:

- solids migration and compression, and
- particle dehydration and cell rupture.

Solids Migration and Compression

The segregation of particles and layers of particles (termed micromigration and macromigration, respectively, by Logsdon and Edgerly[63]) which occur when sludges are deep frozen has been noted in a number of studies. The irreversibility of the changes wrought by freeze-thaw conditioning has led some researchers to suggest that the forces which are responsible for segregation are large enough to destroy cells and to compress particles and flocs, dehydrating and concentrating them.

The behavior of solids in a freezing liquid is a result of the process of crystallization and of the nature of the solids themselves. Ice crystals nucleate and, if unimpeded, proceed to grow in planes. If surrounded by solution, the crystal interface is destabilized by the concentration gradient of the solute. In response, the crystal sends out projections and loses its planar characteristics, becoming dendritic. As the solution is dehydrated at the ice interface, colloidal solutes lose some of their mobility. The interface pushes particles ahead of it, excluding them by surface-energy effects. Solids thus tend to localize at the grain boundaries of the ice crystals[64,67].

Whether or not a particle in the path of the advancing interface is trapped depends upon the size and roughness of the particle, the solids content, and the rate of crystal growth[63,64,67]. The larger the particle, the lower is the velocity required to trap it. While polymers increase the size of particles, they improve the concentration of solids by lowering the resistance of flow through them, thus preventing entrapment of solids. The larger the surface area relative to particle size (i.e., the rougher the particle), the greater is the tendency of the particle to be carried along by the interface.

Ezekwo _et al._[64], from their work with partially digested sewage sludge, noted differences in the behavior of samples of diluted and undiluted sludges upon thawing. The solids from the undiluted sludge (4 percent) formed a rigid mass which retained its longitudinal form, collapsing along the side of the tube in which the sludge was frozen and thawed, during melting and draining. This facilitated the flow of water from the mass. On the other hand, the diluted sludge solids formed a fragile mass which broke apart during collapse, and settling at the bottom of the tube during melting hindered drainage.

From these observations, the researchers hypothesized that slow freezing permitted development of elongated crystals which drained well. Rapid freezing resulted in small ice crystals enveloped by a matrix of dissolved and suspended solids which drained poorly.

Migration of solids was hindered by increased initial solids content, as evidenced by decrease in the size of ice domains. The higher the solids content, the lower the rate at which impurities diffused in the system. At high solids concentrations (greater than 80 percent), nucleation and crystal growth were severely reduced.

Logsdon and Edgerly[63], found that freeze-thaw conditioning had a decreased effect on sludges which had relatively poor dewatering characteristics before conditioning. They suggested that the segregated solids formed a cake similar to that formed during the Buchner funnel test, with ice as the supporting medium. Highly flow-resistant sludges were inclined to entrap solids during freezing.

Particle Dehydration and Cell Rupture

Silvares *et al.*[71] developed a model on freezing injury to cells based on two effects:

- solution effects, predominant in slow freezing, wherein cells are immersed in a concentrated salt solution as ice forms outside the cell. The concentration gradient exerts an osmotic effect upon the water in the cell, drawing water from the cell and thus dehydrating it.

- intracellular freezing, predominant in more rapid freezing, wherein ice forms inside the cell.

Several researchers have suggested that freezing has a dehydrating effect on sludge particles. As water freezes, the unfrozen solution surrounding the crystals becomes increasingly hypertonic. This imbalance causes cellular or bound water to duffuse to the immediate environment of the cells or flocs. Rapid or deep freezing causes cells and flocs to rupture, releasing their contents. Upon thawing, the filtrate contains a higher percentage of dissolved solids because of the material extracted from the particles[30,34].

Farrell[19] speculated that freeze-thaw conditioning removed water from hydroxide flocs, whereas its basic effect on sludge particles was to enhance agglomeration. Sewage sludge particles were thus susceptible to resuspension upon mixing.

Role in Direct-Contact Processes

The role of either of these mechanisms in direct contact conditioning processes is not clear. Large scale migration of particles is not possible in well-mixed systems in which the sludge is maintained as a slurry. Whether local compression and dehydration at the ice-liquid interface is sufficent to cause the irreversible changes noted in previous studies is not known.

III. METHODS AND MATERIALS

Samples of water and wastewater treatment sludges were conditioned using a variety of methods and analyzed to determine the relative effectiveness of direct-contact, freeze-thaw processes. This section describes sludges, conditioning methods, equipment and process variables, and analytical methods used in this study.

SLUDGE SOURCES

Samples of waste activated sludge, primary sewage sludge, and alum water treatment sludge were used in this study. General characteristics of each sludge and the handling protocols developed for each are detailed in this section.

Waste Activated Sludges

Samples of waste activated sludge from the Roanoke Wastewater Treatment Plant (Roanoke, Virginia), and from the Christiansburg Wastewater Treatment Plant (Montgomery County, Virginia) were only used in preliminary experiments. Samples of waste activated sludge from the Stroubles Creek Wastewater Treatment Plant (Montgomery County, Virginia) were used throughout the study.

Samples of Stroubles Creek waste activated sludge were drawn from two sources. Sludge for same-day testing was bled through a tap on the main line returning settled sludge from the secondary clarifiers to the aeration basins. Sludge for use over the course of several days was taken directly from the aeration basin. In both cases, the sludge was allowed to settle and excess supernatant decanted before transport to the laboratory. Sludge from the aeration basin was transferred to 30-liter plastic batch reactors, stored at 20^0 Celsius and aerated. Samples were withdrawn from these basins, settled, and decanted, as needed. The batch reactors were fed approximately 400 mg/L Bactopeptone and supernatant decanted and replaced with tap water daily.

The initial solids concentration of the settled sludge was about 1 percent (varying from 0.6 to 1.6 percent). Specific resistance values generally ranged from 4 to 70 x 10^{11} m/kg. Cake solids concentrations resulting from Buchner funnel tests varied from 9 to 15 percent. Sludge characteristics remained stable over the periods in which the sludge was maintained in the batch reactors. These periods did not exceed four days.

Primary Sewage Sludge

Samples of primary sewage sludge were obtained from the primary clarifier underflow lines at the Stroubles Creek Wastewater Treatment Plant. Sludge was collected during waste pumping and screened through a 1/4-inch plastic mesh to remove fibrous materials. Samples were permitted to settle before testing and excess supernatant decanted.

Initial dry solids concentrations and specific resistance values of primary sludge samples varied greatly. Initial solids concentrations of the settled sludge varied from 1 to 6 percent. Specific resistance values ranged from 80 to 7100 x 10^{11} m/kg, and no cake was formed during Buchner funnel vacuum-filtration tests. Primary sludge samples were conditioned and tested within 8 hours of collection, as specific resistance of the sludge increased greatly with prolonged storage.

Alum Water Treatment Sludges

Samples of alum water treatment sludges were obtained from two sources. One set of samples (used only in preliminary studies) was obtained from an industrial water treatment plant in Philadelphia, Pennsylvania. The other set was collected from the water treatment plant at the Radford Arsenal Ammunitions Plant (RAAP) in Fairlawn, Virginia.

The RAAP alum sludge was drawn from the thickening tank at the solids handling building at the plant. The suspended solids concentration of the thickened sludge was ranged from 1 to 5 percent. The sludge was diluted with tap water to obtain lower initial solids concentrations when necessary.

Specific resistance values for the undiluted sludge ranged from 160 to 310 x 10^{11} m/kg. While cake solids concentrations resulting from Buchner funnel tests varied from 7 to 26 percent, they generally were between 20 and 26 percent. Specific resistance values for samples diluted with tap water to about 1 percent initial solids concentration ranged from 100 to 160 x 10^{11} m/kg; cake solids concentrations varied from 23 to 24 percent.

Storage did not appreciably affect sludge dewatering characteristics for the RAAP sludge. Undiluted sludge settled very slightly during storage periods of over a month, and solids were easily resuspended and stabilized by mixing. Diluted sludge settled moderately over the course of several hours.

CONDITIONING METHODS

Four methods were used to condition samples of Stroubles Creek waste activated and primary sludges, samples of a mixture of these sludges, and samples of RAAP alum sludge to gauge the comparative effectiveness of direct-contact, freeze-thaw conditioning. These included direct-contact, freeze-thaw conditioning with butane and with Freon 12; indirect-contact, freeze-thaw conditioning; and polymer conditioning. The experimental matrix for these studies is presented in Table 4. Information on conditioning agents and equipment and process variables is given below.

Direct-Contact, Freeze-Thaw Conditioning with Butane

Sludge samples were mixed with butane under temperature and pressure conditions conducive to the formation of ice. All experiments were continuous. Predetermined doses of butane were

TABLE 4

EXPERIMENTAL MATRIX

	CONDITIONING METHOD				
				Freon 12 Freeze-Thaw	
Sludge	Polymer	Indirect Freeze-Thaw	Butane Freeze-Thaw	Batch	Continuous
Stroubles Creek Waste Activated (WA)	X	X	X	X	X
Stroubles Creek Primary Sewage (PS)	X	X	X	X	
Stroubles Creek (WA/PS)	X	X		X	
RAAP Alum Sludge					
Undiluted	X	X	X	X	X
Diluted	X	X	X	X	X

introduced into 1-L sludge samples at a set flow rate of 20 mL/min. Butane was introduced into the sludge either as a pure liquid or in the form of colloidal liquid aphrons.

The butane used in this study was "cp" grade, compressed in 30-lb cylinders, and was obtained from an industrial source. Vapor saturation data for butane are given in Table 5. The graph of these data in the relevant temperature range is shown in Figure 5.

Direct-Contact, Freeze-Thaw Conditioning with Dichlorodifluoromethane (Freon 12)

Sludge samples were mixed with dichlorodifluoromethane (marketed as Freon 12 by E.I. DuPont de Nemours & Co., and referred to as such henceforth) under temperature and pressure conditions conducive to the formation of gas hydrates. Two types of experiments were undertaken: batch and continuous. In the batch experiments, selected doses of Freon 12 were rapidly introduced into 1-L sludge samples at pressures too high for hydrate formation. The sample and the refrigerant were mixed vigorously and the pressure lowered to an appropriate level for hydrate formation. Certain samples were subjected to repeated slug doses of Freon 12 for two- and three-stage conditioning. In the continuous experiments, predetermined doses of Freon 12 were introduced into the sample continuously at a set flow rate of 10 mL/min, at temperatures and pressures suitable for hydrate formation.

Freon 12 was obtained compressed in 30-lb disposable jugs from a

TABLE 5

BUTANE VAPOR SATURATION DATA

English Units		SI Units	
Temperature °F	Pressure psia	Temperature °C	Pressure $\times 10^{-5}$ Pa
0	7.30	-18	0.503
5	8.20	-15	0.565
10	9.21	-12	0.635
15	10.33	-9	0.712
20	11.56	-7	0.797
25	12.90	-4	0.889
30	14.35	-1	0.989
31.1	14.70	-0	1.013
35	15.95	2	1.100
40	17.62	4	1.215

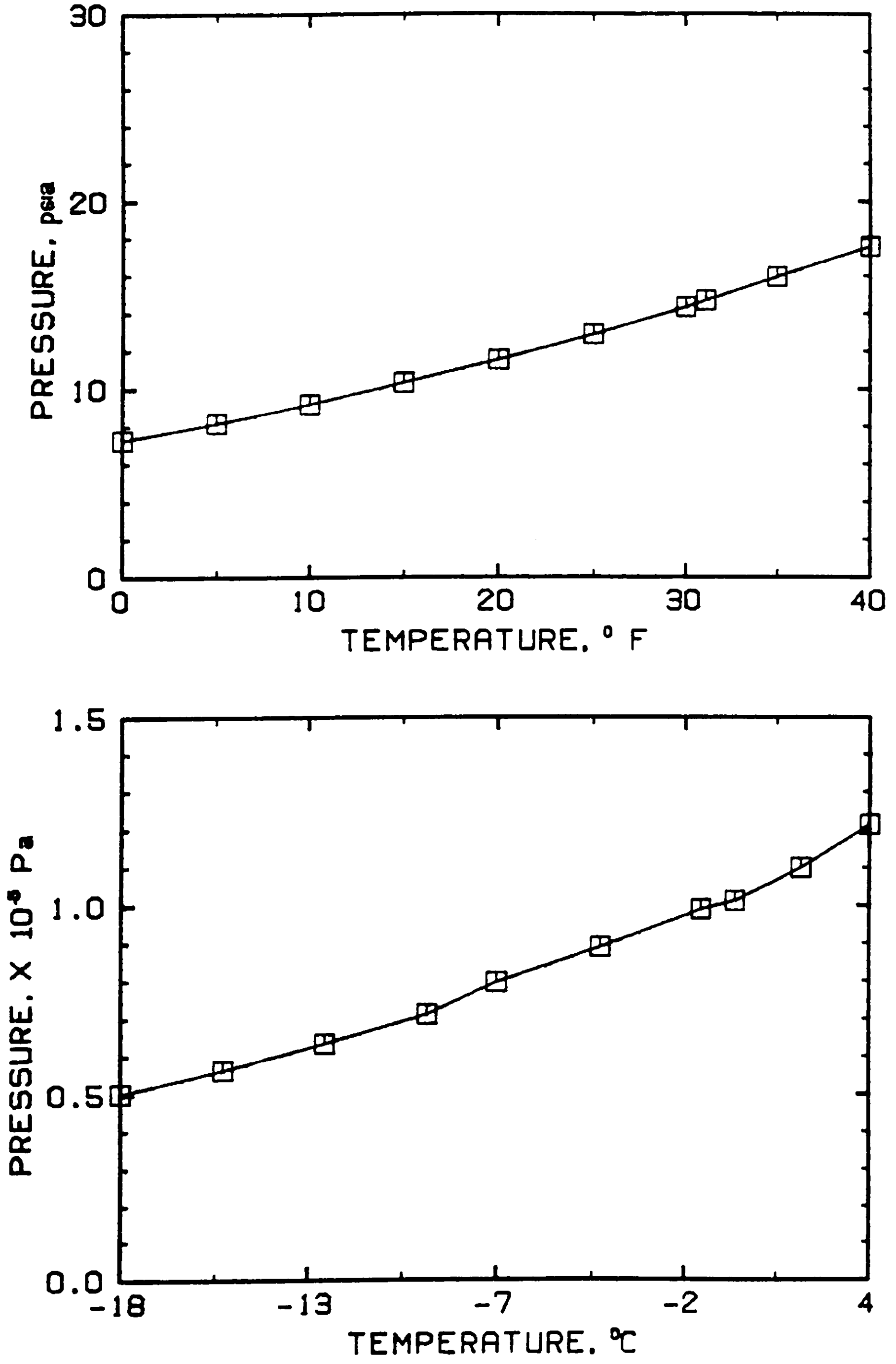


FIGURE 5. BUTANE VAPOR SATURATION CURVE.

commercial source. Vapor saturation and gas hydrate equilibrium data for Freon 12 are given in Table 6. Graphs of these data in the relevant temperature range are shown in Figure 6.

Indirect-Contact, Freeze-Thaw Conditioning

Indirect-contact, freeze-thaw conditioning was used to estimate the maximum potential response of each sludge to other freeze-thaw processes. Indirect freezing of sludge samples was accomplished by placing samples in a conventional deep-freeze unit and allowing them to freeze completely. Two-liter samples initially at room temperature when placed in the unit cooled to $0^{o}C$ in two hours, and froze completely in 24 hours. Completely frozen samples were removed from the unit and thawed at room temperature to approximately $20^{o}C$ before analyses were performed.

Polymer Conditioning

Results of polymer conditioning were used as a conventional standard against which results of freeze-thaw conditioning were compared. Samples of sludge (volume = 500 mL) were dosed with varying amounts of a 0.1-percent solution of Betz 1160, a high-weight cationic polymer, in a standard jar test apparatus. Samples were mixed at 100 rpm for approximately 10 to 15 seconds, and then flocculated for 30 to 60 seconds at 40 rpm.

TABLE 6

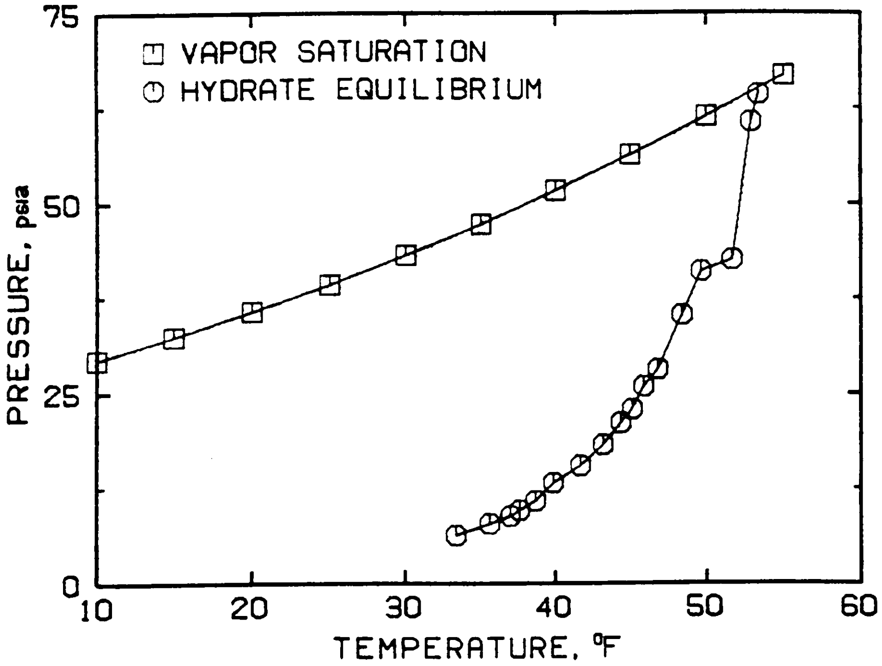
FREON 12 VAPOR SATURATION AND GAS HYDRATE EQUILIBRIUM DATA

VAPOR SATURATION DATA

English Units		SI Units	
Temperature °F	Pressure psia	Temperature °C	Pressure $\times 10^{-5}$ Pa
10	29.33	-12	2.022
15	32.42	-9	2.235
20	35.74	-7	2.464
25	39.31	-4	2.710
30	43.15	-1	2.975
35	47.26	2	3.259
40	51.67	4	3.562
45	56.37	7	3.887
50	61.39	10	4.233
55	66.74	13	4.602

HYDRATE EQUILIBRIUM DATA

English Units		SI Units	
Temperature °F	Pressure psia	Temperature °C	Pressure $\times 10^{-5}$ Pa
33.4	6.38	0.8	0.44
35.6	7.83	2.0	0.54
37.0	8.85	2.8	0.61
37.6	9.57	3.1	0.66
38.7	10.88	3.7	0.75
39.9	13.20	4.4	0.91
41.7	15.52	5.4	1.07
43.2	18.27	6.2	1.26
44.4	21.17	6.9	1.46
45.1	22.92	7.3	1.58
45.9	25.82	7.7	1.78
46.8	28.14	8.2	1.94
48.4	35.24	9.1	2.43
49.6	41.04	9.8	2.83
51.6	42.49	10.9	2.93
52.9	60.62	11.6	4.18
53.4	64.25	11.9	4.43



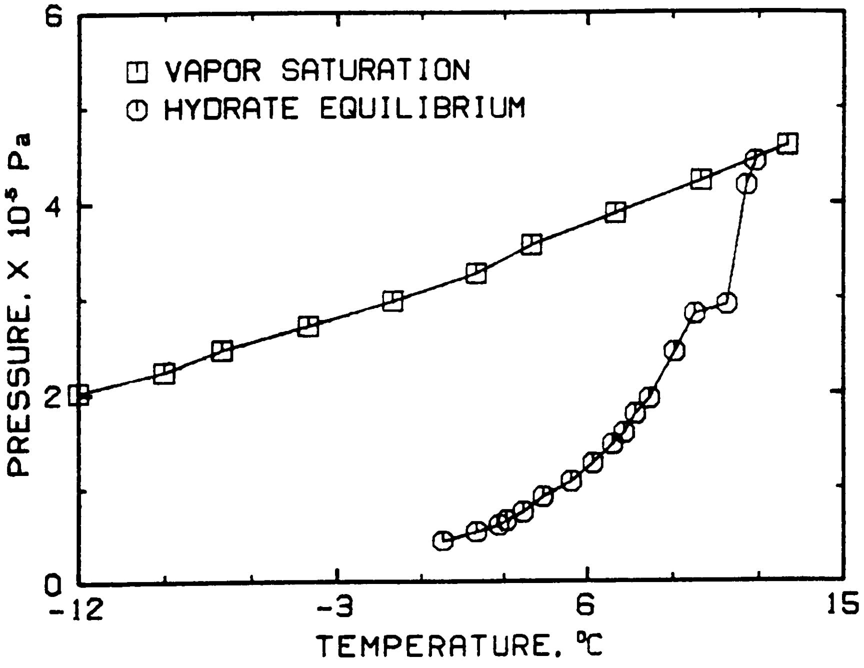


FIGURE 6. FREON 12 VAPOR SATURATION AND GAS HYDRATE EQUILIBRIUM CURVES.

EXPERIMENTAL APPARATUS

The experimental apparatus used in the experiments conducted as part of this study is shown schematically in Figure 7. The main components of the system were the reactor, heat exchange systems, and refrigerant feed systems, which are described in detail in this section.

Reactors

The original reactor used in this study was constructed of 1/4-inch-thick Plexiglas. It had a rectangular 6-inch by 10-inch base and 8-inch side walls. The reactor base had an integral diffuser composed of shallow 1/8-inch-wide channels grooved between two layers of Plexiglas. The channels were laid out in a rectangular grid. Tiny holes (1/32-inch in diameter) were drilled through the top layer of the Plexiglas base to allow liquid refrigerant to bubble up from the channels into the reactor.

The reactor was fitted with a sealed cover. The cover included several ports for vacuum and temperature gauges and for a line through which a vacuum could be drawn and maintained. The cover also had a removable plate fitted with a bearing for a mixer shaft.

Trial experiments using water proved the reactor configuration to be inadequate. Ice formed directly over the diffuser, and mixing was neither sufficiently intense nor the mixer properly positioned to break up the ice and intimately mix the refrigerant with the reactor contents.

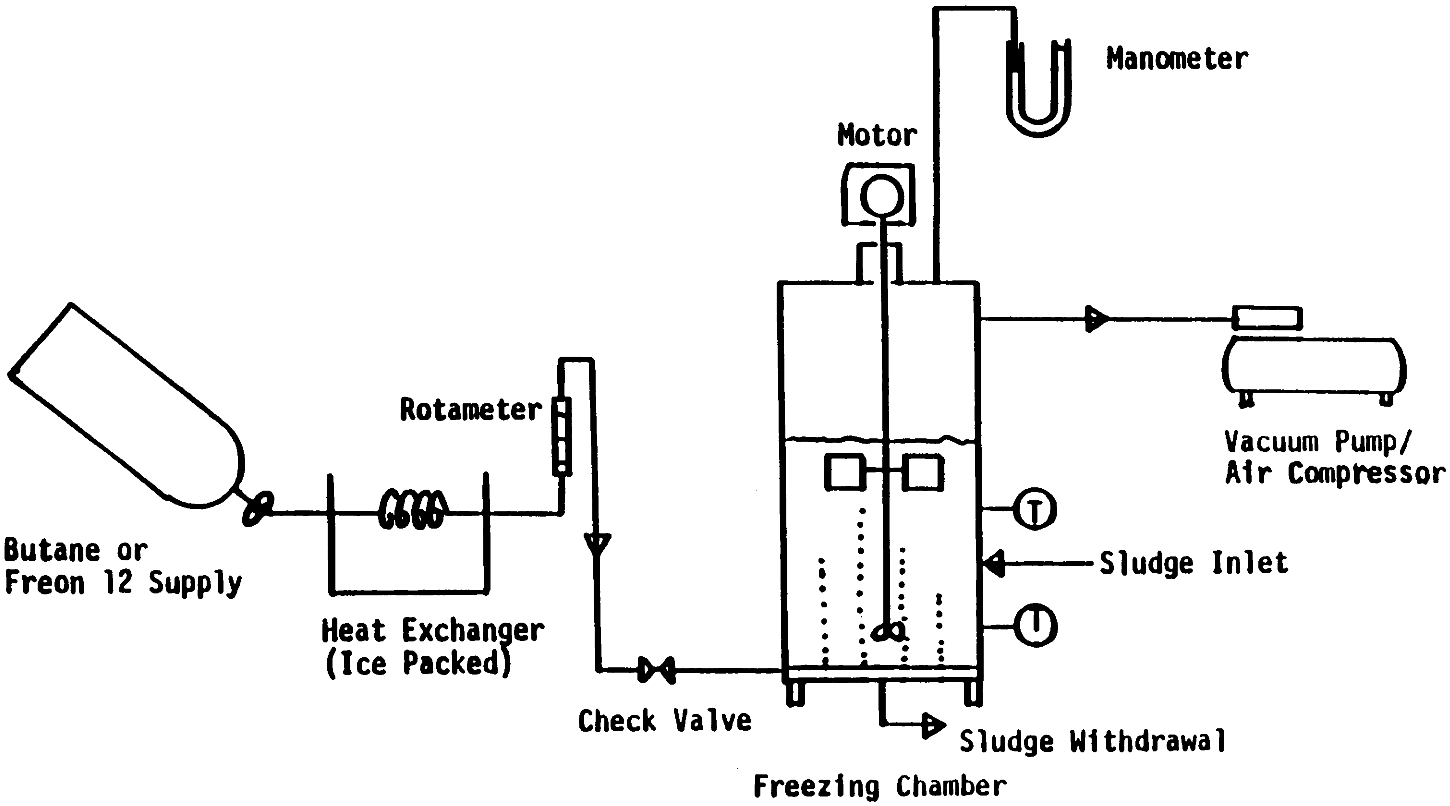


FIGURE 7. SCHEMATIC OF DIRECT-CONTACT FREEZE-THAW CONDITIONING APPARATUS

A cylindrical reactor was designed and built to replace the original reactor. The cylindrical reactor was also constructed of 1/4-inch-thick Plexiglas. It was 5 inches in diameter and 11-1/2 inches tall. Four 1/2-inch diameter ports for temperature measurement, vacuum measurement and maintenance, and miscellaneous other purposes were located along the sidewall. An integral diffuser similar in construction to the diffuser in the rectangular reactor was tooled in the base of the reactor. The channels formed a spiral instead of a rectangular grid.

Another four ports, 1/4-inch in diameter, were located in the reactor cover. Like the original reactor, the new reactor cover also supported a mixer shaft bearing plate.

The reactor was modified several times during the course of preliminary studies. Four 1/4-inch wide baffles running the height of the reactor, equally spaced along the side wall, were added to improve mixing. Modifications were also made to the mixer bearing to accomodate a larger mixer.

Both reactors were originally equipped with integral diffusers. However, these diffusers were prone to clogging. Distribution of refrigerant was uneven, with most issuing from openings along the wall of the reactor, promoting flash freezing at the wall. When the original diffusers were found to be unsuitable, a number of different diffuser types and configurations were tested. An aluminum base was constructed with channels similar to those in the original reactor base. Instead of entering the reactor through small holes, the refrigerant flowed into the reactor through fine, spherical porous diffusers. However, combined head loss through the channels and the diffusers proved too great, causing liquid butane to vaporize before emerging from the diffusers. Similarly, discs of finely divided brass, set into the base, created too much head loss in the system.

Since the aluminum base was a large cold sink, it was ultimately abandoned. The original reactor base was replaced by an unperforated Plexiglas disc. Refrigerant was fed into the reactor through one of the sidewall ports. On the inside of the reactor, a short length of 1/4-inch-diameter Tygon tubing connected the port fitting to a pyramidal coarse bubble diffuser. This diffuser tended to ice, especially at long detention times, and was replaced in later experiments by a coil of 1/4-inch copper tubing perforated with 0.012-inch holes.

Mechanical mixing was provided in all reported experiments to promote intimate contact between sludge and refrigerant or hydrating agent. In initial studies, a small laboratory mixer with a maximum speed of 100 rpm was used. This proved insufficient to prevent the formation of solid ice on the reactor surfaces, along the mixer shaft and blades, and on the diffuser itself.

This mixer was eventually replaced with a Sears 13-inch, 5-speed, 3.0-hp drill press. The drill press not only made high speed mixing up to 2000 rpm possible, but also provided a stable support for the reactor. However, while higher speeds reduced diffuser icing significantly and prevented formation of solid ice along the reactor walls and mixer shaft, they also resulted in deterioration of sludge dewatering characteristics. A constant mixing speed of 400 rpm was selected as a result of a series of mixing tests on samples of RAAP alum sludge. At this speed, both the negative effect on dewatering characteristics and the formation of ice on surfaces were minimized.

Heat Exchange Systems

Heat exchange systems were necessary to maintain reactor and refrigerant temperatures at optimum levels for butane and Freon conditioning during experiments. Sludge samples were precooled to minimize the use of refrigerant for this purpose. Systems for temperature and vacuum/pressure maintenance and methods of sludge and refrigerant precooling are discussed in the following subsections.

Temperature and Vacuum/Pressure Maintenance - To maintain desired temperatures, the reactor was wrapped with uninsulated Tygon tubing and encased by a two-inch-thick styrofoam jacket. Cooled ethylene glycol was pumped from the well of a refrigerating bath (Master Scientific Formaline Model 2095 Bath and Circulator) through Rubatex-insulated tubing, around the reactor and back to the reservoir of glycol.

Process temperature was maintained between -1 and +1°C during butane experiments. The temperature generally dropped over the course of an experiment from the range of +0.5 to +1°C, to the range of -0.5 to -1°C as the sludge froze. A 4-cm Hg vacuum was maintained in the reactor during butane experiments using a Gast air compressor (Model DOA-P106-AA), piped to produce a vacuum. The vacuum insured that the butane evaporated at operating temperatures.

For Freon 12 experiments, precooling the reactor in a commercial refrigerator to 4 to 8^{0}C was sufficient to maintain the temperature at desirable levels. Pressure-temperature conditions during Freon 12 experiments were maintained at points slightly below the vapor saturation curve (Figure 6). (Hydrates form at all points beneath this curve and above the gas hydrate formation curve at temperatures less than 12^{0}C. However, reactions rates are more rapid at points close to the vapor saturation curve.) Process temperature was generally maintained between 7 and 10^{0}C; process pressure was varied accordingly from 56 to 62 psia (3.9 to 4.3×10^{5} Pa), using a Gast Super Series air compressor (Model ROA-P101-AA).

After conditioning, the temperature of the sludge was allowed to rise above 14^{0}C in order to decompose the hydrates. The pressure in the reactor was subsequently increased to compress the Freon 12 to a liquid state, as allowing it to bubble through the sludge resulted in foaming. The liquid Freon floated to the surface and was then allowed to evaporate.

Refrigerant Precooling - Butane was precooled to temperatures ranging from -10 to -5^{0}C by feeding it through a 1/4-inch-diameter copper coil (approximately two meters total length) submerged in a bath of ethylene glycol and ice. Low temperatures were necessary to prevent premature volatilization of butane due to heat gains in the refrigerant feed system. Excessively low temperatures were avoided to prevent exacerbating diffuser icing.

Freon 12 was precooled to 2-1/2 to $3^{o}C$ by immersing the copper coil in ethylene glycol contained in the well of the refrigerating bath.

Sludge Precooling - Samples of sludge were precooled before introduction into the reactor. For butane experiments, two-liter samples of sludge were precooled in a conventional commercial deep-freeze unit for approximately four hours, until the sludge temperature dropped to between +0.5 and $+1^{o}C$. For Freon 12 experiments, samples were precooled to 4 to $8^{o}C$ in a commercial refrigerator.

Refrigerant Feed Systems

Two types of refrigerant feed systems were utilized in preliminary experiments: a conventional liquid system and a polyaphron system. The polyaphron system was not used in later experiments due to mechanical difficulties and foaming problems. Both methods are discussed in the following subsections.

Conventional Liquid System - Butane and Freon 12 were pumped through the feed system using the compressive force of the pressurized containers in which the refrigerants were purchased. Butane pressure varied from 22 psi to 37 psi (1.5 to 2.6×10^{5} Pa), and Freon 12 pressure from 70 to 95 psi (4.8 to 6.6×10^{5} Pa), depending on room temperature. The tanks were tilted or turned upsidedown, placing the feed valve below the bulk of the container contents to insure that the refrigerant emerged from the cylinder as a liquid.

The feed system was constructed of 1/4-inch-diameter Polyflo tubing, insulated with Rubatex. Liquid refrigerant flowed from the tank through a precooling copper coil to a Gilmont rotameter for flow measurement. Butane flow rate was adjusted with a union bonnet metering valve. Freon 12 flow rate was adjusted with an ultra-fine low-flow metering valve. A check valve in the line just prior to the reactor prevented backflow of the reactor contents into the feed line.

Butane flow rates between 5 and 35 mL/min were used in preliminary experiments. Based on the results of these experiments, a flow rate of 20 mL/min was selected for the remaining studies. Higher flow rates resulted in flash freezing, while it proved difficult to maintain a constant vacuum at lower flow rates.

Freon 12 flow rates between 5 and 25 mL/min were used in preliminary experiments. A flow rate of 10 mL/min was selected for the remaining studies. Higher flow rates resulted in an excessively foamy product, while lower flow rates resulted in very long detention times.

Polyaphron System - As an alternative method of introducing butane into the sludge, experiments were conducted to incorporate liquid butane into colloidal aphrons. Colloidal aphrons are fine droplets of water-insoluble gas or liquid, each encapsulated in a thin surfactant film[72]. They exhibit unusual foam-like properties, including great stability, and have been shown effective in separation techniques[73]. Potential benefits in using liquid butane in a polyaphron included storage and feeding at ambient pressure and improved contact between butane and sludge.

The standard procedure used to produce aphrons is to add an oil to a surfactant in solution. Initially one or two drops are added at a time, with vigorous shaking between additions. Once a milky foam begins to form, indicating the presence of aphrons, larger quantities of oil are added.

The ultimate ratio of oil to water is approximately 10:1. Thus, if 500 mL of oil aphrons are desired, 500 mL of the selected oil are added to 50 mL of the surfactant solution.

Certain new techniques had to be developed to produce butane aphrons since liquid butane vaporizes at ambient temperature and pressure. To maintain butane as a liquid at atmospheric pressure, its temperature must be maintained below 0°C. Glycerol must be added to the surfactant solution to prevent it from freezing during production and storage.

The procedure developed was as follows:

1. Three to four gallons of ethylene glycol were chilled to -20°C. A plastic container and a dropper bottle were also chilled. The plastic container was weighted so that it could not float when submerged in the glycol.

2. Two coolers were prepared to hold the glycol. One gallon of the chilled glycol was poured into one cooler, and the rest into the second cooler.

3. A solution of 5 g/L sodium dodecyl benzene sulfonate (SDBS) was prepared. To make 250 mL of oil aphrons, 25 mL of 5 g/L SDBS, 10 mL of glycerol, and 2.5 mg of lauric acid were added to the plastic container. Solution temperature was allowed to decrease to $-10^{o}C$ in the larger cooler.

4. Liquid butane was fed into the dropper bottle until it was three-quarters full. The dropper bottle was then attached to the side of the cooler that contained the gallon of glycol, with the bottle immersed in the glycol.

5. The butane was added to the surfactant solution with the dropper one drop at a time, with vigorous shaking maintained for about one minute between drops. After five drops were added in this manner, two to three drops could be added at a time. The amount of butane added was gradually increased to 5 mL. However, this much was not added until the solution had a thick, milky appearance. Adding too much butane too soon caused the aphrons to destabilize and fall apart.

6. Once formed, the aphrons were stored in a commercial deep-freeze unit.

It was discovered that too low a storage temperature caused the surfactant solution to freeze and settle to the bottom, leaving the liquid butane floating at the surface. If the solution was vigorously shaken and warmed so that the solution thawed, the aphrons reformed, as long as the temperature did not rise above $0^{o}C$.

Based on this discovery, a new method was devised to produce the aphrons. The surfactant solution, glycerol, and lauric acid were added to a plastic container. Butane was added gradually as described above until four to five drops of butane were added at a time, with vigorous shaking between additions. The solution was then put in a freezer and the surfactant solution allowed to freeze. The aphrons reformed after five to ten minutes of vigorous shaking. Relatively large amounts of butane (up to 10 mL per addition) were then added to produce the desired quantity of aphrons.

The butane aphrons proved difficult to pump. Contact with the pump and tubing, which could not be maintained satisfactorily below $0^{o}C$, caused the aphrons to volatilize prematurely. Similar problems with premature volatilization were encountered with gravity feed.

Conditioning Agent Removal

Various techniques were used during the early stages of this study in an attempt to remove spent butane and Freon 12 from the product sludge. Neither vacuum stripping nor aeration resulted in any observable improvement in dewatering characteristics for either butane- or Freon-conditioned sludges.

Overnight storage at 40°F, on the other hand, improved the dewatering characteristics of both butane- and Freon-conditioned sludges. Product sludges, which in general exhibited very poor settling characteristics immediately after thawing, usually separated into sludge and supernatant fractions with storage. Certain butane-conditioned samples produced a third fraction, a stable, high-solids foam with poor dewatering characteristics.

ANALYTICAL METHODS

Table 7 lists analyses and determinations used to quantify the results of conditioning experiments. Descriptions of analytical methods are presented in this section.

Particle Size Distribution

Particle size distributions of sludge and supernatant samples were analyzed to gauge any changes which occurred during conditioning which might impact dewatering characteristics. Particle counts were made using a HIAC Particle Size Analyzer Model PC-320[74]. The sensor used in this study was a HIAC Standard Sensor Model CMB-300, which is capable of detecting and counting particles in the range of 5 to 300 microns (μm).

TABLE 7

EXPERIMENTAL ANALYSES AND DETERMINATIONS

Analysis/Determination	Reference
Total Particle Counts	74
Particle Size Distributions	74
Weight Fractions	75
Specific Resistance	6
Blinding Index	9
Vacuum-Filtered Cake Solids Concentration	75
Initial Solids Concentration	75
Centrifuged Solids Concentration	75
Floc Density	76
Supernatant TOC	75
Sludge pH	75

Samples were diluted, if required, to meet the particle concentration limit of the sensor. If available, filtered supernatant was used to dilute samples. If not, tap water was used for dilution. Usually sludge samples were diluted to 1/1000, and supernatant to 1/10, if at all. Three 10-mL aliquots of each sample were analyzed for particle size distribution, and the results of the three averaged.

Results are reported as totals per "mean particle diameter (MPD)." MPD was calculated by averaging the end points of each size range (e.g., if the particle sensor limits for a given range were set at 35 and 45 μm, the MPD is 40 μm.) (This nomenclature is not intended to imply that particles are spherical or that the measurement reported is a characteristic length as determined by Knocke and Wakeland[10]. Rather it is a convenient term to describe the dimension of the particle sensed by the analyzer.)

Prior to analysis, samples were filtered through a brass screen (250 μm pore openings) to prevent clogging of the sensor. A sample of the filtrate was weighed before and after drying at 103°C and the percentage of solids passing through the filter determined (in accordance with Section 209A of Standard Methods[75]. This calculated value was reported as percent of sludge solids passing a 250-μm sieve.

Specific Resistance, Initial and Vacuum-filtered Solids Concentrations, and Blinding Coefficients

Specific resistance was calculated using the results of time vs. volume data obtained using Grade 40 filter paper (8 μm particle retention) in a Buchner funnel apparatus as described in Vesilind[6]. A vacuum of 20 in Hg (508 mm Hg) was drawn on the filtering apparatus during the procedure. At cake failure, a sample of the sludge cake was scraped from the filter, and the dry solids concentration determined according to procedures described in Section 209A of Standard Methods[75]. If no cake was produced within 30 minutes, a representative cake solids concentration was used to calculate specific resistance. Generally, this value was that determined for the cake produced at the lowest conditioning dose for which a cake formed. Initial dry solids concentration was determined according to the same procedure.

The blinding coefficient, as defined by Huang[9], was determined by plotting the natural logarithm of the time and volume data from the Buchner funnel test and calculating the slope of the resultant line.

Centrifuged Solids Concentration

Samples of sludge were distributed equally between 2 plastic 50-mL test tubes and placed in a Beckman Model J-21C centrifuge. Samples were centrifuged at 9000 rpm for ten minutes. Supernatant was then decanted, the solids removed from the tube, and the dry solids concentration of the resultant cake determined by drying at 103^oC[75].

Floc Density

The floc density of selected sludge samples was measured to determine if conditioning had any effect on the relative water content of flocs. Density was analyzed using the method described by Vollrath-Vaughn[76]. Small droplets of sludge were introduced beneath the surface of stratified layers of various concentrations of Percoll contained in a 10-mL test tube. (Percoll is a polymer-coated silica sol manufactured by Pharmacia Fine Chemicals, which can be concentrated to specific gravities of up to 1.3.) The test tubes were centrifuged in an International Clinical Centrifuge Model CL at 850 RPM for two minutes. Upon removal, the samples were observed and the location of flocs noted. Flocs tended to concentrate either within a particular gradient step or between two adjoining gradient steps. Commonly, particles concentrated in bands at several locations, indicating a range of densities. The samples were returned to the centrifuge for another two minutes and then removed. Location of floc bands was again noted.

Total Organic Carbon

The total organic carbon (TOC) content of supernatant samples was measured to assess the effect of conditioning on supernatant quality. TOC was analyzed using a Horiba Total Organic Carbon Analyzer Model PIR-2000. This analyzer utilizes the persulfate-ultraviolet oxidation method described in Section 505A of Standard Methods[75].

Sludge pH

The pH of sludge samples was measured using a Fischer Scientific Accumet pH meter Model 610, according to the procedure described in Section 423 of Standard Methods[75].

IV. RESULTS

The results of direct-contact, freeze-thaw conditioning experiments are presented together with the results of polymer and indirect-contact experiments in this chapter. Each of the following sections is devoted to a specific sludge.

STROUBLES CREEK WASTE ACTIVATED SLUDGE

Samples of unconditioned waste activated sludge obtained from the Stroubles Creek Wastewater Treatment Plant dewatered rapidly to a moderate solids concentration. As the specific resistance of the sludge was already low prior to conditioning, the main benefit anticipated from conditioning was an increase in dewatered solids concentration.

Polymer conditioning typically increases filtration rates while having little effect on final dewatered solids concentrations. Freeze-thaw conditioning, in contrast, was expected to produce significant increases in solid concentration. Certain improvements in filtration rates were also anticipated.

Polymer Conditioning

Samples of Stroubles Creek waste activated sludge were conditioned with 10, 20, 30 and 50 mg/L Betz 1160. There was little change in dewatering characteristics for any polymer dose. The primary conditioning effect of polymer addition was an increase in sludge floc size. The limited improvements observed when polymer was added to this particular sludge suggested that an increase in floc size does not automatically result in significant improvements in sludge dewatering characteristics.

The results of analyses and determinations on polymer-conditioned samples of waste activated sludge are presented in Table 8.

Particle and Chemical Characteristics - The main effect of polymer conditioning on waste activated sludge was a shift in particle size distribution to size ranges with larger mean particle diameter (MPD). As can be seen from Figure 8, conditioning reduced the total number of particles with MPD less than 55 μm, especially in the size ranges with MPD less than 30 μm. Reduction in the percentage of small particles varied consistently with polymer dose. The greatest reduction was achieved at the highest polymer dose: the number of particles with MPD less than 55 μm was reduced from 95 percent for the unconditioned sample to 84 percent for the sample conditioned with 50 mg/L polymer. Also, 10 percent of the particles in this sample were retained when filtered through a 250-μm sieve, compared to no measurable percentage for all other samples. These results indicate a substantial shift towards larger sizes in the distribution of particles.

Polymer conditioning had little effect on the supernatant, other

TABLE 8

RESULTS OF ANALYSES
POLYMER-CONDITIONED WASTE ACTIVATED SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Polymer Dose, mg/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.03	16,500	18,000	0	8	6.9
10	1.03	14,900	12,900	0	10	7.0
20	1.03	8,100	9,700	0	9	7.0
30	1.03	10,400	13,500	0	9	7.0
50	1.03	7,200	13,200	10	9	7.0

DEWATERING CHARACTERISTICS

Polymer Dose, mg/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	1.0	13.6	8.8	49	0
10	1.0	10.5	8.4	38	-0.4
20	1.0	12.2	8.2	61	0.3
30	1.1	12.6	8.3	54	-0.1
50	1.2	12.0	8.0	42	-0.2

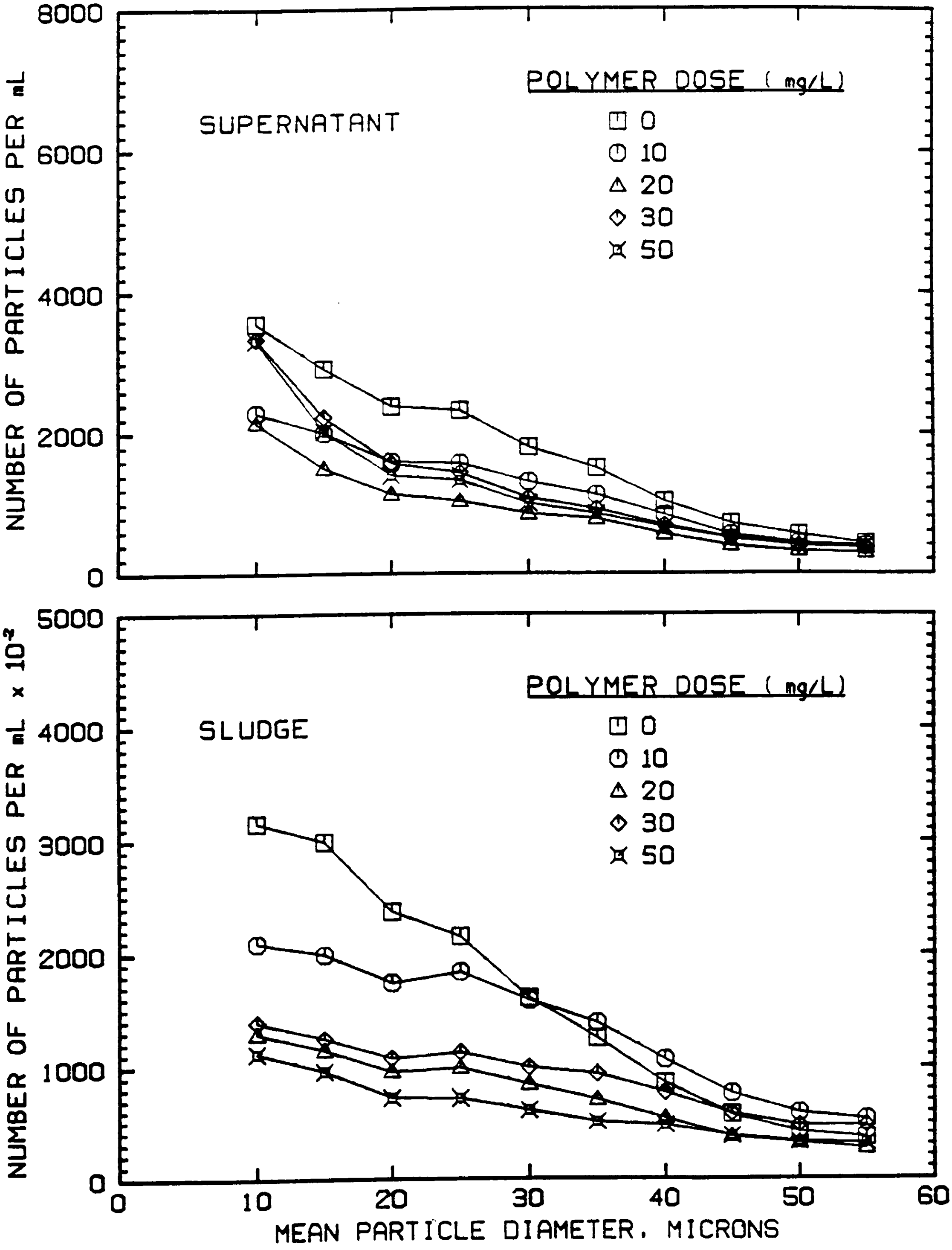


FIGURE 8. PARTICLE SIZE DISTRIBUTIONS. POLYMER-CONDITIONED WASTE ACTIVATED SLUDGE.

than slightly reducing the total number of particles with MPD less than 250 μm.

Dewatering Characteristics - The overall effect of polymer conditioning on the dewatering characteristics of waste activated sludge was minimal. The dewatered solids concentration obtained from both vacuum filtration and centrifugation decreased slightly for all conditioned samples. Contrary to expectations, specific resistance did not decrease with increasing polymer dose or with increases in particle size, showing instead only slight variations from the value calculated for the unconditioned sludge. All calculated specific resistance values were less than 100 x 10^{11} m/kg.

The altered appearance of sludge flocs observed during floc density analyses suggested that the decreases in dewatered solids concentration resulted from retention of previously free water within the polymer-enhanced floc structure. When polymer was added to the sludge, formerly fine, isolated flocs aggregated together into large, amorphous clumps. As small amounts of free water were incorporated into the growing aggregates, the amount of moisture available for extraction by dewatering was reduced, resulting in decreased dewatered solids concentration.

Other parameters were unaffected by the restructuring of particle groups. Free water still drained through the new structures at similar rates, as measured by the specific resistance, and changes in the amount of water associated with the particle were not sufficient to affect floc density.

Changes in blinding coefficient supported the indications of increased sludge floc size observed in particle size data. Three of the four conditioned sludges had negative blinding coefficients in contrast to the unconditioned sludge, which had a blinding coefficient of zero. The decrease in this parameter may have resulted from an increasing homogeneity in particle size, as particles were bound together by polymer, as suggested by Notebaert[5].

Indirect Contact, Freeze-Thaw Conditioning

The major effects of indirect-contact, freeze-thaw conditioning of Stroubles Creek waste activated sludge on parameters of interest were large increases in initial and vacuum-filtered solids concentration and in floc density. These changes signalled major alterations in floc structure and substantial decreases in floc water content. There were also moderate increases in specific resistance, most likely related to increases in solids content.

Results of these and other analyses and determinations on the sample of indirect-contact, freeze-thaw conditioned waste activated sludge are presented in Table 9.

Experimental Observations - Certain distinct changes in the appearance and gross settling characteristics of indirectly frozen waste activated sludge were observed. After thawing, the conditioned sludge settled rapidly, and a large volume of supernatant was decanted easily. The freeze-thaw solids were large, grainy, and dense, similar in appearance to freeze-dried coffee granules.

TABLE 9

RESULTS OF ANALYSES
INDIRECT-CONTACT, FREEZE-THAW-CONDITIONED WASTE ACTIVATED SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Conditioning Method	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen	Sludge pH
		Sludge x 10^{-2}	Supernatant		
None (Control)	1.03	16,500	18,000	0	6.9
Indirect Freeze	1.055	3,100	1,900	76	9.3

DEWATERING CHARACTERISTICS

Conditioning Method	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
None (Control)	1.0	13.6	8.8	49	0
Indirect Freeze	4.3	20.5	10.1	120	0.6

Particle and Chemical Characteristics - The overwhelming difference between the particle distributions of indirect-contact, freeze-thaw conditioned and unconditioned samples of waste activated sludge, depicted in Figure 9, was in the total number of particles represented by the distributions. The conditioned sludge sample had 20 percent fewer particles with MPD less than 250 μm. Similar reductions in the number of particles in the supernatant with MPD less than 250 μm were noted.

The small particles eliminated by conditioning from the distributions measured by the particle counts constituted part of the mass of larger particles retained on a 250-μm sieve. Particles with MPD greater than 250 μm represented 76 percent by weight of the total solids of the conditioned sludge sample, compared to the unconditioned sample, which had no measurable percentage in that size range.

Changes in waste activated sludge pH with freezing indicated that physical disruption of particles during freezing may have occurred. Sludge pH increased from 7.0 for the unconditioned sample to 9.3 for the conditioned sample. Chemically neutral particles might have broken apart during freezing to release alkaline components into the supernatant, causing the sludge pH to increase.

Indirect freezing resulted in a large increase in floc density, from 1.03 to 1.05 g/L. The increase in density was readily apparent from the greatly improved settling characteristics of the freeze-thaw solids, as well as the appearance of individual particles. Mass

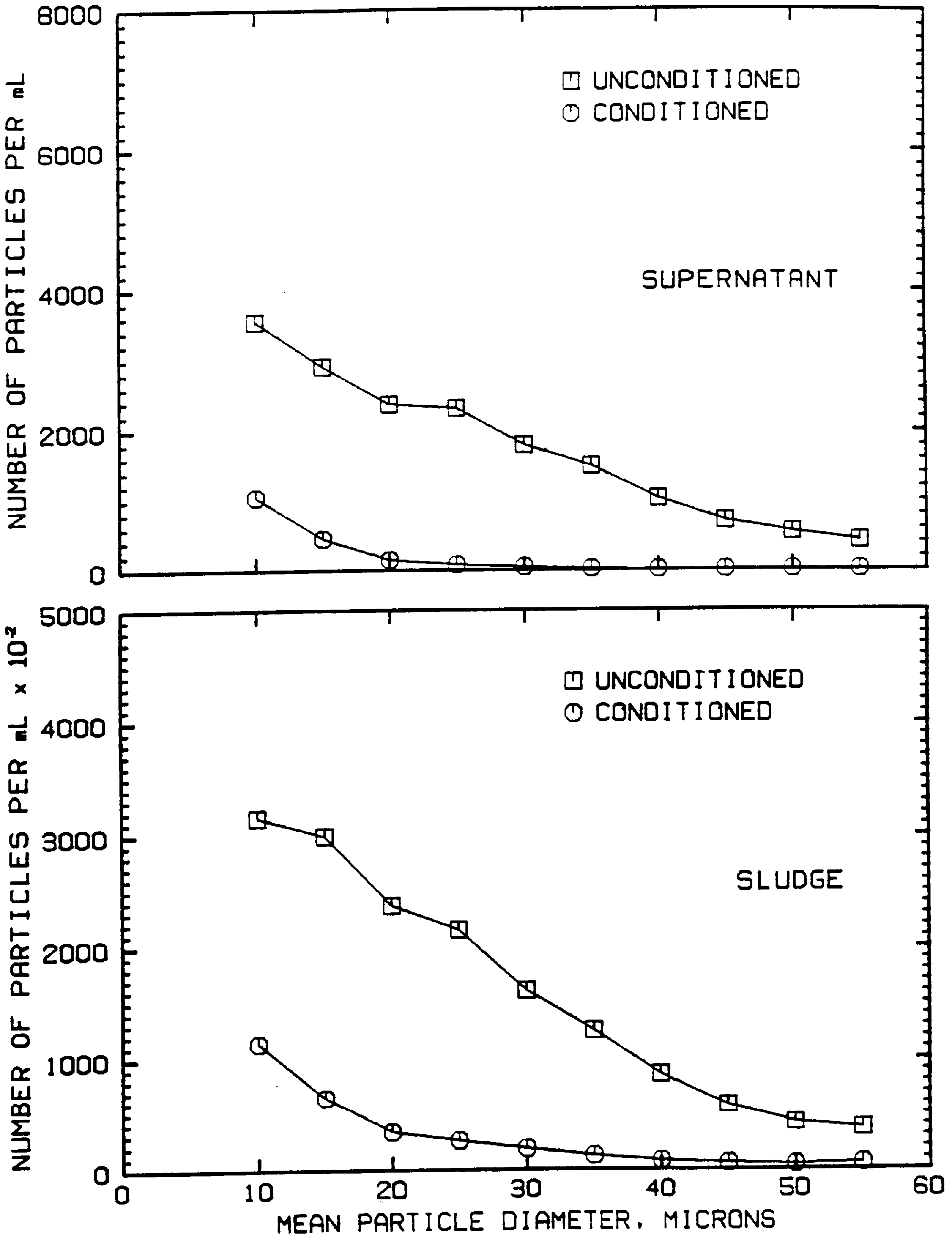


FIGURE 9. PARTICLE SIZE DISTRIBUTIONS. INDIRECT-CONTACT FREEZE-THAW CONDITIONED WASTE ACTIVATED SLUDGE.

balance calculations showed that this represented the release of 53 percent of the floc water.

Dewatering Characteristics - Indirect-contact, freeze-thaw conditioning of waste activated sludge resulted in a large increase in initial and vacuum-filtered dry solids concentration and moderate increases in specific resistance. The process released a large amount of water as supernatant, increasing the initial solids concentration of the sludge over 300 percent. Vacuum-filtered solids increased by 51 percent, and centrifuged solids posted a smaller but still sizable increase of 15 percent.

The concomitant increases in dewatered solids concentration and floc density were probably related. Arundel[77], in her study of the dewatering behavior of sludges exposed to high pressures, observed increases in floc density with increased dry solids above a sludge-specific concentration. She concluded that internal water was released from the flocs, causing floc density to increase, as pressure deformed the floc matrix. The intense pressures developed during freezing have been suggested as possible causes of similar results by other researchers[63,78].

Specific resistance more than doubled with indirect freezing, although the value calculated for the conditioned sample was still moderate (120 x 10^{11} m/kg). Increased solids content has been shown to increase specific resistance[4], and it is likely that the large change induced by freezing in initial solids affected the sludge's response to filtration.

The change in blinding coefficient with indirect-contact freeze-thaw conditioning suggested that conditioning enhanced the tendency of the sludge cake to blind. The blinding coefficient increased from zero for the unconditioned sludge to a positive value for the conditioned sludge. The usual interpretation of a positive blinding coefficient---the blocking of cake pores by small particles---was not suggested by particle size analysis data, which showed a definite increase in particle size. Considered with the increased specific resistance, the positive blinding coefficient may have indicated changes in cake structure. Under vacuum, larger flocs may have compressed, resulting in a more tightly packed cake less conducive to drainage.

Direct-Contact, Freeze-Thaw Conditioning with Butane

One-L samples of Stroubles Creek waste activated sludge were conditioned with 20 mL/min butane for contact times of 20, 30, and 40 minutes, for total butane doses of 400, 500 and 800 mL/L, respectively. Direct-contact freeze-thaw conditioning of Stroubles Creek waste activated sludge with butane produced no significant improvements in dewatering characteristics. Only small increases in centrifuged solids were observed. Changes in vacuum-filtered solids were variable, and specific resistance increased for all butane doses.

Indirect freezing of waste activated sludge also resulted in increased centrifuged solids and increased specific resistance.

Evaluation of particle size distributions suggested, however, that different mechanisms were responsible for similar results.

Analyses were performed on unconditioned and conditioned samples of waste activated sludge conditioned with butane to determine particle and dewatering characteristics. Results of analyses and determinations are presented in Table 10.

Experimental Observations - Conditioning produced a foamy, poorly settling product sludge. The foam, high in solids content and difficult to dewater, was stable, dissipating only slightly with gentle mixing.

Particle and Chemical Characteristics - The main result of direct-contact, freeze-thaw conditioning of waste activated sludge with butane was an increase in the number of small particles in the product sludge. The changes in particle size distribution were not likely caused by the conditioning mechanisms of the freeze-thaw process alone, however, but influenced by other factors.

The particle size distribution for the sludge conditioned with 400 mL/L butane, shown in Figure 10, is representative. The distribution of the conditioned sludge sample, similar in shape and magnitude to that of the unconditioned sample, comprised a much larger number of particles in size ranges with mean particle diameter (MPD) less than 25 μm. The total number of sludge particles with MPD less than 250 μm nearly doubled for the 600 mL/L and 800 mL/L butane doses.

Conditioned supernatant samples also had more small particles

TABLE 10

RESULTS OF ANALYSES
BUTANE-CONDITIONED WASTE ACTIVATED SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Butane Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge $\times 10^{-2}$	Supernatant			
0	1.05	14,800	20,400	0	7	7.1
400	1.05	17,400	29,500	0	153	7.2
0	1.03	10,500	26,500	0	8	6.9
600	1.03	20,600	25,000	0	17	6.9
0	1.03	9,400	3,500	0	7	7.4
800	1.03	18,900	27,300	0	19	7.3

DEWATERING CHARACTERISTICS

Butane Dose, mL/L	Solids Concentration, %			Specific Resistance, $m/kg \times 10^{11}$	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	1.0	12.9	9.1	36	-0.2
400	1.2	13.3	9.3	290	0.1
0	0.6	15.5	8.8	57	-0.5
600	1.3	12.8	9.9	150	-0.5
0	0.9	12.8	9.1	36	-0.3
800	1.2	11.5	9.6	120	-0.3

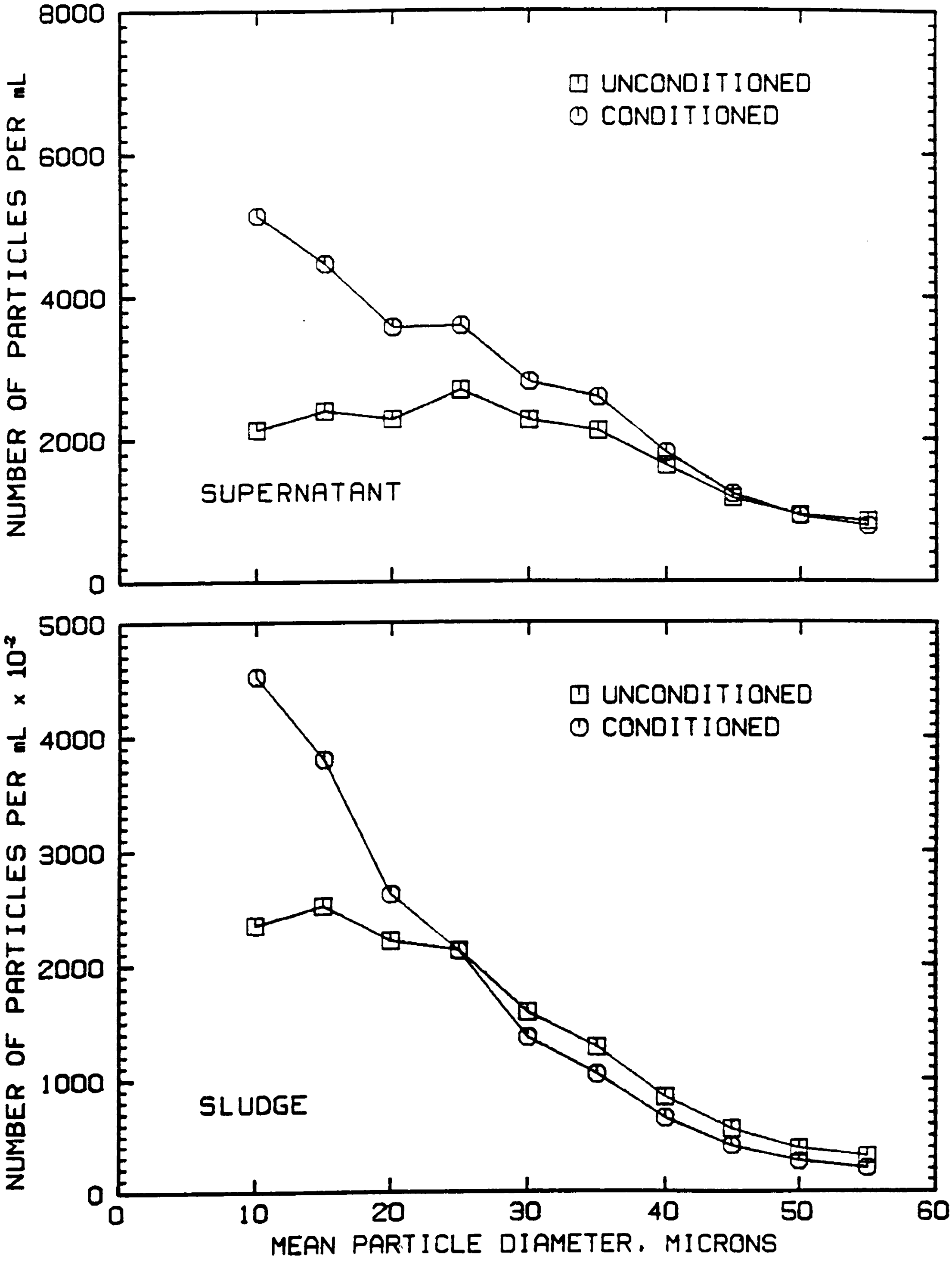


FIGURE 10. PARTICLE SIZE DISTRIBUTIONS. WASTE ACTIVATED SLUDGE CONDITIONED WITH 400 mL/L BUTANE.

than unconditioned supernatant samples. The particle size distribution of the conditioned samples comprised a much greater number of particles in size ranges with MPD less than 30 μm, and exceeded the unconditioned distribution in all size ranges with MPD less than 50 μm.

The changes observed in the particle size distributions of conditioned samples may have been caused by (1) the reduction of particle size during freezing, either through compression or disruption; and/or (2) floc shear induced by mixing applied during experiments. Compression of particles was not substantiated by floc density measurements, which did not change with conditioning. Certain evidence of particle disruption was observed in the results of indirect freezing of waste activated sludge, although the particle size data from those experiments seemed to indicate that these fractionated particles reaggregated upon thawing. If the butane conditioning experiment likewise resulted in particle disruption, it is possible that reaggregation was prevented by the foam generated during the experiment. Mixing could also have contributed to reduced particle size through floc shear or by preventing smaller particles created by freezing from reaggregating. (Mixing tests of equal intensity and duration conducted in the experimental apparatus used in this study produced similar changes in particle size distributions.)

Increases in supernatant TOC were noted for all conditioned samples. The increases for the samples conditioned with 600 mL/L butane were moderate, while the increase for the sample conditioned with 400 mL/L was excessively large. Moderate increases in TOC concentration might be attributed to any of several causes, including the release of organics as particles ruptured during freezing, the suspension of fines in the supernatant as a result of mixing, or entrainment of butane. The large TOC increase observed at the lowest butane dose was likely due to the entrainment of excessive amounts of butane in the sludge during this experiment, which generated large amounts of foam.

Dewatering Characteristics - There was no overall improvement in the dewatering characteristics of butane-conditioned waste activated sludge. While centrifuged solids increased slightly for all butane doses, the response to vacuum filtration was poor. Specific resistance increased for all butane doses. Final vacuum-filtered cake solids increased only slightly with the application of 400 mL/L butane and decreased with the application of 600 mL/L and 800 mL/L butane.

The deterioration of specific resistance with conditioning is shown in Figure 11. The increase in specific resistance in the indirect-contact, freeze-thaw experiment was attributed to the increased solids content, which resulted from the release of internal water. Thus the change in specific resistance for indirectly frozen sludge, though undesirable, was assumed to be part of the conditioning effect of the freeze-thaw process.

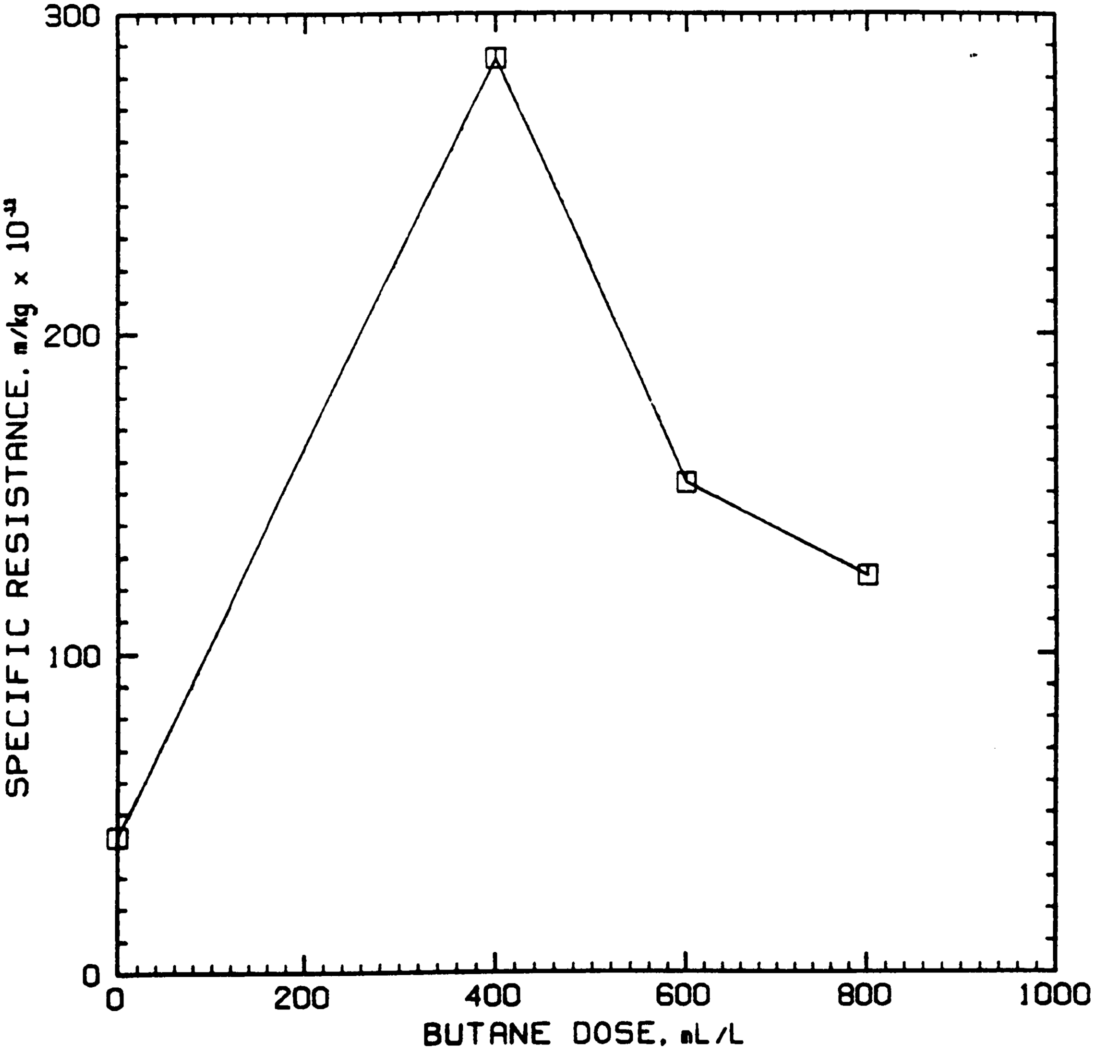


FIGURE 11. SPECIFIC RESISTANCE VS BUTANE DOSE.
BUTANE-CONDITIONED WASTE ACTIVATED SLUDGE.

In contrast, changes in particle size distribution in the direct-contact, freeze-thaw experiments suggested that the increase in specific resistance for butane-conditioned sludge was related to process variables independent of or extraneous to the actual conditioning process, i.e., mixing and foaming.

In considering the causes of the increases in specific resistance, it is interesting to note that higher butane doses resulted in relatively lower specific resistances. In addition, a positive blinding coefficient was calculated for the sludge treated with 400 mL/L butane, in contrast to the other samples, conditioned and unconditioned, which showed no evidence of cake blinding. Since higher butane doses were administered over longer contact times, and thus longer mixing times, specific resistance would be expected to increase with butane dose if deterioration was due to mixing alone. The decrease observed in specific resistance with high butane dose suggests that (1) deterioration of dewatering characteristics was not caused by mixing alone, but by some other factor as well; and (2) higher butane doses and/or longer mixing times mitigated the negative effect of this other factor.

Certain observations suggest that the foam generated during the process was the factor. First, the foam, produced whether mixing was provided or not, tended to dissipate at longer mixing times. Therefore, foam would be more likely to affect specific resistance at shorter contact times. Second, the characteristics of foam make it a likely cause of poor dewatering.

The changes in vacuum-filtered solids---an increase at 400 mL/L butane and decreases at 600 mL/L and 800 mL/L butane---suggested that the extent to which conditioned sludge dewatered upon vacuum filtration depended less upon the foam content of the sludge than did filtration rate. The variability in size and direction of these changes precludes any conclusions as to their meaning.

The slight increase in centrifuged solids probably resulted from the separation of previously bound water from sludge solids as flocs were broken apart by freezing pressures or by mixing turbulence. Certain factors, such as altered particle size distributions and the flow-inhibiting characteristics of the foam, which prevented the removal of this water by vacuum filtration, did not affect its removal by centrifugation, which tends to enhance foam drainage.

In summary, butane conditioning of waste activated sludge resulted in a poorly dewatering product. The effects of mixing and of foaming were severe enough to counteract any beneficial effect of the freeze-thaw process. Longer conditioning times resulted in less deterioration of specific resistance values, but no overall improvement in dewatering characteristics.

Results were disappointing when compared to the increases in vacuum-filtered solids obtained with indirect freezing, but it must be recalled that neither polymer conditioning nor indirect freezing improved specific resistance, and that polymer conditioning actually resulted in small decreases in the vacuum-filtered cake solids concentration.

Direct-Contact, Freeze-Thaw Conditioning with Freon 12

One-L samples of Stroubles Creek waste activated sludge were conditioned with Freon in batch and continuous experiments. In the batch experiments, samples were treated in one- and two-stage conditioning, with 250 mL Freon applied at each stage. In the continuous experiments, samples were fed 10 mL/min Freon for contact times of 25, 50, and 75 minutes. Thus the samples treated in one-stage batch and 25-min continuous experiments were fed 250 mL/L Freon; the two-stage batch- and 50-min continuously conditioned samples, 500 mL/L; and the three-stage batch- and 75-min continuously conditioned samples, 750 mL/L. It should be noted as well that batch-conditioned samples were mixed for very short periods at the beginning of each experiment to insure intimate contact with the refrigerant, while continuously conditioned samples were mixed throughout the defined contact time.

The effects of direct-contact, freeze-thaw conditioning of Stroubles Creek waste activated sludge with Freon 12 on dewatering characteristics were varied. Conditioning resulted in large increases in vacuum-filtered solids and smaller, but still sizable, increases in centrifuged solids. Increases in specific resistance were very large. Changes in particle distributions were not straightforward, and were likely influenced by handling inconsistencies.

Although increases in solids concentration were similar to those obtained in indirect freezing, changes in particle characteristics for Freon-conditioned samples suggested that mixing and foaming effects interfered with the rate of dewatering.

The results of analyses and determinations from batch and continuous experiments on Freon-conditioned samples of waste activated sludge are presented in Tables 11 and 12, respectively.

Experimental Observations - The Freon-conditioning process resulted in a foamy product sludge; the foam, however, was not produced in the large quantities noted in the butane-conditioning experiments, nor was it stable, tending to disperse with overnight storage.

Particle and Chemical Characteristics - Unlike the changes noted as a result of polymer addition, indirect freezing, and direct freezing with butane, changes in particle size distributions for Freon-conditioned waste activated sludge samples followed no distinct trend.

In general, particle size distributions for both batch- and continuously conditioned samples were very similar in shape and magnitude to those of unconditioned samples, as can be seen from Figures 12 and 13. All continuously conditioned samples had a greater number of particles with mean particle diameter (MPD) of 10 μm, suggesting that, as for butane conditioning, there was some mixing-induced floc shearing.

The total number of particles with MPD of 250 μm or less in Freon-conditioned samples generally decreased, however, in contrast to the sizable increases observed in butane-conditioned samples.

TABLE 11

RESULTS OF ANALYSES
FREON-CONDITIONED WASTE ACTIVATED SLUDGE
(BATCH EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.03 - 1.04	14,900	4,100	0	12	7.4
250	1.02	13,700	27,400	0	43	7.6
500	1.01 - 1.05 (1.02)*	9,700	20,900	0	54	7.2

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	0.8	8.3	8.8	210	0.2
250	0.6	13.5	9.4	360	-0.2
500	0.4	12.6	10.9	2,800	0.7

Note:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

TABLE 12

RESULTS OF ANALYSES
FREON-CONDITIONED WASTE ACTIVATED SLUDGE
(CONTINUOUS EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.03 - 1.04	27,500	15,800	0	8	7.9
250	-	29,700	23,300	0	34	7.9
500	1.02 - 1.04	17,100	20,300	0	34	7.6
750	1.02 - 1.04	16,500	5,700	0	45	7.8

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	0.8	9.9	8.8	69	-0.3
250	0.7	11.7	-	320	-0.1
500	0.7	10.4	9.7	1,100	0.2
750	0.7	*	9.5	3,000	0.7

Note:

* No cake produced in 30 minutes of dewatering.

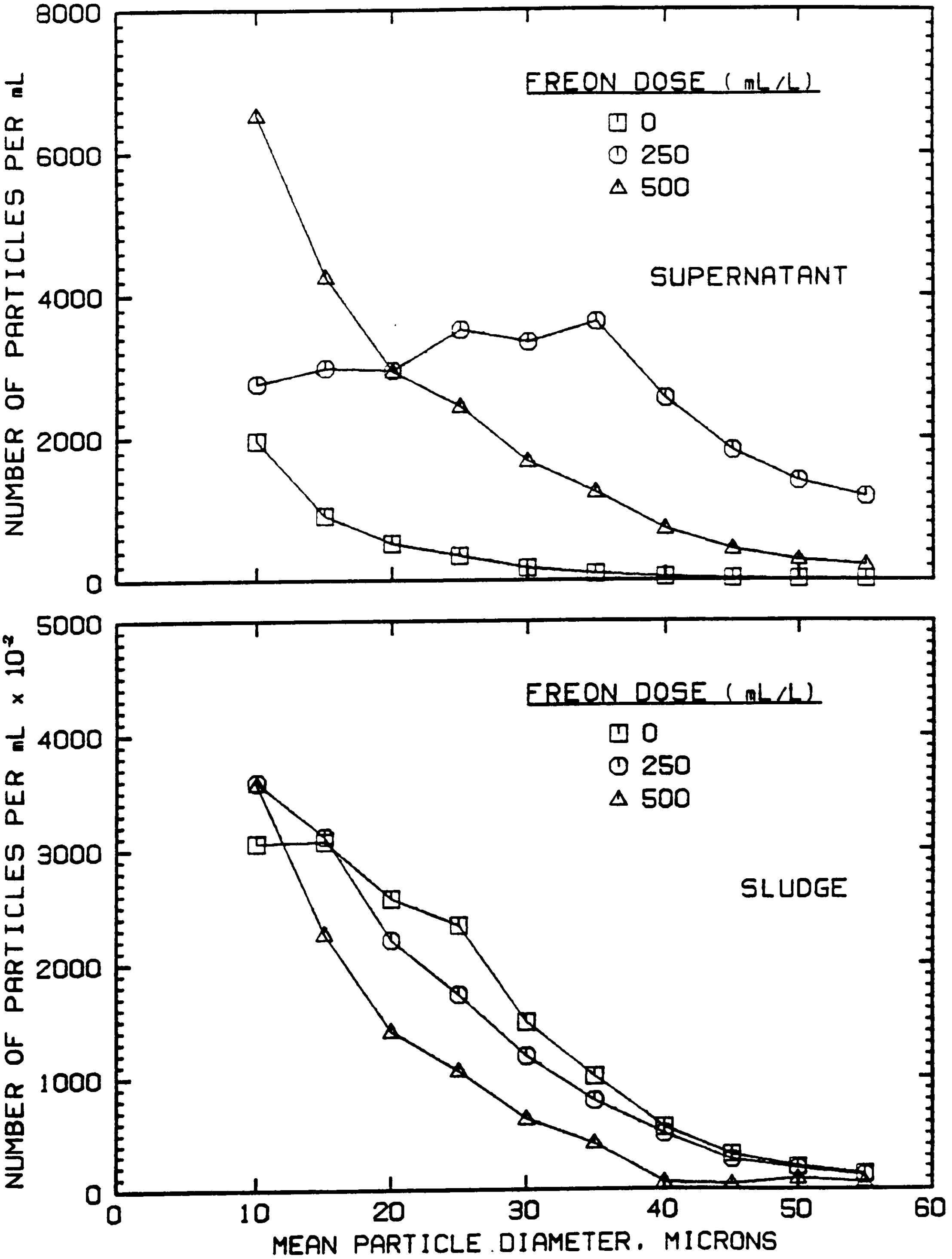


FIGURE 12. PARTICLE SIZE DISTRIBUTIONS. FREON-CONDITIONED WASTE ACTIVATED SLUDGE (BATCH EXPERIMENTS)

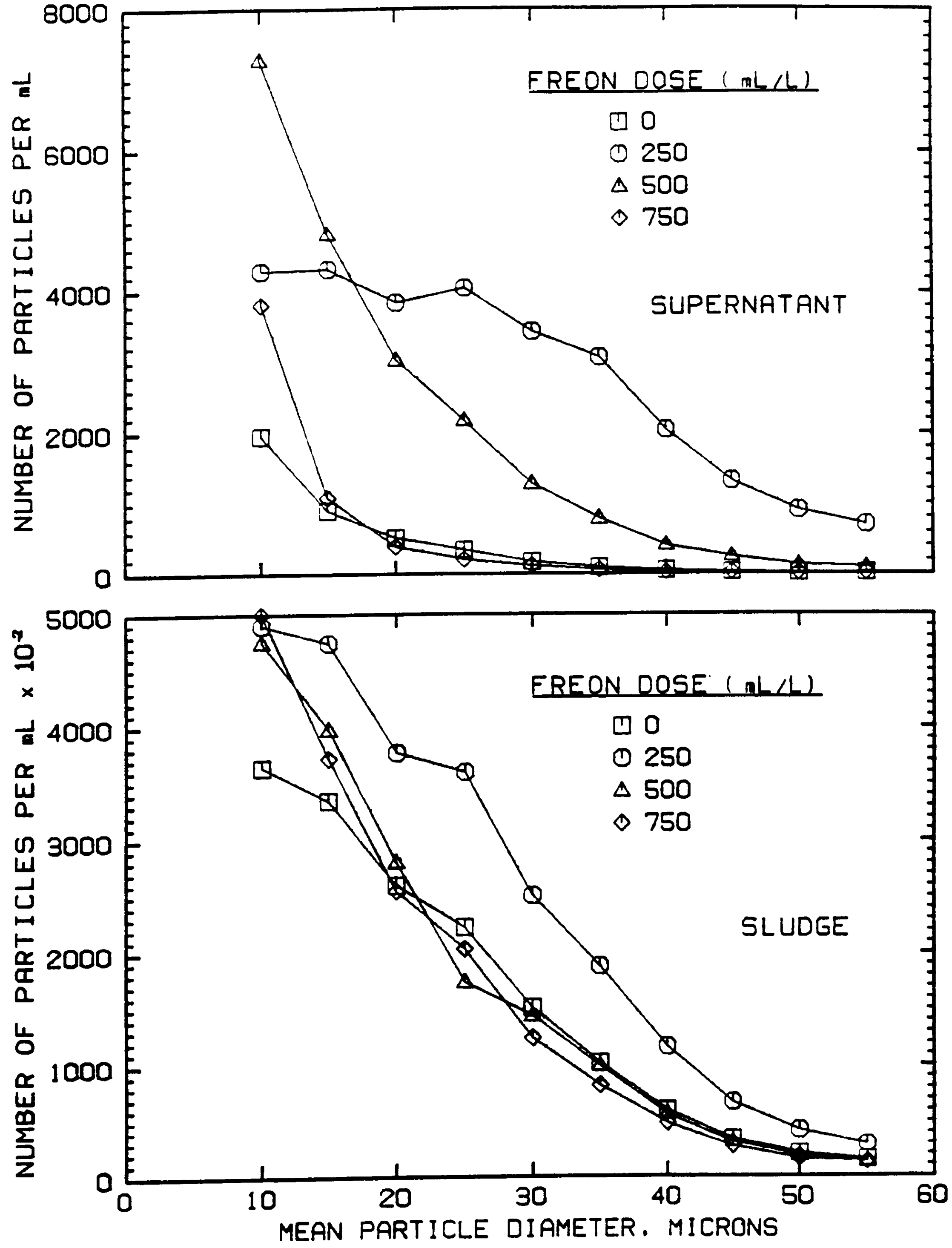


FIGURE 13. PARTICLE SIZE DISTRIBUTIONS. FREON-CONDITIONED WASTE ACTIVATED SLUDGE (CONTINUOUS EXPERIMENTS)

This suggests that there may have been an increase in the number of particles with MPD between 55 and 250 μm. (There was no measurable solids fraction with MPD greater than 250 μm.)

Batch-conditioned supernatant samples had a very large total number of particles, up to seven times that of the unconditioned samples. Most continuously conditioned samples also had large numbers of particles in the supernatant.

Supernatant particle size distributions had two distinct shapes. The first decreased steadily, at a decreasing rate, as particle size increased, and was similar to distributions observed in other experiments for both conditioned and unconditioned samples. The second was relatively flat for size ranges with MPD less than 35 μm, and then decreased in a similar manner to the first distribution. Each of the two distributions were observed for both conditioned and unconditioned samples, and the second was characteristic of supernatant which has been allowed to settle, suggesting that these differences were the result of unintentional inconsistencies in sample preparation prior to particle analysis.

There were small decreases in floc density noted for both batch and continuously conditioned samples. These decreases would imply the association of previously unbound water with sludge flocs, if that conclusion were not contradicted by the increase in dewatered solids concentrations discussed below. Given the increase in dewatered solids, it is more likely that any decrease in floc density resulted from the association of Freon bubbles with the flocs, giving rise to the foam observed in all samples.

TOC increased moderately with conditioning, from values of 8 to 12 mg/L for unconditioned samples, to values of 34 to 54 mg/L for conditioned samples. TOC tended to increase with increasing total Freon volume applied. TOC had also increased for butane-conditioned samples, and it was speculated that the source of a certain fraction of the TOC was entrained butane. Unlike butane, however, Freon is not measured by TOC analyses. The increase in organic carbon must have originated from a different source, either from particles ruptured during freezing or as fines produced by mixing.

Dewatering Characteristics - There were increases in vacuum-filtered and centrifuged solids respectively for certain batch- and continuously Freon-conditioned samples of waste activated sludge. Vacuum-filtered solids increased 63 percent for one-stage conditioning, approaching the level of improvement established by indirect conditioning. Continuous conditioning with 250 and 500 mL/L Freon resulted in smaller increases. In contrast, the sample conditioned with 750 mL/L Freon produced no cake at all in 30 minutes of dewatering.

Centrifuged solids concentration increased by percentages similar to that obtained with indirect freezing. Smaller increases were obtained with higher doses, whether administered continuously or in stages. Improvement in dewatered solids for indirectly frozen sludge was attributed to the removal of floc moisture. As water was squeezed from the floc, the floc became more compact and, thus, more dense. According the the alternative interpretation, particle structuress were broken apart, releasing water, and then recoalesced in new floc structures of higher density. In either case, increases in dewatered solids were accompanied by increases in floc density.

As suggested above, the decrease in floc density observed in Freon-conditioned samples was likely the result of the foam formed by the Freon bubbling through the sludge during the freeze-thaw process. The conditioning effect of the Freon might have resulted in net increases in density, had the conditioning process not been compromised by the effects of foaming.

As can be seen from Figure 14, Freon conditioning of waste activated sludge resulted in large increases in specific resistance, which varied directly with Freon dose. Increases were very large for Freon doses of 500 mL/L or more. The order-of-magnitude increases in specific resistance, which worsened with higher Freon dose for both batch- and continuously conditioned samples, were not likely the results of changes in particle size distributions, which were minimal, but more likely caused by the inclusion of Freon bubbles in the sludge as foam. The increase was greatest for the two-stage batch-conditioned sample, mixed only intermttently, than for the continuously conditioned sample also treated with 500 mL/L, mixed throughout the contact time. This is consistent with the interpretation of the interplay of mixing and foaming developed in the results of butane conditioning of waste activated sludge reported in the preceding section; that is, longer mixing times ameliorated

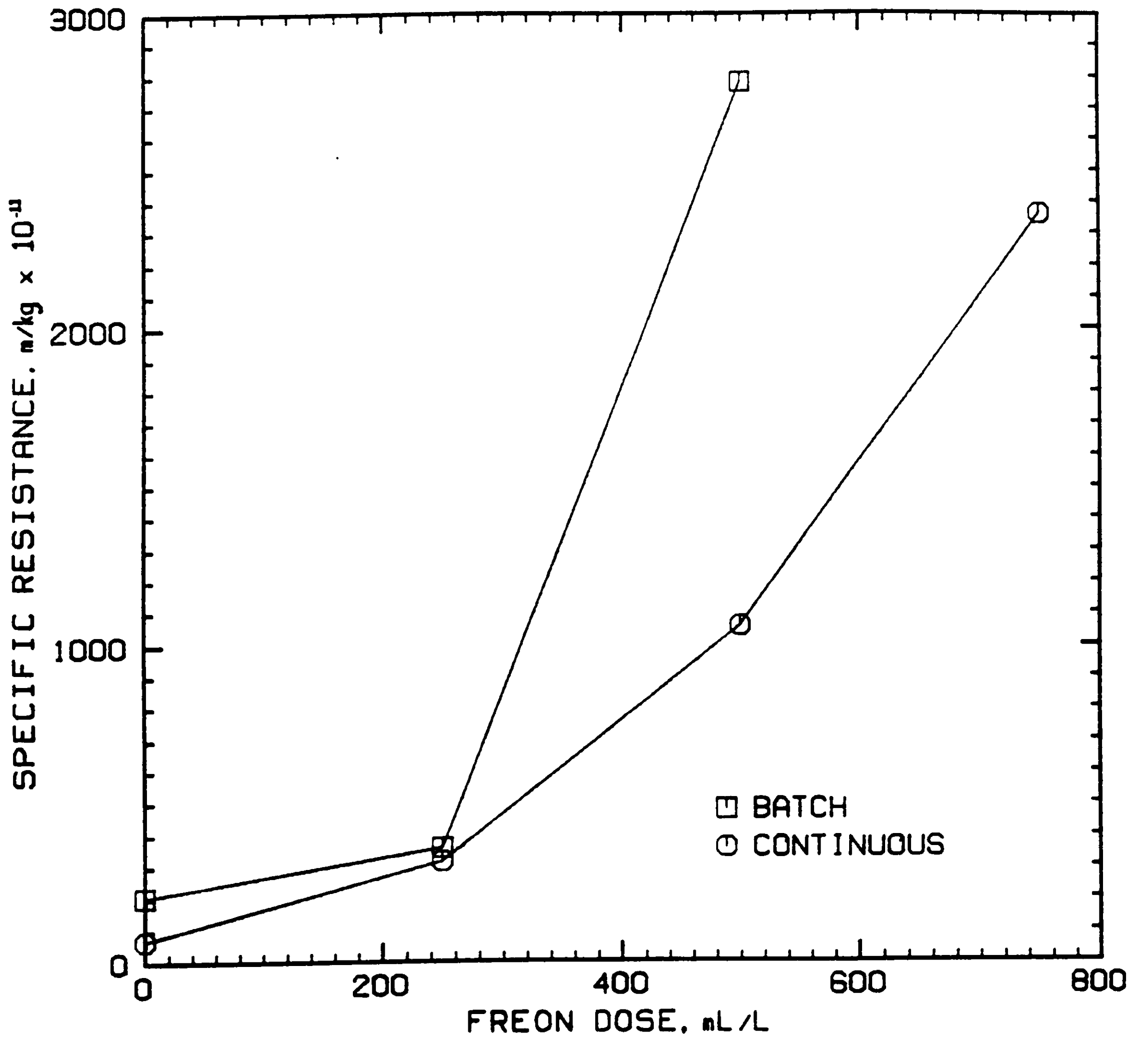


FIGURE 14. SPECIFIC RESISTANCE VS FREON DOSE.
FREON-CONDITIONED WASTE ACTIVATED SLUDGE.

the negative effects of foaming.

STROUBLES CREEK PRIMARY SEWAGE SLUDGE

Samples of unconditioned primary sewage sludge from Stroubles Creek Wastewater Treatment Plant dewatered poorly. Not only did the sludge filter very slowly, with high specific resistance, but no cake formed during the Buchner funnel test. Conditioning was expected to improve filtration rates and cake quality.

Polymer Conditioning

Samples of dry solids Stroubles Creek primary sewage sludge were conditioned with 10, 20, 75, 100, 150, and 200 mg/L Betz 1160. Polymer conditioning was successful in greatly decreasing specific resistance, as well as producing a cake of moderate solids concentration upon vacuum filtration at higher polymer doses. The results of analyses and determinations on conditioned and unconditioned samples of primary sewage sludge are presented in Table 13.

Particle and Chemical Characteristics - Polymer conditioning of Stroubles Creek primary sewage sludge resulted in reductions of the total number of particles with mean particle diameter (MPD) less than 250 µm, as determined by particle counts, and in decreases in the relative number of very small particles (MPD = 10 µm).

As can be seen from Table 13, there was a steady decrease with

TABLE 13

RESULTS OF ANALYSES
POLYMER-CONDITIONED PRIMARY SEWAGE SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Polymer Dose, mg/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.05 - 1.06	26,800	7,900	25	299	6.4
10	-	17,300	5,000	37	311	6.3
20	-	16,100	13,700	21	285	6.3
75	-	10,400	15,100	30	268	6.5
100	1.05 - 1.06	7,200	9,300	67	288	6.5
150	1.07	5,300	9,400	85	289	6.5
200	1.07	3,700	7,900	83	294	6.5

TABLE 13 (cont'd)

DEWATERING CHARACTERISTICS

Polymer Dose, mg/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	1.5	*	17.4	7,100	0.3
10	1.5	*	-	5,300	-0.2
20	1.3	*	-	5,200	-0.6
75	1.1	*	17.9	160	-0.8
100	1.6	22.0	17.2	210	-0.6
150	1.9	25.9	17.4	340	-0.1
200	1.7	27.0	17.7	64	-0.6

Note:

* No cake produced in 30 minutes of dewatering.

increasing polymer dose in the total number of particles represented by the particle distributions of sludge samples. There were only slight changes in the weight fraction of total solids retained on a 250-μm sieve in samples conditioned with less than 100 mg/L polymer; however, samples conditioned with 100 mg/L or more showed large gains in this fraction. Successively greater doses of polymer resulted in fewer numbers of particles in each analyzed size range, especially in size ranges with MPD less than 25 μm, as can be seen from Figure 15.

Like sludge samples, conditioned supernatant samples had many fewer particles than the unconditioned supernatant sample, especially in the size range with MPD equal to 10 μm. The total number of particles with MPD less than 250 μm in most conditioned supernatant samples did not decrease strictly with increasing polymer dose, however. Anomalies may have resulted from handling inconsistencies prior to settling. Large reductions in the number of small particles (MPD less than 20 μm) in the supernatant at all polymer doses were noted.

Floc density of the primary sewage solids increased slightly with polymer conditioning, with the bulk of particles increasing in density from 1.05 and 1.06 g/L for the unconditioned sample and samples conditioned with 100 mg/L polymer or less, to 1.07 g/L for samples conditioned with 150 and 200 mg/L polymer.

Dewatering Characteristics - Dewatering characteristics of Stroubles Creek primary sewage sludge improved greatly with polymer conditioning. Specific resistance decreased for all polymer doses,

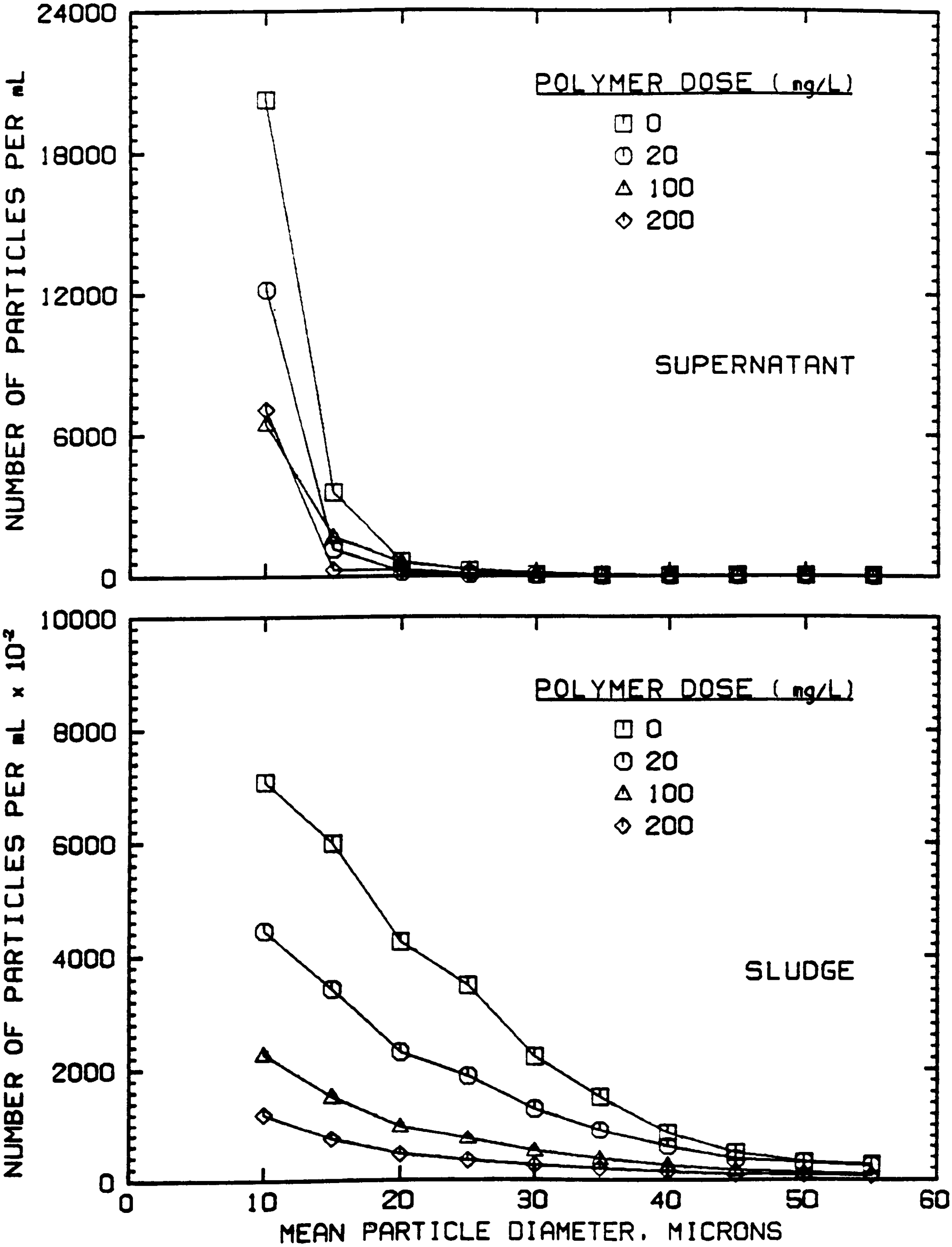


FIGURE 15. PARTICLE SIZE DISTRIBUTIONS, POLYMER-CONDITIONED PRIMARY SEWAGE SLUDGE.

as shown in Figure 16. Also, higher polymer doses succeeded in producing a vacuum-filtered cake of moderate solids content, and specific resistance was much reduced. It was likely that the increasing improvement in dewatering characteristics of primary sewage sludge conditioned with increasing amounts of polymer resulted from the changes in particle size distribution; specifically, the reduction in the number of small particles in sludge and supernatant. Small particles are generally responsible for cake blinding, and their presence and interference in the unconditioned sample was signalled by a positive blinding coefficient.

The reversal of the sign of the blinding coefficient for all conditioned samples as well as the ability of samples conditioned with higher polymer doses to form a cake during vacuum filtration probably resulted from an increase in the size of the particles constituting the sludge.

Centrifuged solids, dewatered by different mechanisms and less susceptible to changes in particle size distribution, remained stable for all polymer doses. Had changes in floc density been associated with changes in the water balance, centrifuged solids might have varied accordingly.

Indirect-Contact, Freeze-Thaw Conditioning

Indirect-contact, freeze-thaw conditioning of Stroubles Creek primary sewage sludge resulted in a substantial decrease in specific resistance. Although initial solids concentration more than doubled,

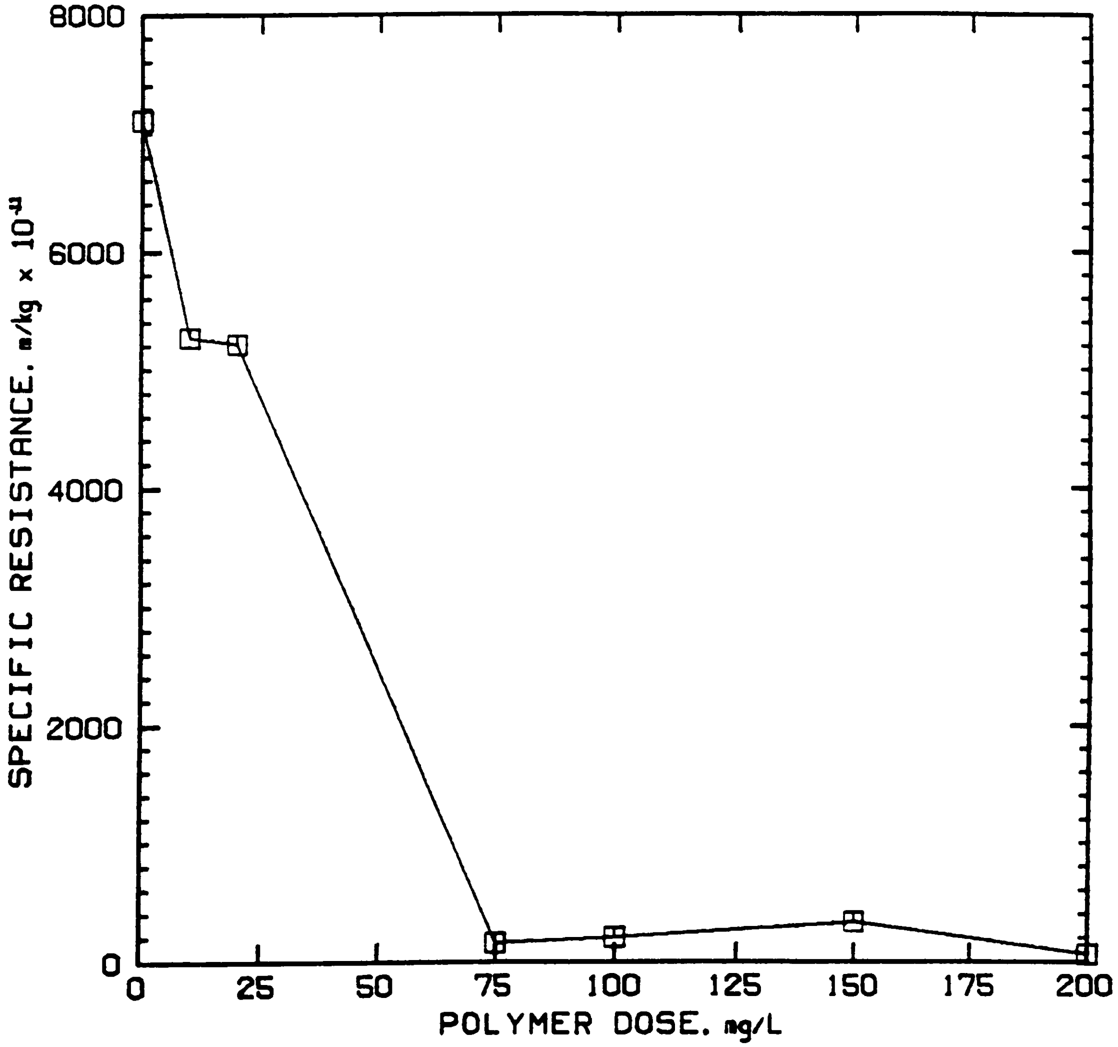


FIGURE 16. SPECIFIC RESISTANCE VS POLYMER DOSE.
POLYMER-CONDITIONED PRIMARY SEWAGE SLUDGE.

and particle characteristics showed a shift towards larger, more dense particles, cake solids concentrations showed no improvement. In general, indirect freezing was not as effective as polymer addition in improving the dewatering characteristics of primary sludge.

Results of analyses and determinations for an indirectly frozen sample and an unconditioned sample of Stroubles Creek primary sewage sludge are presented in Table 14.

Particle and Chemical Characteristics - Indirect-contact, freeze thaw conditioning of primary sewage sludge resulted in reduction of the total number of particles represented by the particle size distribution and in a decrease of the relative number of very small particles (mean particle diameter (MPD) = 10 μm). As can be seen from Table 14, the total number of particles represented by the distribution decreased sharply with conditioning, as did the weight fraction of total solids passing through a 250-um sieve. As can be seen from Figure 17, there were many less particles with MPD equal to 10 μm in the conditioned sludge and supernatant samples, with the conditioned samples also having fewer particles than the unconditioned samples in each size range.

Average floc density of indirectly frozen primary sewage sludge increased from 1.045 to 1.06 g/mL. The range of densities broadened, with the lower limit extended from 1.055 to 1.03 g/mL, and the upper limit from 1.10 to 1.11 g/mL.

The changes in floc density suggested that the increase in

TABLE 14

RESULTS OF ANALYSES
INDIRECT-CONTACT, FREEZE-THAW-CONDITIONED PRIMARY SEWAGE SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Conditioning Method	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
None (Control)	1.055 - 1.10 $(1.045)^*$	22,200	144,000	57	56	6.9
Indirect Freeze	1.03 - 1.11 $(1.06)^*$	8,300	11,500	87	103	6.3

DEWATERING CHARACTERISTICS

Conditioning Method	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
None (Control)	2.1	**	16.9	2,600	-0.1
Indirect Freeze	4.8	**	11.3	500	3.3

Notes:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

** No cake produced in 30 minutes of dewatering.

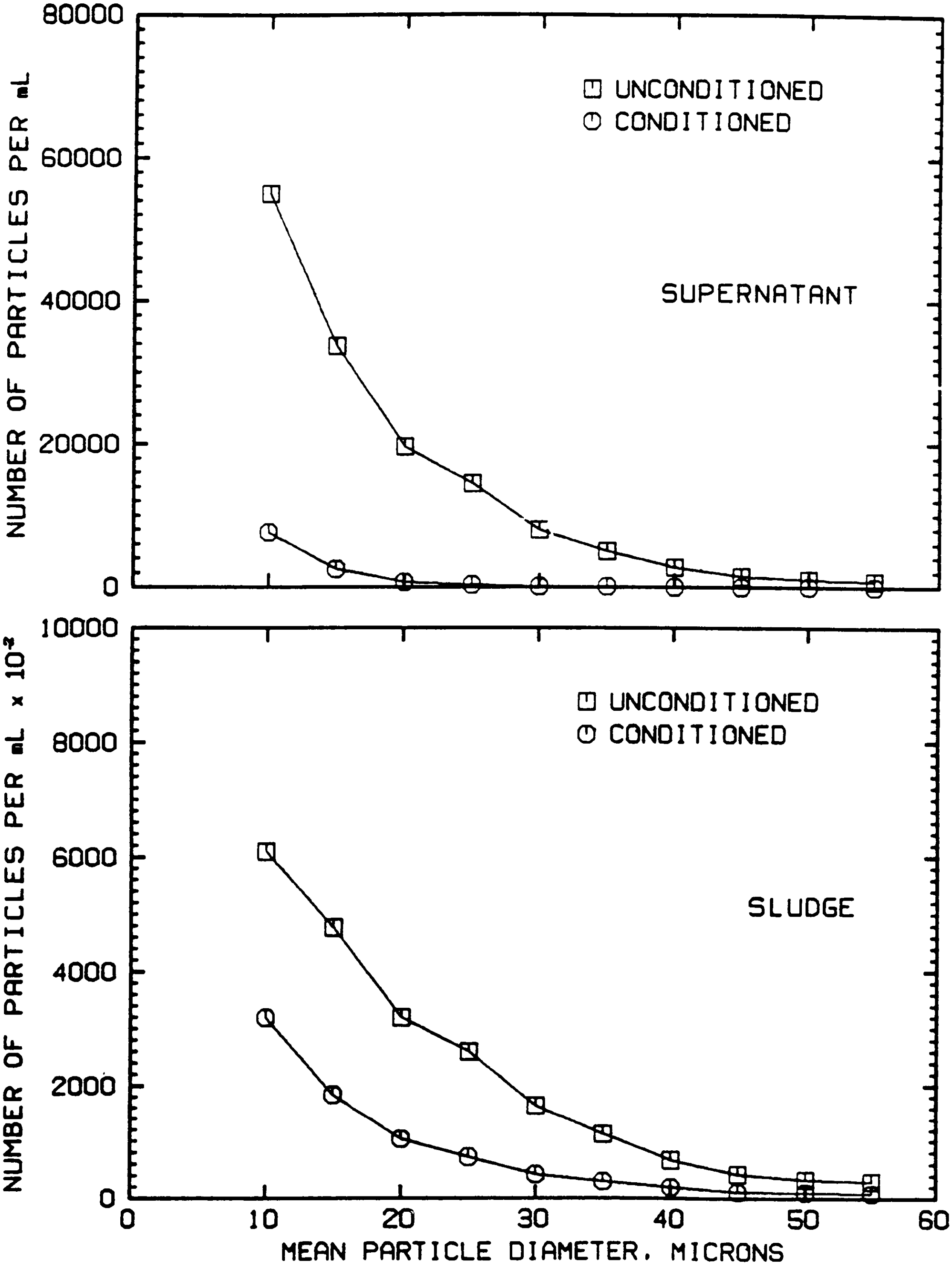


FIGURE 17. PARTICLE SIZE DISTRIBUTIONS, INDIRECT-CONTACT FREEZE-THAW CONDITIONED PRIMARY SEWAGE SLUDGE.

particle size was not a simple amalgamation of existing flocs, as occurred during polymer conditioning. Particle size changes were more likely caused by destruction of existing floc structures during freezing, resulting in the freeing of previously bound water, and ensuing consolidation of released particles during thawing and storage. This interpretation would explain the change in the range of floc densities, which increased to encompass both less and more dense flocs, created as old particle attachments were broken and new ones formed, and the general increase in floc density, resulting from the release of floc water.

Dewatering Characteristics - Indirect-contact, freeze-thaw conditioning had varying effects on the dewatering characteristics of Stroubles Creek primary sewage sludge. Initial dry solids concentration increased over 100 percent, from 2.1 to 4.8 percent solids, with indirect freezing. Neither the conditioned nor the unconditioned sample, however, produced a cake after 30 minutes of dewatering. Centrifuged solids actually decreased over 30 percent with conditioning, from 17 to 11 percent solids.

There was a substantial decrease in specific resistance for the conditioned sludge. As for the polymer-conditioned sludge, the decrease was related to the increase in particle size. The decrease was not, however, as large as that obtained by the higher doses of polymer in comparative experiments. Changes in floc structure would account for the decrease in specific resistance and the increase in initial solids content. Likewise, the change in the blinding coefficient from negative to positive could result from a more tightly packed, and hence more compressible, cake structure, facilitated by floc restructuring.

Direct-Contact, Freeze-Thaw Conditioning with Butane

A 1-L sample of Stroubles Creek primary sewage sludge was fed 20 mL/min butane for a contact time of 40 minutes, resulting in a cumulative butane dose of 800 mL/L. Direct-contact, freeze-thaw conditioning of primary sewage sludge with butane resulted in a moderate reduction in specific resistance. Other parameters showed only slight changes. A shift in floc density range was observed; it was, however, dissimilar to the change in floc density which occurred upon indirect freezing.

Results of analyses and determinations on samples of primary sewage sludge conditioned with butane are presented in Table 15.

Particle and Chemical Characteristics - The major effect of butane conditioning on the particle size distributions of primary sewage sludge samples was a change in distribution shape. Although, as can be seen from Table 15, there was little difference in the total number of particles with mean particle diameter (MPD) less than 250 μm, as determined by particle counts, the conditioned sample had more particles than the unconditioned sample in size ranges with MPD less than 20 μm, and fewer particles in size ranges with larger MPD. In addition, the conditioned sample had a smaller percentage of sludge solids retained on a 250-μm sieve.

TABLE 15

RESULTS OF ANALYSES
BUTANE-CONDITIONED PRIMARY SEWAGE SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Butane Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen
		Sludge x 10^{-2}	Supernatant	
0	1.055 - 1.10 (1.045)*	22,200	144,000	57
800	1.035 - 1.045	21,500	86,000	36

DEWATERING CHARACTERISTICS

Butane Dose, mL/L	Solids Concentration, %		Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered		
0	2.1	**	4,100	-0.1
800	1.4	**	3,200	0.0

Notes:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

** No cake produced in 30 minutes of dewatering.

The quality of the conditioned supernatant sample as evaluated by particle concentration improved. The distribution of the conditioned supernatant sample represented fewer particles than that of the unconditioned supernatant sample in all size ranges, as can be seen from Figure 18. The number of particles in the size range with mean particle diameter of 10 μm were very close, however, with the major difference in magnitude noted in size ranges with mean particle diameter between 15 and 35 μm.

The average floc density of primary sewage sludge samples changed little with butane conditioning, but the distribution of density was altered. The unconditioned sample had particles ranging in density from 1.055 to 1.10 g/mL, with most particles forming a heavy band at 1.045 mg/mL, while particles in the conditioned sample were concentrated at densities of 1.035 and 1.045 mg/mL. This narrowing of the range of floc density was in contrast to the opposite effect resulting from indirect freezing.

Certain changes in particle characteristics, including deviations from the results of indirect-contact, freeze-thaw conditioning, can be explained as the influence of mixing, which served to mask changes that could be directly attributed to conditioning.

<u>Dewatering Characteristics</u> - Direct-contact, freeze-thaw conditioning with butane resulted in a moderate decrease of 22 percent in the specific resistance of primary sewage sludge. Initial solids content did not increase, as it had for indirectly frozen

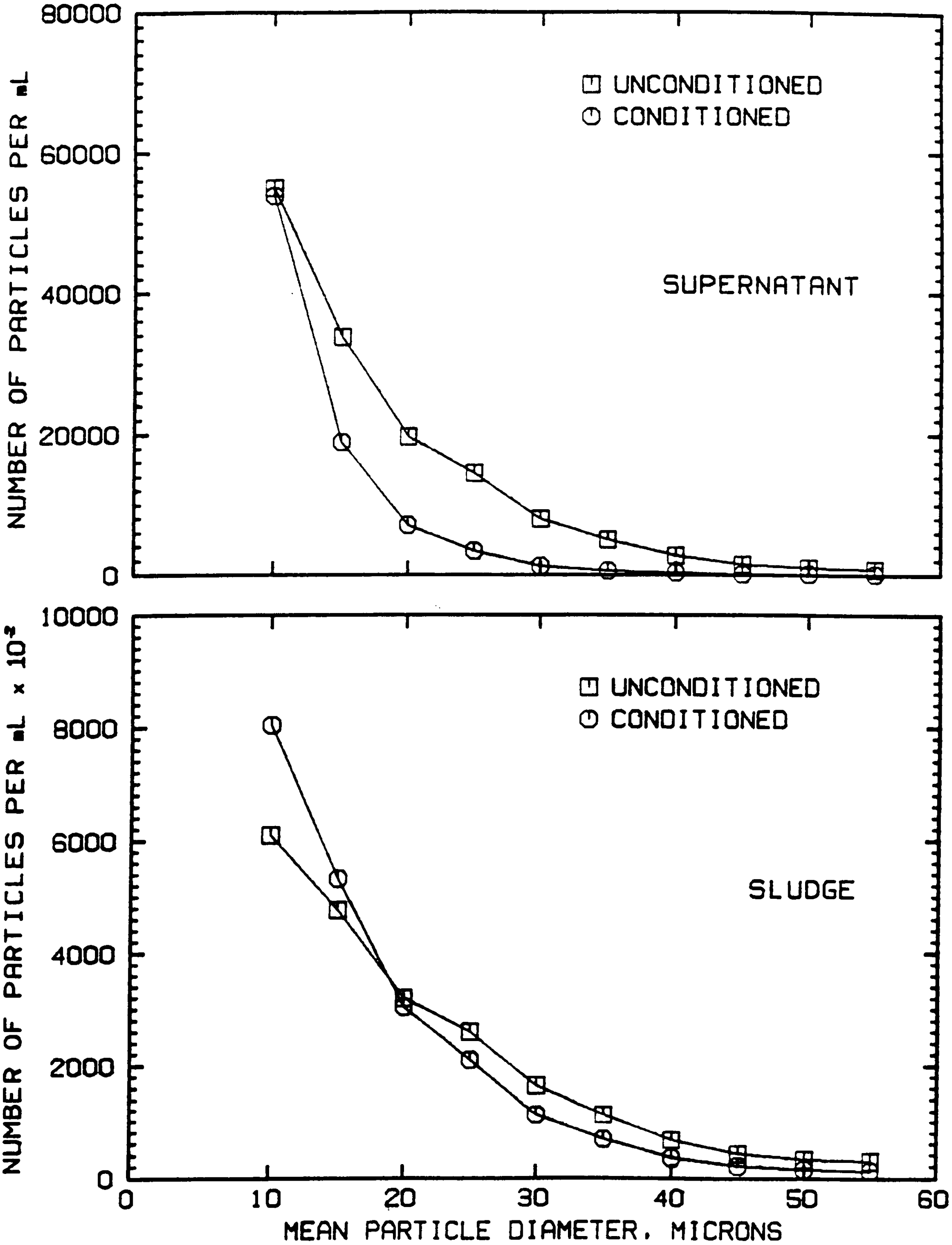


FIGURE 18. PARTICLE SIZE DISTRIBUTIONS. PRIMARY SLUDGE CONDITIONED WITH 800 mL/L BUTANE.

sludge. (Initial solids actually showed a slight decrease, but it is probably that the difference between the conditioned and unconditioned samples resulted from the difficulty in obtaining a representative sample.)

The blinding coefficient increased from zero for the unconditioned sample to a positive value for the conditioned sludge. However, the blinding coefficient varied from negative to zero to positive for different samples of unconditioned primary sludge, so the change may not have been significant.

The effects attributed to mixing and its effects on parameters of interest were discussed in detail in reporting earlier results of experiments with waste activated sludge. Like particle changes, changes in dewatering characteristics caused by conditioning may have been masked or neutralized by the effects of mixing. While floc restructuring caused by the freeze-thaw process probably resulted in reduced specific resistance, the decrease was not accompanied by the increase in initial dry solids content and strong change in blinding coefficient that characterized the indirectly frozen sample.

Direct-Contact, Freeze-Thaw Conditioning with Freon 12

A 1-L sample of Stroubles Creek primary sludge was subjected to 1-stage batch conditioning with 250 mL/L Freon. The main effect of direct-contact freeze-thaw conditioning with Freon 12 on primary sewage sludge was a large increase in specific resistance. Other measurable changes in dewatering and particle characteristics were small, with the exception of a large increase in the total number of particles in the supernatant.

Results of analyses and determinations on samples of primary sewage sludge conditioned with Freon 12 are presented in Table 16.

Particle and Chemical Characteristics - There was little change in sludge particle size distributions of primary sewage sludge samples conditioned with Freon 12, as can be seen from Figure 19. As can be seen from the data presented in Table 16, the total numbers of particles with mean particle diameter (MPD) less than 250 μm for the conditioned and unconditioned samples were similar. As for the butane-conditioned sludge, however, the number of particles in the Freon-conditioned sample in the size ranges with MPD less than 20 μm was greater than that in the unconditioned sample, and smaller in size ranges with larger mean particle diameter. As for butane-conditioned samples of primary sludge, this change probably resulted from combined effects of freeze-thaw conditioning and mixing.

Oddly, the supernatant from the conditioned sample had an excessively large number of particles, about 10 times that of the unconditioned sample, reflected in all size ranges of the distribution.

As it had for indirect-contact, freeze-thaw conditioning with butane, the range of floc densities of sludge conditioned with Freon 12 increased from a single band at 1.03 g/L, to two bands at 1.02 and 1.04 g/mL. This change, similar to that noted for indirect freezing

TABLE 16

RESULTS OF ANALYSES
FREON-CONDITIONED PRIMARY SEWAGE SLUDGE
(BATCH EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen
		Sludge x 10^{-2}	Supernatant	
0	1.03	26,700	25,000	25
250	1.02 - 1.04	28,300	241,000	-

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	1.5	*	17.4	7,100	0.3
250	1.1	*	15.9	23,200	0.1

Note:

* No cake produced in 30 minutes of dewatering.

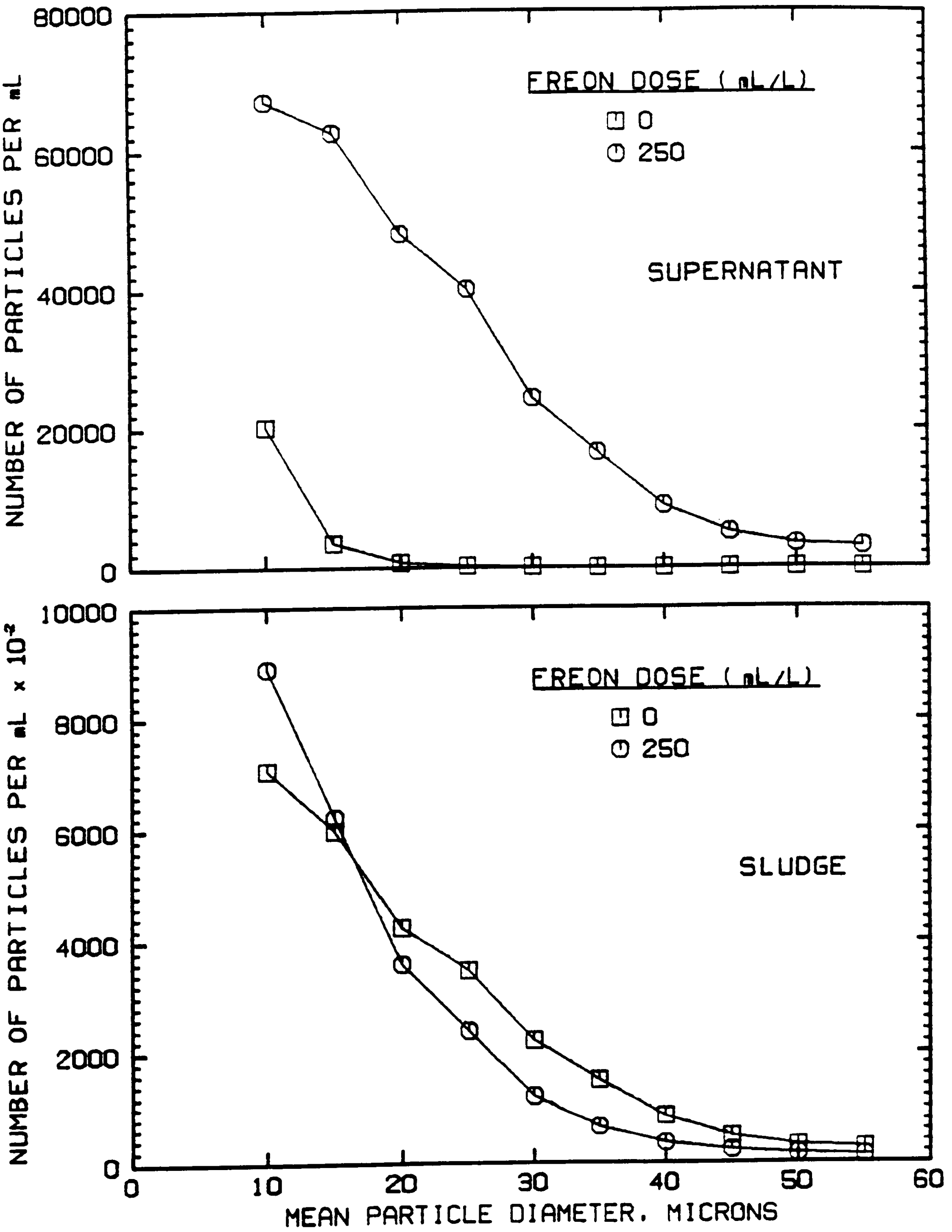


FIGURE 19. PARTICLE SIZE DISTRIBUTIONS. FREON-CONDITIONED PRIMARY SLUDGE (BATCH EXPERIMENTS)

of primary sludge samples, was the only indication that some conditioning effect had occurred.

Dewatering Characteristics - There was a threefold increase in specific resistance with conditioning, from 7100 to 23000 x 10^{11} m/kg. The general resistance to dewatering, evidenced by the decrease in both rate and extent of filtration, may have been caused, in part, by the increased number of small particles in the supernatant, which is generally recognized as a factor in poor response to dewatering[8]. Since mixing was minimal in batch experiments, it is likely that these small particles were generated by the freeze-thaw process.

Neither the conditioned nor the unconditioned sample produced a cake upon vacuum filtration, while centrifuged solids decreased slightly (less than 10 percent) with Freon addition.

STROUBLES CREEK PRIMARY SEWAGE SLUDGE/WASTE ACTIVATED SLUDGE MIXTURES

Unconditioned samples of a 50/50 mixture of Stroubles Creek primary sewage sludge and waste activated sludge showed dewatering characteristics similar to those of primary sludge. Specific resistance was high, and no cake formed upon vacuum filtration.

Polymer Conditioning

Samples of a 50/50 mixture of Stroubles Creek primary sewage and waste activated sludges were conditioned with 10, 30, and 50 mg/L Betz 1160. Polymer conditioning of the sludge mixture resulted both in greatly decreased specific resistance and in cake formation upon vacuum filtration. The major effect of polymer addition on particle characteristics was an increase in floc size and a small increase in floc density.

Results of analyses and determinations on mixtures of Stroubles Creek sludges are presented in Table 17.

Particle and Chemical Characteristics - Polymer conditioning increased the size of flocs constituting the mixture of Stroubles Creek primary sewage and waste activated sludges. As can be seen from Table 17, the total numbers of particles with mean particle diameter (MPD) less than 250 µm decreased with increasing polymer dose, as did the percent of sludge solids passing through a 250-µm sieve. The distributions for all sludge samples, conditioned and unconditioned, were similar in shape, with samples conditioned with increasing polymer doses having fewer particles in each size range. The same held true in general for the supernatant samples.

Floc density distributions shifted to represent increased average densities for polymer-conditioned solids. Particles in the unconditioned sample banded at densities of 1.02 and 1.04 g/mL. Samples conditioned with 30 and 50 mg/L showed a slight increase in particle density, with particles banding at 1.03 and 1.05 g/mL. The particles in the sample conditioned with 50 mg/L concentrated in a single band at 1.04 g/mL.

Dewatering Characteristics - The specific resistance of mixtures of Stroubles Creek primary sewage and waste activated sludges was

TABLE 17

RESULTS OF ANALYSES
POLYMER-CONDITIONED, PRIMARY SEWAGE/WASTE ACTIVATED SLUDGE MIXTURE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Polymer Dose, mg/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.02, 1.04	20,500	25,800	26	31	7.6
10	1.03, 1.05	12,100	11,200	38	26	7.2
30	1.03, 1.05	7,900	5,300	70	27	7.1
50	1.04	4,300	4,600	82	27	7.4

DEWATERING CHARACTERISTICS

Polymer Dose, mg/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	1.3	*	13.3	150	0.9
10	1.4	21.9	11.9	36	-0.6
30	1.5	18.8	12.2	8	-0.9
50	1.6	18.1	12.3	5	-1.0

Note:

* No cake produced in 30 minutes of dewatering.

greatly reduced by polymer addition, and in contrast to the unconditioned samples, conditioned samples formed a cake upon vacuum filtration. Centrifuged solids concentrations decreased slightly. It is interesting to note that while sludge specific resistance continued to decrease with increasing polymer dose, the corresponding cake solids concentration decreased slightly. This decrease was thought to be related to incorporation into the floc structure of previously free water by the amalgamation of flocs. (This concept was introduced and discussed in reporting results of experiments with waste activated sludge.)

The change in the blinding coefficient from positive to negative, considered in conjunction with the particle size increase, suggested that small, potentially cake-blinding particles were coagulated by the polymer into large, more homogenous flocs.

Indirect-Contact, Freeze-Thaw Conditioning

Indirect-contact, freeze-thaw conditioning resulted in major changes in the dewatering characteristics of a sample of a 50/50 mixture of Stroubles Creek primary sewage and waste activated sludges. Sludge specific resistance was substantially reduced, and a cake of moderate solids content formed upon vacuum filtration. Indirect freezing increased both the characteristic size and density of sludge particles.

Results of analyses and determinations on the indirectly frozen sample of the sludge mixture are presented in Table 18.

TABLE 18

RESULTS OF ANALYSES
INDIRECT-CONTACT, FREEZE-THAW-CONDITIONED PRIMARY SEWAGE/WASTE ACTIVATED SLUDGE MIXTURE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Conditioning Method	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
None (Control)	1.04	20,500	25,800	26	31	7.6
Indirect Freeze	1.05 - 1.07	3,600	11,000	78	152	6.7

DEWATERING CHARACTERISTICS

Conditioning Method	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
None (Control)	1.3	*	13.3	1,500	0.9
Indirect Freeze	2.1	24.2	7.9	130	-0.5

Note:

* No cake produced in 30 minutes of dewatering.

Particle Characteristics - Indirect-contact, freeze-thaw conditioning of a mixture of primary sewage and waste activated sludges resulted in a shift to larger particle size. As can be seen from particle totals in Table 18, the number of particles with mean particle diameter (MPD) less than 250 μm decreased, and, correspondingly, the weight fraction of sludge solids retained on a 250-μm sieve increased. The reduction in particle concentration with conditioning spread across the particle size distribution (Figure 20), with the conditioned sample having fewer particles than the unconditioned sample in each size range.

The density distribution of sludge mixture flocs changed with conditioning. Flocs from the unconditioned sample concentrated at 1.04 g/mL, while conditioned flocs were divided into a light band at 1.05 mg/mL and a heavy band at 1.07 g/mL. The increase in average density and widening of range were also noted for indirectly frozen samples of primary sludge.

Supernatant TOC increased substantially with conditioning from 31 to 152 mg/L, while pH decreased from 7.6 to 6.7. The changes in supernatant TOC and sludge pH suggested, as mentioned in reporting results of experiments with other sludges, that the freeze-thaw process disrupted existing flocs, resulting in the release of intrafloc components.

Dewatering Characteristics - Indirect-contact, freeze-thaw conditioning of the mixture of primary sewage and waste activated sludges resulted in a much improved response to vacuum-filtration.

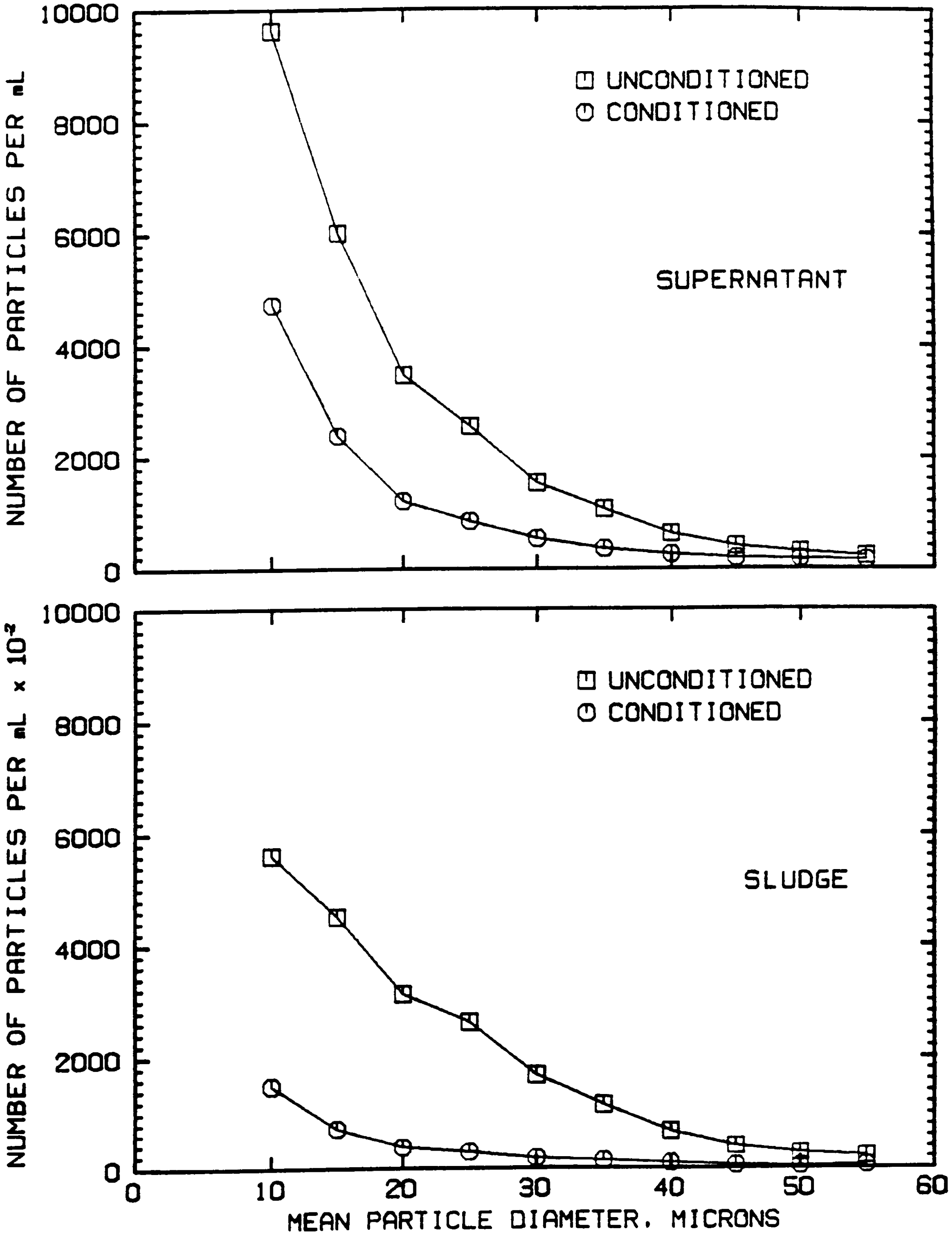


FIGURE 20. PARTICLE SIZE DISTRIBUTIONS, INDIRECT-CONTACT FREEZE-THAW CONDITIONED PRIMARY SEWAGE WASTE ACTIVATED SLUDGE MIXTURE.

The conditioned sampled dewatered with little resistance to a cake of moderate solids content. Conditioning reduced specific resistance to less than 10 percent of its value for the unconditioned sample, from 1500 to 130 x 10^{11} m/kg. The cake formed upon vacuum filtration was 24 percent solids, significantly higher than that produced with any polymer dose. (Centrifuged solids concentration, on the other hand, decreased 41 percent, from 13 percent solids for the unconditioned sample to 8 percent solids for the conditioned sample.)

These improvements, as well as the reversal of the blinding coefficient from a positive to a negative value, were attributed to the changes in floc structure drawn from the particle data. Freezing produced a denser, larger floc structure. This in turn resulted in a greater amount of water being outside the floc in the free water fraction, where it was drained more rapidly via vacuum filtration.

Direct-Contact, Freeze-Thaw Conditioning with Freon 12

Samples drawn from two mixtures of equal volumes of Stroubles Creek primary sewage and waste activated sludges were direct-contact freeze-thaw conditioned with Freon 12. The mixtures differed in solids content because of daily variablity in the primary sewage sludge. The first sludge mixture ("A"), with an initial dry solids concentration of about 1 percent, was subjected to 250 mL/L Freon 12 administered in a one-stage batch experiment. The second sludge mixture ("B"), with an initial dry solids concentration of about 3 percent, was subjected to Freon doses of 250 mL/L and 500 mL/L in one- and two-stage batch experiments, respectively.

The primary effect of Freon conditioning on these sludge mixtures was an increase in specific resistance. The main change in particle characteristics was an increased number of small particles and an increase in the range of floc densities. These changes were likely caused by a combination of conditioning and mixing effects.

The results of analyses and determinations on 1-liter samples of these 50/50 mixtures of Stroubles Creek primary and waste activated sludges are presented in Table 19.

Particle Characteristics - In general, Freon conditioning increased the concentration of small sludge particles in the primary sewage/waste activated sludge mixture. As can be seen from Table 19, the concentration of particles with mean particle diameter (MPD) less than 250 μm increased for each conditioned sample, although this increase was negligible for sludge mixture A. As a rule, the conditioned samples had more particles in the size ranges with mean particle diameter less than 20 μm, and fewer particles in size ranges with larger mean particle diameter (Figure 21). Otherwise, the particle size distributions for the conditioned and unconditioned samples were similar in shape. There was an increase with conditioning in the weight fraction of sludge solids retained on a 250-μm sieve for sludge mixture A, and a decrease for sludge mixture B.

As reported for other freeze-thaw experiments with primary sludge and primary/waste activated sludge mixtures, changes in floc

TABLE 19

RESULTS OF ANALYSES
FREON-CONDITIONED PRIMARY SEWAGE/WASTE ACTIVATED SLUDGE MIXTURE
(BATCH EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
Sample A						
0	1.04	20,500	25,800	26	31	7.6
250	1.03, 1.05	21,000	228,700	43	59	7.5
Sample B						
0	1.02 - 1.05	22,100	-	56	-	-
250	1.02 - 1.05	28,500	-	35	-	-
500	1.02	29,100	-	28	-	-

Table 19 (cont'd)

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
Sample A					
0	1.3	*	13.4	1,500	0.9
250	1.3	*	11.4	4,000	0.9
Sample B					
0	3.0	*	-	2,900	0.3
250	2.5	*	-	11,000	-0.3
500	2.1	*	-	15,000	-0.2

Note:

* No cake produced in 30 minutes of dewatering.

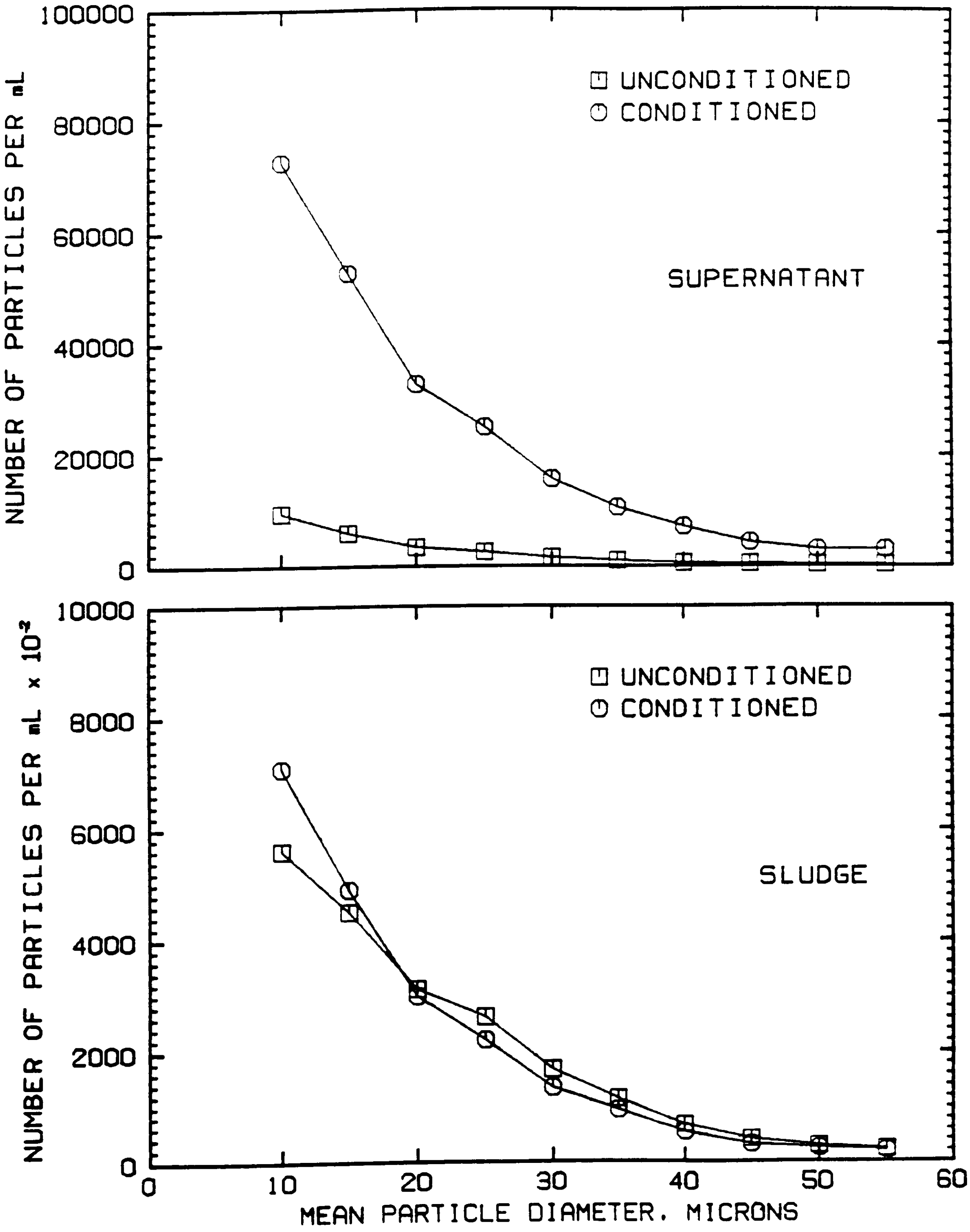


FIGURE 21. PARTICLE SIZE DISTRIBUTIONS. FREON-CONDITIONED PRIMARY SEWAGE/WASTE ACTIVATED SLUDGE MIXTURE (BATCH EXPERIMENTS)

density for sludge mixture A indicated increased heterogeneity in floc characteristics. While flocs in the unconditioned sample concentrated at a single density, flocs from the conditioned sample separated into two distinct bands. The unconditioned sample of sludge B already showed a range of floc densities, and there was no observable change with conditioning. The difference in the characteristic floc density profile for the two mixtures probably stemmed from the varying ratio of solids contributed by the primary fraction, with mixture B, having the larger percentage of primary solids, showing the greater variation in floc density.

The supernatant from conditioned sludge mixture A had an excessively high number of particles in each size range (Figure 21), with almost nine times the total number of particles when compared to the unconditioned sample. Supernatant TOC also increased. These results were similar to those reported for Freon-conditioned primary sludge, and seemed to point to combined effects from mixing and conditioning. The increase in the number of small particles in sludge mixture A outweighed the potential benefits of the general increase in particle size, as evidenced by the increase in the weight fraction of larger particles for sludge mixture A.

Dewatering Characteristics - Direct-contact, freeze-thaw conditioning of samples of the mixture of primary sewage and waste activated sludge with Freon 12 resulted in large increases in resistance to dewatering. Specific resistance values increased with conditioning from 1500 to 4000 x 10^{11} m/kg for the sludge mixture A sample, and from 2900 to 11000 and 15000 x 10^{11} m/kg for the sludge mixture B one- and two-stage samples, respectively. Neither the conditioned nor the unconditioned sample produced a cake upon vacuum filtration, while centrifuged solids decreased slightly with conditioning.

As for Freon-conditioned primary sludge, deterioration of dewatering characteristics could be ascribed to higher particle concentrations in the supernatant resulting from conditioning.

RAAP ALUM SLUDGE

Unconditioned samples of undiluted RAAP alum sludge dewatered to high solids concentration upon vacuum filtration and centrifugation, although they were moderately resistant to filtration. It was anticipated that polymer addition would improve filtration rate, and that freeze-thaw conditioning might improve both rate and extent of dewatering.

Effects of Dilution

Diluting different sludges has been observed to induce varying effects on dewatering characteristics. Ademiluyi et al.[12] found that specific resistance increased or decreased with increasing dilution, depending upon the sludge type and specific range of solids concentration. For example, specific resistance gradually increased for domestic sewage sludge diluted from 7 percent to 3 percent solids, and then decreased rapidly at higher dilutions. Water treatment plant sludge, in contrast, showed a decrease in specific resistance for dilutions from 8 to 3 percent solids, and then an increase at higher dilutions. It was speculated that at certain concentrations, conditions were favorable for release of fine particles, which then blinded the sludge upon filtration.

In this study, certain samples of RAAP alum sludge was diluted approximately 3 to 1 with tap water prior to conditioning to reduce solids concentration to about one percent. Dilution had little effect on the dewatering characteristics of unconditioned sludge. Specific resistance remained moderate, and the sludge samples dewatered to a high dry solids concentration. The sludge showed no tendency towards cake blinding, either with or without dilution. Particle size distributions varied, but there was no evidence of an increase in the number of smaller particles with dilution.

Polymer Conditioning

Samples of undiluted RAAP alum sludge were polymer-conditioned with 50, 75, 100, and 125 mg/L Betz 1160. Polymer addition resulted in substantial decreases in specific resistance and in slight changes in dewatered solids concentration. Likewise, increases in the characteristic size and density of sludge flocs were also observed.

The results of analyses and determinations on polymer-conditioned samples of undiluted RAAP alum sludge are presented in Table 20.

Particle and Chemical Characteristics - The main effect of polymer conditioning on particle characteristics of undiluted alum sludge was an increase in particle size. As can be seen from Table 20, the weight fraction of sludge solids retained on a 250-μm sieve increased, and the number of particles with mean particle diameter (MPD) less than 250 μm decreased. This shift towards larger particle size was also apparent across the size ranges represented by the particle size distributions depicted in Figure 22. For polymer doses of 100 mg/L and less, there was a decrease in the number of particles with MPD less than 20 μm, and an increase in the number of particles with MPD greater than 20 μm.

The 125 mg/L dose seemed to represent a threshold value for substantive conditioning. The total number of particles per mL with MPD less than 250 μm decreased sharply while the weight fraction of sludge solids retained on a 250-μm sieve increased to 75 percent.

Like particle size, floc density increased substantially with polymer conditioning. Mass balance calculations indicated that the increase reflected a 20 percent loss of floc water. Floc structure observed during floc density analyses also changed. The small, uniform flocs observed in unconditioned sludge were replaced by large, bulky aggregates.

The polymer could have caused the apparent release of floc water by reducing surface charge, thus permitting particles to draw closer together, and/or by physically trapping particles in a more tightly

TABLE 20

RESULTS OF ANALYSES
UNDILUTED, POLYMER-CONDITIONED ALUM SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Polymer Dose, mg/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen
		Sludge x 10^{-2}	Supernatant	
0	1.16 - 1.18 (1.17)*	29,700		3
50	-	29,000		42
75	-	25,500		53
100	-	23,500		40
125	1.18 - 1.22	5,500		75

DEWATERING CHARACTERISTICS

Polymer Dose, mg/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	4.5	20.4	15.5	230	0
50	3.8	21.0	14.6	85	-0.1
75	3.6	22.1	15.3	19	0
100	3.7	22.9	14.9	82	-0.5
125	3.7	19.6	16.3	12	-1.1

Note:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

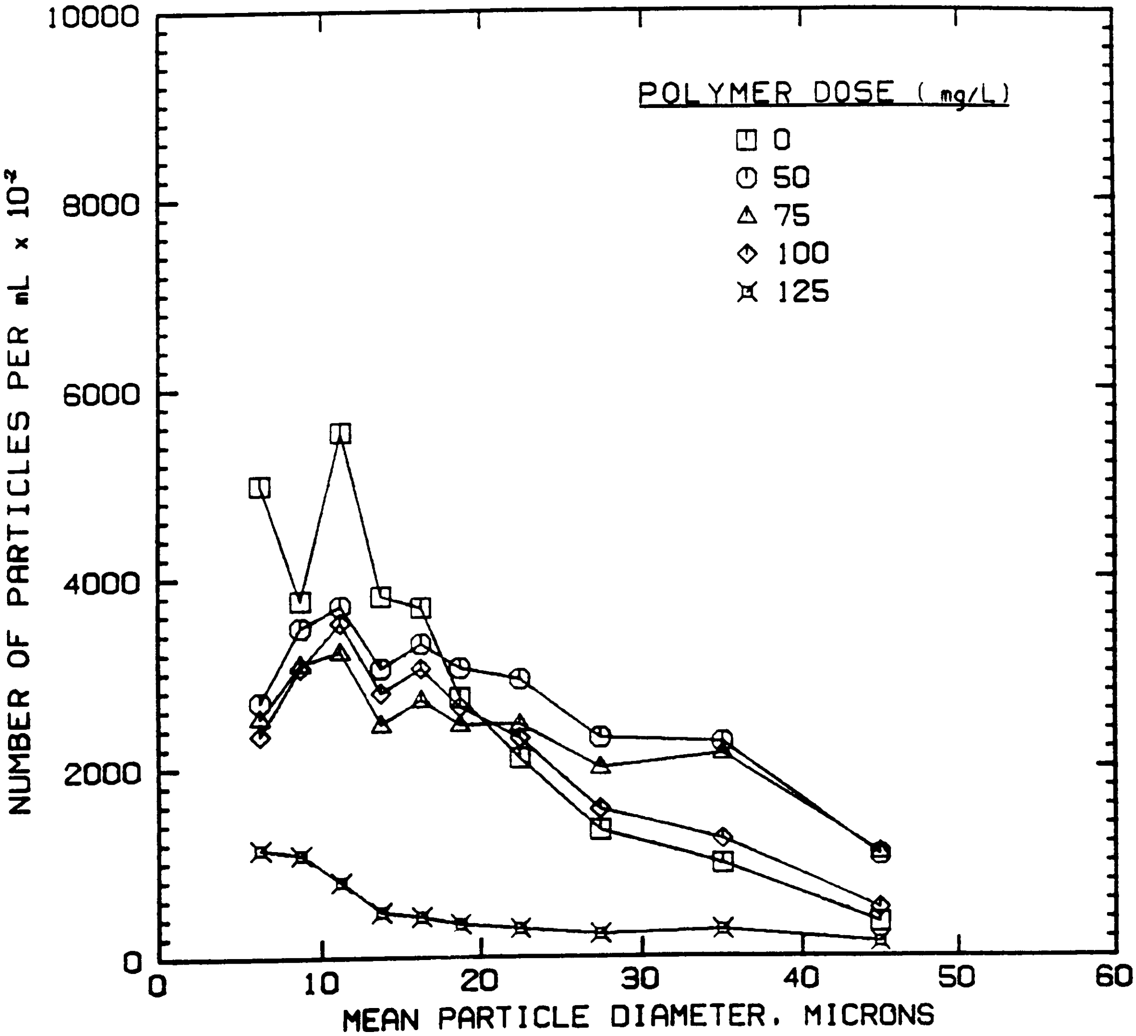


FIGURE 22. PARTICLE SIZE DISTRIBUTION. UNDILUTED POLYMER-CONDITIONED ALUM SLUDGE.

packed structure. Water originally measured as integral to the floc would have been displaced as particles drew, or were drawn, closer together.

Dewatering Characteristics - Changes in dewatering characteristics of polymer-conditioned samples of alum sludge were typical. Large decreases in specific resistance were observed, while improvements in dewatered cake solids concentration were slight.

Polymer conditioning resulted in only small changes in vacuum-filtered solids concentration. The unconditioned sample had a final cake solids concentration of 20 percent; the greatest improvement, noted for the sample conditioned with 100 mg/L polymer, was a 15 percent increase to 23 percent solids.

The specific resistance of all polymer-conditioned samples was reduced by at least 63 percent, to values of 85 x 10^{11} m/kg or less, when compared to the unconditioned sludge, which had a specific resistance of 230 x 10^{11} m/kg. Reductions in specific resistance did not vary with polymer dose, nor with the number of particles with MPD less than 250 μm, although there did appear to be a general inverse relationship between specific resistance and the weight fraction of sludge solids retained on a 250-μm sieve.

Effects of Dilution - Samples of diluted RAAP alum sludge were conditioned with 10, 50, and 100 mg/L Betz 1160. Polymer conditioning resulted in decreased specific resistance at all doses. Vacuum-filtered cake solids concentration remained stable, except at the highest polymer dose, where it decreased, while centrifuged solids concentration increased slightly for all polymer doses.

Floc density and particle size increased with increasing polymer dose. The largest change in particle characteristics was the sharp decrease in the number of small particles in the supernatant.

Results of analyses and determinations on samples of diluted alum sludge conditioned with polymer are presented in Table 21.

As can be seen from Figure 23, a major effect of polymer addition on the particle characteristics of diluted alum sludge was the decrease in the number of particles with mean particle diameter (MPD) of 10 μm. Particle size shifted towards more particles in the 25 to 35 μm range for the 10 and 50 mg/L polymer doses. As can be seen from Table 21, the 100 mg/L dose resulted in a more definite shift towards larger particles, with the weight fraction of sludge solids retained on a 250-μm sieve increasing from zero for the unconditioned sample to 50 percent.

The most striking result of polymer conditioning was in the reduction of the number of particles in the supernatant. Concentrations dropped at least two order of magnitude for all polymer doses, to less than 4 percent of the numbers in the unconditioned samples.

The 100 mg/L dose produced substantially different results in other areas as well. Whereas TOC had decreased and the floc density and sludge pH had remained virtually unchanged for lesser doses, the sample treated with 100 mg/L polymer showed an increase in TOC and floc density, and a decrease in pH.

TABLE 21

RESULTS OF ANALYSES
DILUTED, POLYMER-CONDITIONED ALUM SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Polymer Dose, mg/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.16 - 1.22 (1.17)*	12,000	25,600	0	20	7.7
10	1.16 - 1.22	13,100	900	7	8	7.8
50	1.16 - 1.22 (1.18)*	9,200	700	0	11	7.5
100	1.17 - 1.22 (1.21)*	10,400	500	59	33	6.7

DEWATERING CHARACTERISTICS

Polymer Dose, mg/L	Solids Concentration, %			Specific Resistance, m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	0.9	22.3	9.6	160	-0.2
10	1.4	22.0	11.2	13	-0.7
50	1.3	22.2	10.8	10	-0.9
100	1.4	20.8	11.2	6	-0.9

Note:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

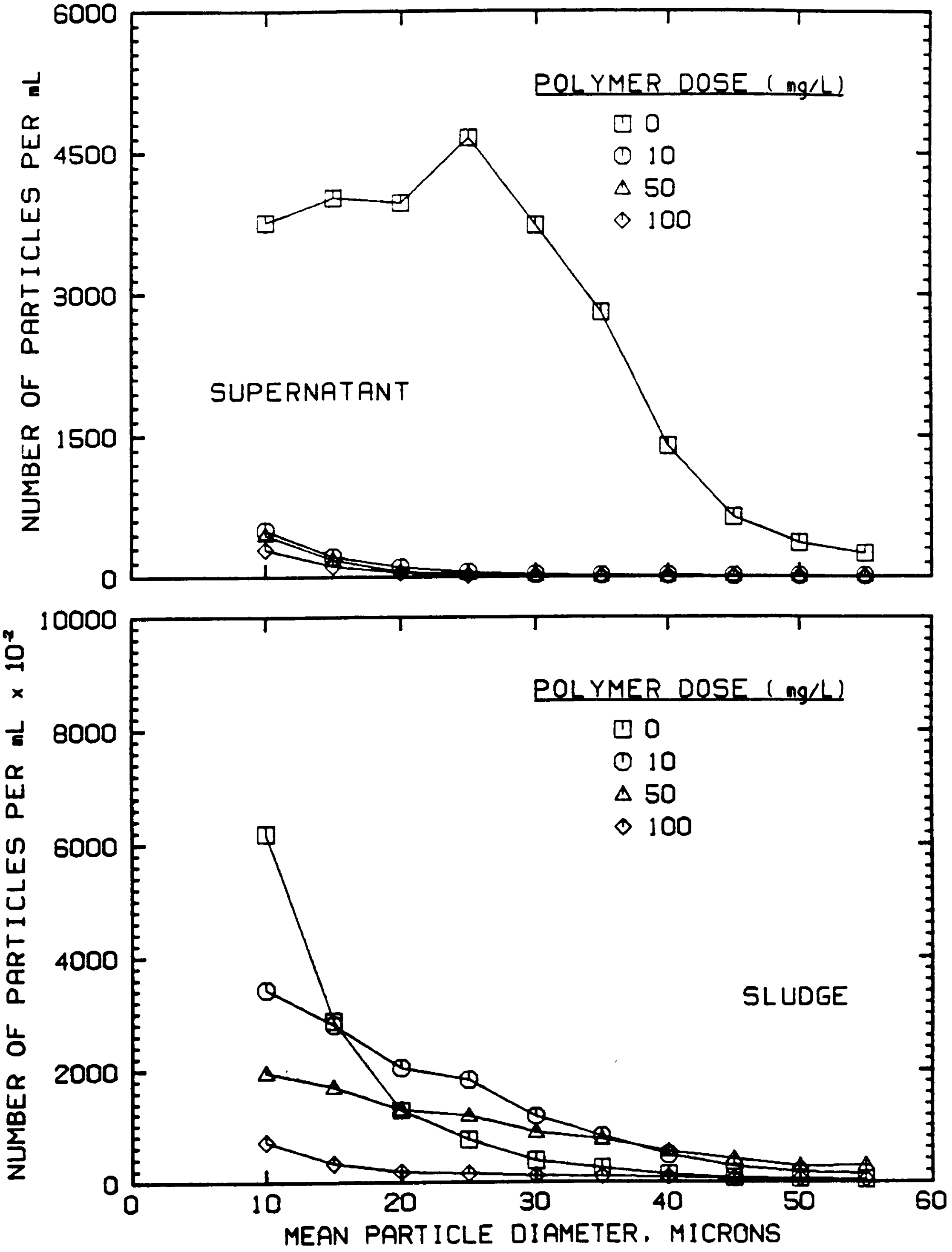


FIGURE 23. PARTICLE SIZE DISTRIBUTIONS, DILUTED POLYMER-CONDITIONED ALUM SLUDGE.

The effects of polymer conditioning on the dewatering characteristics of samples of diluted alum sludge were similar to those observed for undiluted sludge. There was a large decrease in specific resistance for all polymer-conditioned samples, while variations in dewatered solids concentrations were small.

Specific resistance decreased to approximately the same level at each polymer dose, from an unconditioned value of 160 x 10^{11} m/kg to 13 x 10^{11} m/kg and less for conditioned samples.

Indirect-Contact, Freeze-Thaw Conditioning

Indirect-contact, freeze-thaw conditioning greatly improved the dewatering characteristics of undiluted RAAP alum sludge, outperforming polymer conditioning in all areas. Specific resistance decreased greatly, while vacuum-filtered and centrifuged solids concentrations increased 200 and 150 percent, respectively. Decreased specific resistance was associated with large, concommitant increases in particle size and floc density.

The results of analyses and determinations for an indirectly frozen sample of undiluted RAAP alum sludge are presented in Table 22.

Experimental Observations - Thawed alum sludge solids had the granular, gritty appearance typical of freeze-thaw conditioned sludge. A large amount of supernatant was decanted from the product sludge, resulting in a fivefold increase in initial dry solids content.

TABLE 22

RESULTS OF ANALYSES
UNDILUTED, INDIRECT-CONTACT, FREEZE-THAW-CONDITIONED ALUM SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Conditioning Method	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
None (Control)	1.16 - 1.22 (1.17)*	27,500	17,700	0	13	8.2
Indirect Freeze	)1.3	24,500	17,400	73	14	7.5

DEWATERING CHARACTERISTICS

Conditioning Method	Solids Concentration, %			Specific Resistance m/kg x 10^{11}
	Initial	Vacuum-Filtered	Centrifuged	
None (Control)	3.2	21.0	10.0	190
Indirect Freeze	14.6	39.9	25.5	1

Note:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

Particle and Chemical Characteristics - The large increase in particle size resulting from indirect-contact, freeze-thaw conditioning of undiluted alum sludge was apparent from the large amount of sludge solids retained on a 250-μm sieve for the conditioned sludge. No measurable fraction was retained upon sieving the unconditioned sample, while 76 percent of the conditioned sludge solids fell in this size range.

The similarities in distributions of particles with mean particle diameter (MPD) less than 250 μm (Figure 24), as well as the total number of particles represented by these distributions, for conditioned and unconditioned samples were belied by comparison of the weight fractions of total sludge solids that the distributions represented. The particle distribution depicted for the unconditioned sample represented approximately 100 percent of sludge solids, while the distribution depicted for the conditioned sample represented a much smaller fraction of solids---approximately 24 percent---from a more concentrated sludge. The number of particles in these size ranges would have decreased with conditioning, had supernatant not been removed from the sample, thereby increasing initial solids content.

Floc density increased greatly with conditioning, from 1.17 g/mL to more than 1.3 g/mL, representing the release of up to 46 percent of floc water.

Dewatering Characteristics - Indirect-contact, freeze-thaw conditioning of undiluted alum sludge resulted in large increases in

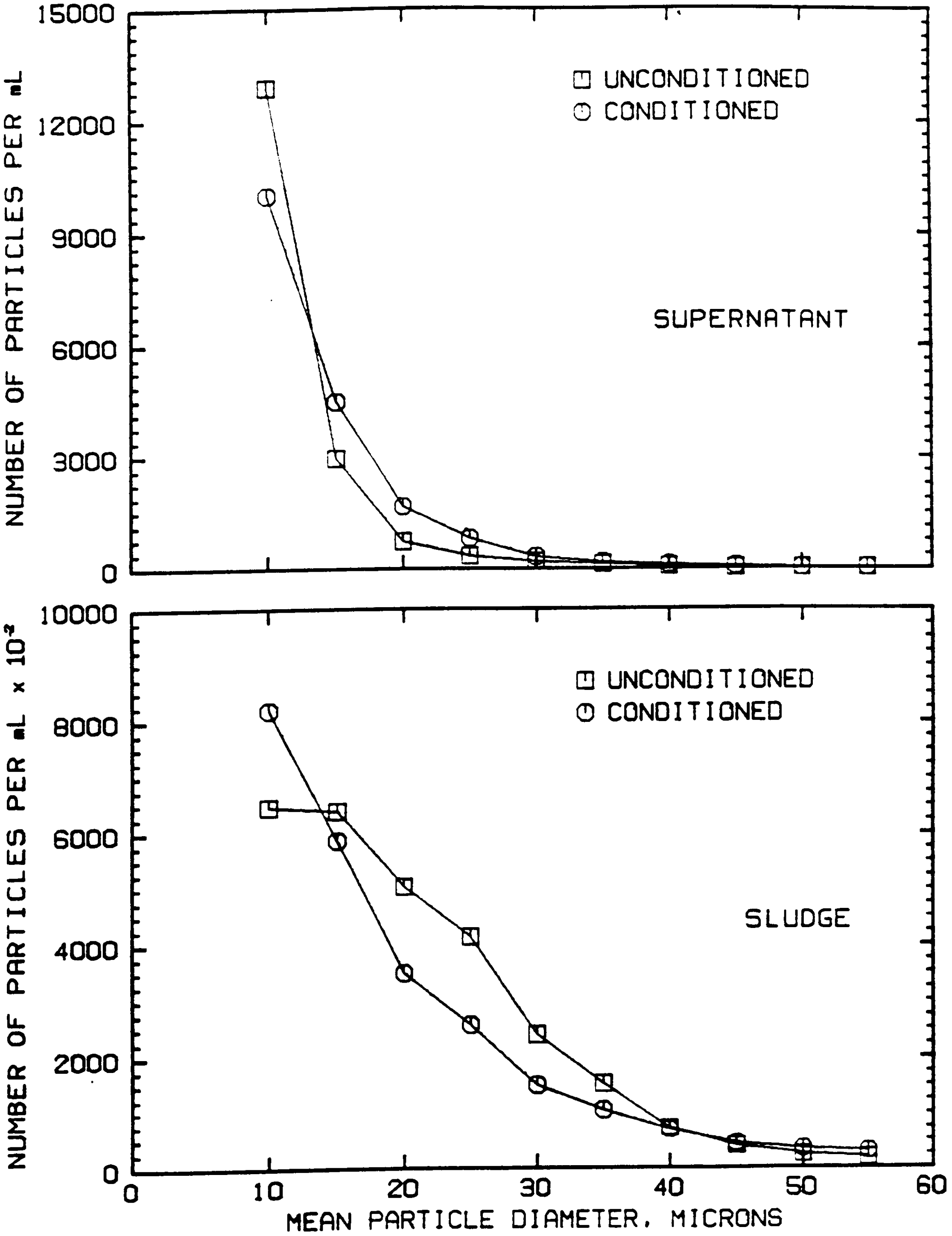


FIGURE 24. PARTICLE SIZE DISTRIBUTIONS, UNDILUTED INDIRECT-CONTACT FREEZE-THAW CONDITIONED ALUM SLUDGE.

initial and dewatered solids concentrations and a large decrease in specific resistance. Initial solids content increased 450 percent, from 3.2 to 14.7 percent solids. Conditioned vacuum-filtered cake solids concentration nearly doubled, from 21 percent solids for the unconditioned sludge to 40 percent solids. Centrifuged solids almost tripled, from 10 to 26 percent. The change in specific resistance was correspondingly large, with a decrease from 190 x 10^{11} m/kg for the unconditioned sample, to less than 1 x 10^{11} m/kg for the conditioned sample.

These results were the classic response to indirect-contact, freeze-thaw conditioning: a dramatic increase in particle size and density, accompanied by large improvements in specific resistance and in initial and dewatered solids concentration. All evidence indicated that a large amount of water previously unavailable for removal was released by the freeze-thaw process, and that the removal of this water, reduction of surface charge, compression or rupture of particles, and/or other changes resulting from the freeze-thaw process, enhanced the formation of large, dense flocs with remarkable settling and dewatering properties.

Effects of Dilution - The dewatering characteristics of diluted RAAP alum sludge were greatly improved by indirect-contact, freeze-thaw conditioning. Specific resistance was reduced to less than one percent of its initial value, and there were large increases in initial and dewatered solids concentrations. Floc density and particle size increased, and there was a large reduction in the number of particles in the supernatant.

The results of analyses and determinations for an indirectly frozen sample of RAAP alum sludge diluted to one percent are given in Table 23.

The main change in particle characteristics, as can be seen from Table 23, was an increase in the percent of sludge solids larger than 250 μm. Approximately 78 percent of the conditioned sludge solids were retained on a 250-μm sieve, as compared to none for the unconditioned sample. Particle size distributions, while apparently similar, as can be seen from Figure 25, were fundamentally different, in that the initial solids concentration of the conditioned sludge was 15 times that of the unconditioned sludge. These results were similar to those observed for undiluted sludge. Initial solids for conditioned samples of diluted and undiluted sludges were practically identical, as were weight fractions of solids retained on a 250-μm sieve.

Supernatant distributions for the two samples were also quite different. There were very few particles in the indirectly frozen supernatant sample, less than five percent of the total number of particles counted for the unconditioned sample. In contrast, the undiluted sludge had shown no such improvement. Also, conditioning of diluted sludge resulted in a moderate decrease in supernatant TOC, from 20 to 8 mg/L, while there had been no improvement for undiluted sludge.

The changes in dewatering characteristics of diluted alum sludge

TABLE 23

RESULTS OF ANALYSES
DILUTED, INDIRECT-CONTACT, FREEZE-THAW-CONDITIONED ALUM SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Conditioning Method	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
None (Control)	1.16 - 1.17	12,000	25,600	0	20	7.7
Indirect Freeze	)1.3	8,000	700	78	8	7.3

DEWATERING CHARACTERISTICS

Conditioning Method	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
None (Control)	0.9	22.3	9.6	160	-0.2
Indirect Freeze	15.1	41.0	27.9	3	-1.0

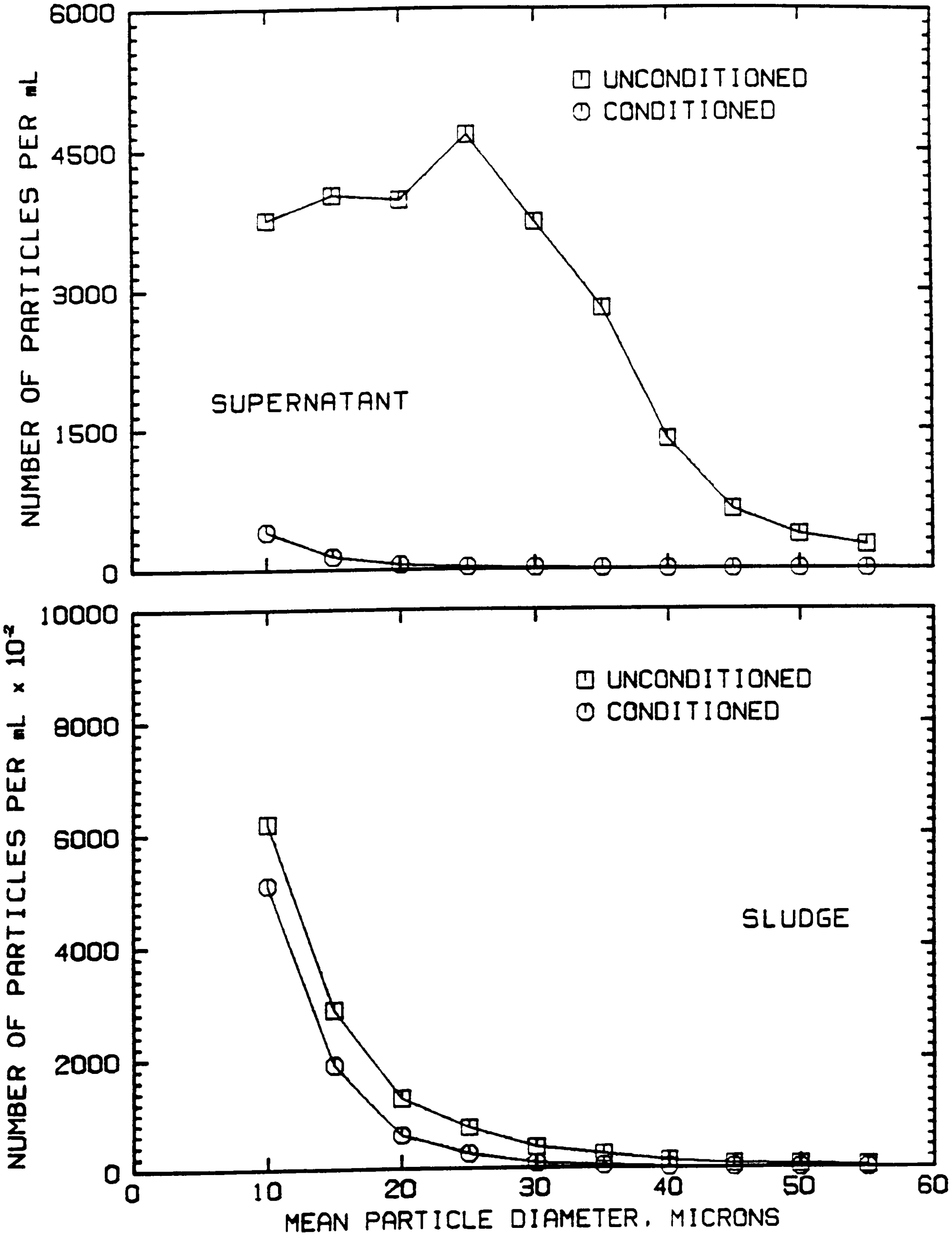


FIGURE 25. PARTICLE SIZE DISTRIBUTIONS. DILUTED INDIRECT-CONTACT FREEZE-THAW CONDITIONED ALUM SLUDGE.

with indirect-contact freeze-thaw conditioning were striking, as they had been for the undiluted sludge. The increases in solids concentration, both initial and dewatered, for the indirectly frozen sample of diluted alum sludge were very large. Initial dry solids concentration increased from 1 to 15 percent. Vacuum-filtered cake solids concentration nearly doubled with conditioning, from 22 percent dry solids for the unconditioned sample to 41 percent dry solids for the indirectly frozen sample. Centrifuged dry solids concentration nearly tripled, from 10 to 28 percent dry solids. The specific resistance of the sludge decreased sharply following freeze-thaw conditioning.

Direct-Contact, Freeze-Thaw Conditioning with Butane

One-L samples of undiluted RAAP alum sludge were conditioned with 20 mL/min butane for contact times of 20, 30, and 40 minutes, resulting in butane doses of 400, 600, and 800 mL/L, respectively. The only improvement noted in dewatering characteristics was a slight increase in vacuum-filtered solids concentrations at the highest butane dose. Specific resistance increased to similar values for all conditioned samples. The only consistent change in other parameters, including particle characteristics, was a moderate decrease in pH.

Results of analyses and determinations on samples of butane-conditioned, undiluted alum sludge are presented in Table 24.

Experimental Observations - The butane conditioning process generated large amounts of foam in alum sludge samples. In general,

TABLE 24

RESULTS OF ANALYSES
UNDILUTED, BUTANE-CONDITIONED ALUM SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Butane Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 µm)		% Sludge Solids Retained on 250 µm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge x 10^{-2}	Supernatant			
0	1.14 - 1.21 (1.17, 1.19)*	29,700	3,000	3	13	8.8
400	1.15 - 1.19 (1.19)*	30,400	1,900	9	20	7.1
0	1.175 - 1.195 (1.175)*	23,200	-	0	10	8.1
600	1.175 - 1.185	79,000	26,100	0	16	7.3
0	-	30,500	-	6	-	8.2
800	1.17 - 1.20 (1.175)*	30,400	19,200	0	25	7.2

TABLE 24 (cont'd)

DEWATERING CHARACTERISTICS

Butane Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	2.0	26.2	15.1	170	-0.6
400	2.0	26.9	28.1	290	-0.4
0	1.3	24.0	14.3	160	-0.2
600	2.8	23.7	14.3	290	-0.2
0	2.3	23.2	14.3	170	-0.1
800	2.0	26.0	15.4	360	-0.1

Note:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

the foam had a higher initial solids content (about 4 percent) and dewatered to a lower vacuum-filtered solids concentration (about 20 percent) than either the unconditioned or conditioned sludge.

Particle Characteristics - Changes in particle characteristics varied considerably and inconsistently; there were no general trends observed which could be related to increasing butane dose. The cause of certain changes were suggested by the results of previous experiments with other types of sludge.

There was little change in the distribution of particles with mean particle diameter (MPD) less than 50 μm for the sample conditioned with 400 mL/L butane (Figure 26), and the total number of particles per mL with MPD less than 250 μm also remained about the same. However, the weight fraction of sludge solids retained on a 250-μm sieve increased slightly and the floc density distribution narrowed, shifting towards a typically more dense particle. The changes in floc density and weight fraction reflected an increase in the percentage of larger, more dense particles, suggesting that some freeze-thaw conditioning might have occurred.

The changes in the particle characteristics of the undiluted alum sludge sample conditioned with 600 mL/L (Figure 27), while different from those resulting from the 400 mL/L dose, also indicated that certain freeze-thaw effects might have occurred. Initial solids content more than doubled, accounting for a certain part of the increase in the total number of particles per mL with MPD less than 250 μm. Although most of the increase was in the size ranges of MPD

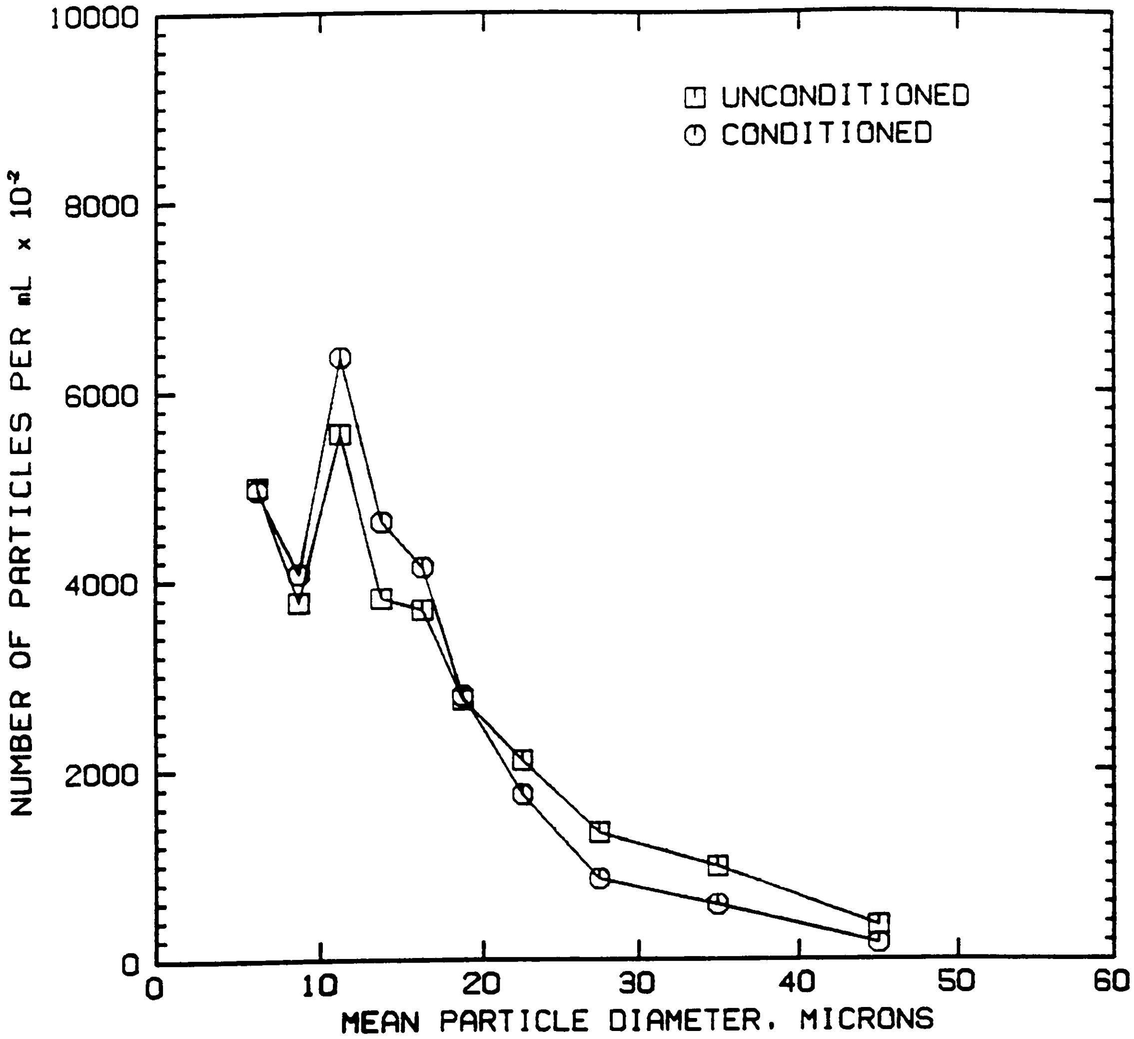


FIGURE 26. PARTICLE SIZE DISTRIBUTIONS. UNDILUTED ALUM SLUDGE CONDITIONED WITH 400 mL/L BUTANE.

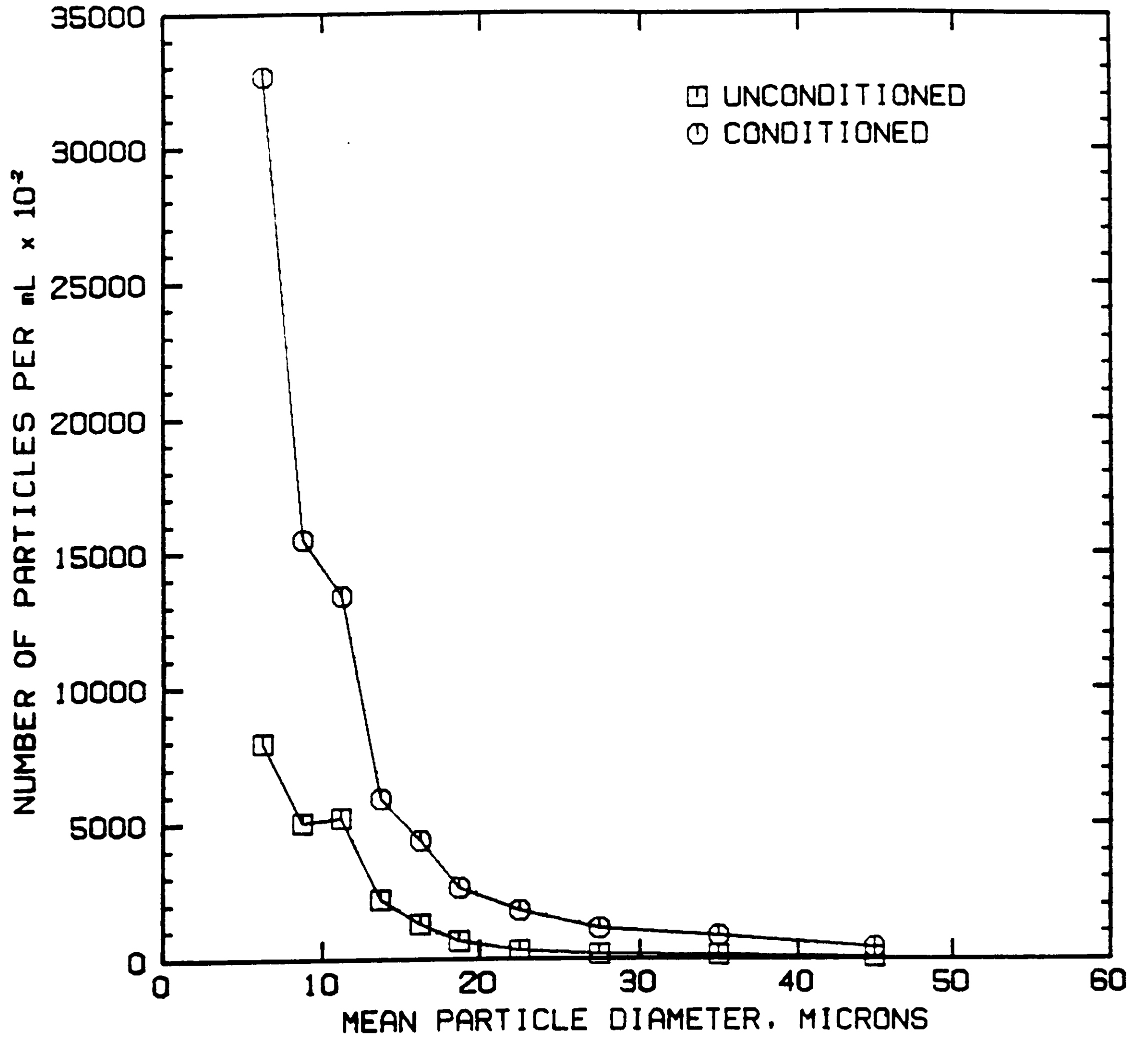


FIGURE 27. PARTICLE SIZE DISTRIBUTIONS. UNDILUTED ALUM SLUDGE CONDITIONED WITH 600 mL/L BUTANE.

of 10 µm or less, suggesting mixing-related changes, particle compression may have been responsible for a fraction of these smaller particles. The supernatant also contained a large number of small particles, most with MPD less than 10 µm.

The only noticeable change in particle characteristics for the sample conditioned with 800 mL/L butane was a decrease in the amount of solids retained on a 250-µm sieve, which may have resulted from the production of fines through freezing.

Dewatering Characteristics - The effects of butane conditioning on the dewatering characteristics of alum sludge were variable, with certain changes in dry solids concentration obtained upon vacuum filtration and centrifugation and increases in specific resistance. For butane doses of 400 and 600 mL/L, there was a small increase and decrease, respectively, in vacuum-filtered cake solids concentration, while cake solids concentration increased 13 percent for the 800 mL/L dose. Centrifuged dry solids concentration of the sample conditioned with 400 mL/L butane showed a large (perhaps anamolous) increase, but did not change for the sample conditioned with 600 mL/L butane, and decreased for the 800 mL/L dose.

Changes in specific resistance with butane conditioning were more consistent, as shown in Figure 28. Specific resistance increased for all butane-conditioned samples, from 160 to 170 x 10^{11} m/kg for the unconditioned samples, to more than double that value. Conditioning had no effect on the sign of the blinding coefficient, which was negative for all samples.

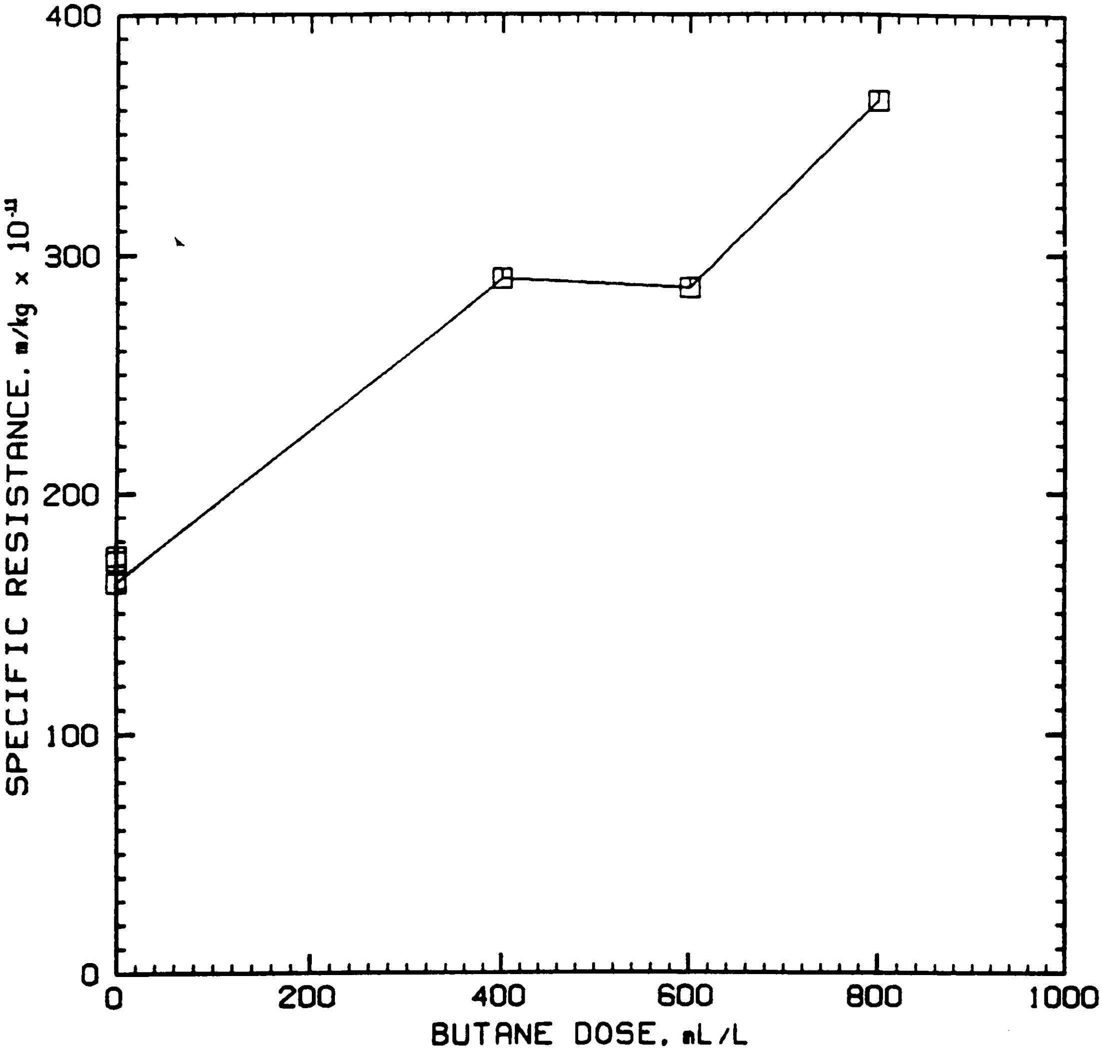


FIGURE 28. SPECIFIC RESISTANCE VS BUTANE DOSE, UNDILUTED BUTANE-CONDITIONED ALUM SLUDGE.

Contact times for these experiments were relatively short and the degree of freezing taking place indeterminate. This may explain the absence of any clear trends. The large increase in floc density, in the number of particles with MPD greater than 250 µm, and in centrifuged solids concentration for the sample treated with 400 mL/L butane, and the increase in initial solids concentration for the sample treated with 600 mL/L may have been indications of the conditioning effect of the freeze-thaw process. As suggested in reporting results of earlier experiments, the vacuum filtration process might have been more sensitive to interference from the foam generated during application of the butane, thus explaining the limited response in vacuum filtered solids and the increase in specific resistance. Improvement may also have been obscured by the detrimental effects of mixing.

The only trend consistent with the results of indirect freezing was a decrease in sludge pH for all conditioned samples.

Effects of Dilution - A one-liter sample of diluted RAAP alum sludge was conditioned with 20 mL/min butane for a contact time of 75 min, resulting in a butane dose of 1500 mL/L. This experiment represented an attempt to determine the effects of larger butane doses. The results were very similar to those obtained for smaller doses applied to samples of undiluted sludge. There were slight increases in vacuum-filtered and centrifuged solids concentrations, while the specific resistance of the sludge doubled. The range of floc density increased, while other particle characteristics remained unchanged.

Results of analyses and determinations on samples of butane-conditioned, diluted alum sludge are presented in Table 25.

Direct-Contact Freeze-Thaw Conditioning with Freon 12

One-L samples of undiluted RAAP alum sludge were conditioned with Freon 12 in batch and continuous experiments. In the batch experiments, samples were treated in one and two stages, with 250 mL Freon applied at each stage. In the continuous experiment, the sample was treated with 10 mL/min Freon for a contact time of 50 min. Thus, the sample treated in the one-stage batch experiment was exposed to 250 mL/L Freon; and the samples treated in the two-stage batch experiment and in the continuous experiment were exposed to 500 mL/L Freon.

In general, the application of Freon 12 to undiluted alum sludge samples had little effect on particle or dewatering characteristics. Specific resistance increased, whether the Freon was applied continuously or as a slug dose. The increase in specific resistance was smaller for batch experiments than for the continuous experiment, suggesting mixing effects. Vacuum-filtered solids concentration decreased for all conditioned samples. Centrifuged solids concentration increased slightly for samples batch-conditioned with Freon, but decreased for the continuously conditioned sample.

Results of analyses and determinations on samples of undiluted alum sludge conditioned with Freon are presented in Tables 26 and 27

TABLE 25

RESULTS OF ANALYSES
DILUTED, BUTANE-CONDITIONED ALUM SLUDGE

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Butane Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)	
		Sludge x 10^{-2}	Supernatant
0	1.16 - 1.17	18,700	30,300
1500	1.15 - 1.18	21,800	27,400

DEWATERING CHARACTERISTICS

Butane Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	1.1	21.3	10.0	121	-0.3
1500	1.2	23.1	10.9	205	0

TABLE 26

RESULTS OF ANALYSES
UNDILUTED, FREON-CONDITIONED ALUM SLUDGE
(BATCH EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)	
		Sludge x 10^{-2}	Supernatant
0	1.16 - 1.18 (1.17)*	24,500	25,700
250	1.16 - 1.18 (1.18)*	20,700	28,700
500	1.16 - 1.18 (1.18)*	28,100	230,000

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	3.3	16.1	10.0	150	-0.1
250	3.6	13.1	10.8	260	-0.3
500	3.1	15.1	11.1	250	-0.2

Note:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

TABLE 27

RESULTS OF ANALYSES
UNDILUTED, FREON-CONDITIONED ALUM SLUDGE
(CONTINUOUS EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density,* g/mL	Particles per mL (MPD less than 250 μm)	
		Sludge x 10^{-2}	Supernatant
0	1.16 - 1.18 (1.17)*	24,500	25,700
500	1.18	26,100	-

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	3.3	16.1	10.0	150	-0.1
500	3.4	**	9.5	500	4

Notes:

* Value in parentheses indicates concentration gradient where bulk of particles were observed.

** No cake produced in 30 minutes of dewatering.

for batch and semicontinuous experiments, respectively.

Particle Characteristics - Effects of Freon conditioning on the particle characteristics of samples of undiluted alum sludge were small. Average floc density increased slightly with Freon addition in both batch and continuous experiments, while there were no notable changes in other particle characteristics. Supernatant quality deteriorated considerably, with an order-of-magnitude increase in the number of particles with mean particle diameter (MPD) less than 250 μm in the supernatant from the sample conditioned in two stages with 500 mL/L total Freon, and the absence of any removable supernatant at all from the sample conditioned with 500 mL/L in the continuous experiment.

Dewatering Characteristics - Freon conditioning of undiluted alum sludge resulted in slight increases in centrifuged solids for batch experiments. The response to vacuum filtration, however, was uniformly poor. Specific resistance increased for all doses and conditioning regimes, and vacuum-filtered solids decreased. The continuously conditioned sample failed to form a cake upon filtration.

A few tenuous relationships can be drawn from the experimental data. For batch experiments, increased centrifuged solids concentrations were accompanied by increases in floc density. This relationship suggested that the addition of Freon to the sludge had some conditioning effect. This relationship was not observed for the semicontinuously conditioned sample, which had an increase in floc density but no change in centrifuged dry solids concentration. Since this sample was mixed for a much longer time than the batch-conditioned samples, this results might have been caused by the detrimenal effects of mixing. It is interesting to note that this sample was also the only one not to form a cake upon vacuum filtration, and had the highest specific resistance.

Effects of Dilution - One-liter samples of RAAP alum sludge previously diluted to a 1 percent dry solids concentration were conditioned with Freon, in batch and continuous experiments. In the batch experiments, samples were treated with 1-, 2-, and 3-stage conditioning, with 250 mL Freon applied at each stage. In the continuous experiments, samples were fed 10 mL/min Freon for contact times of 25, 50, and 75 minutes. The samples treated in 1-stage batch and 25-min continuous experiments were fed 250 mL/L Freon; the 2-stage batch- and 50-min continuously conditioned samples, 500 mL/L; and the 3-stage batch- and 75-min continuously conditioned samples, 750 mL/L. Results of analyses are presented in Tables 28 and 29 for batch and continuous experiments, respectively.

Particle size distributions for conditioned and unconditioned samples of diluted alum sludge were similar in shape and magnitude, with the exception of the samples batch-conditioned with 500 mL/L Freon (Figure 29) and continuously with 250 mL/L (Figure 30). These samples had greater numbers of particles in the size ranges with mean particle diameter less than 40 μm. The total number of particles per mL represented by the distribution of the batch-conditioned sludge

TABLE 28

RESULTS OF ANALYSES
DILUTED, FREON-CONDITIONED ALUM SLUDGE
(BATCH EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
	Sludge x 10^{-2}	Supernatant			
0	16,700	29,200	0	10	8.4
250	14,900	31,500	0	38	8.2
500	30,900	31,100	0	21	7.7
750	14,200	30,400	0	29	7.4

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %		Specific Resistance, m/kg x 10^{11}	Blinding Coefficient
	Initial	Vacuum-Filtered		
0	0.8	23.4	110	-0.5
250	0.8	27.2	100	-0.2
500	0.8	28.0	120	-0.5
750	0.6	28.2	100	-0.6

TABLE 29

RESULTS OF ANALYSES
DILUTED, FREON-CONDITIONED ALUM SLUDGE
(CONTINUOUS EXPERIMENTS)

SLUDGE, SUPERNATANT, AND PARTICLE CHARACTERISTICS

Freon Dose, mL/L	Floc. Density, g/mL	Particles per mL (MPD less than 250 μm)		% Sludge Solids Retained on 250 μm Screen	Supernatant TOC, mg/L	Sludge pH
		Sludge $\times 10^{-2}$	Supernatant			
0	-	19,800	29,200	0	8	7.8
250	-	26,000	20,700	0	12	7.6
0	1.16 - 1.17	14,700	15,100	0	9	7.8
500	1.16 - 1.18	17,300	14,500	0	14	7.7
750	1.16 - 1.18	15,900	30,000	0	13	8.0

DEWATERING CHARACTERISTICS

Freon Dose, mL/L	Solids Concentration, %			Specific Resistance m/kg $\times 10^{11}$	Blinding Coefficient
	Initial	Vacuum-Filtered	Centrifuged		
0	0.9	23.9	-	100	-0.9
250	0.8	22.8	-	170	-0.6
0	1.0	23.5	10.0	140	0.2
500	0.9	23.9	12.3	200	-0.6
750	0.7	24.2	11.6	270	-0.2

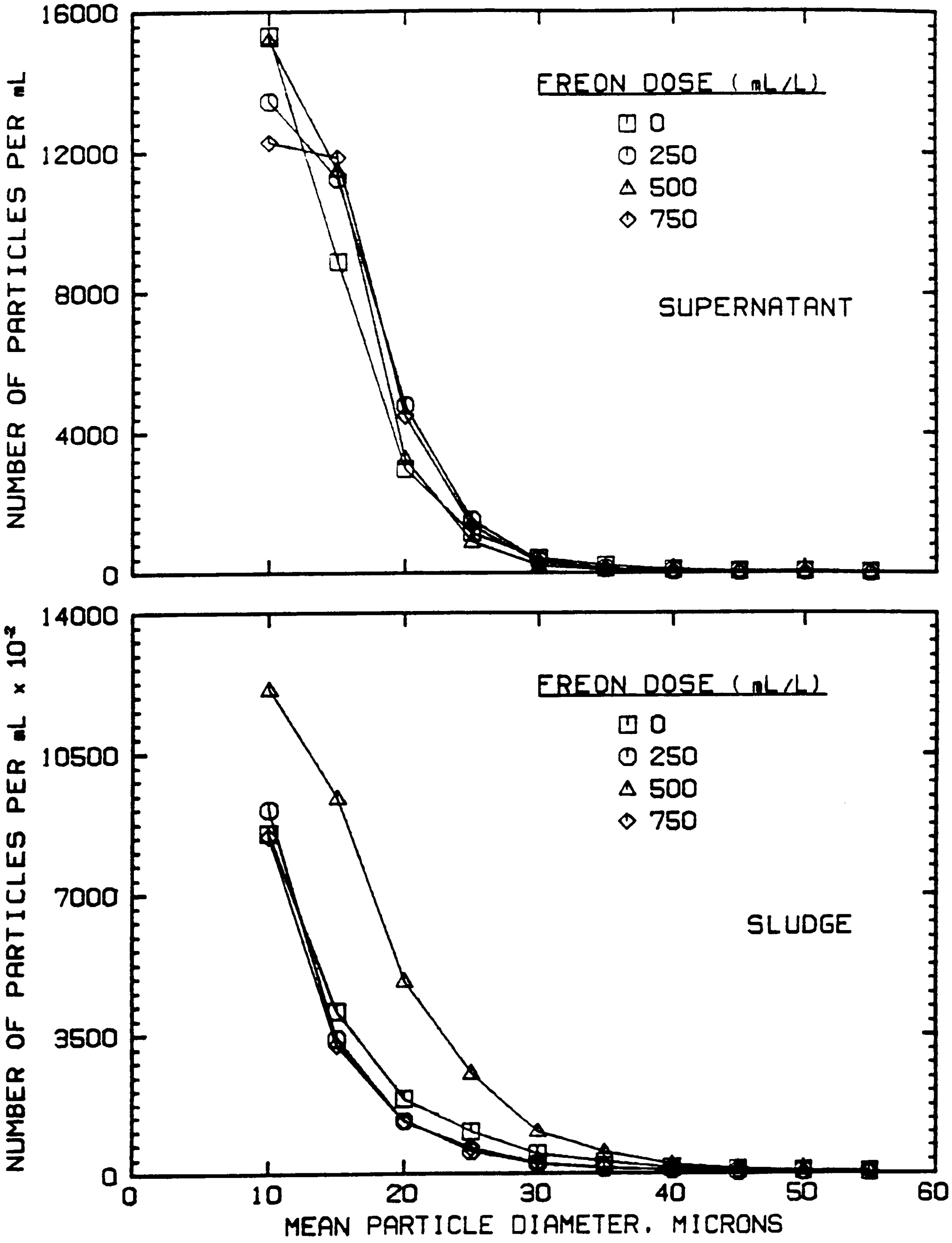


FIGURE 29. PARTICLE SIZE DISTRIBUTIONS, DILUTED, FREON-CONDITIONED ALUM SLUDGE (BATCH EXPERIMENTS)

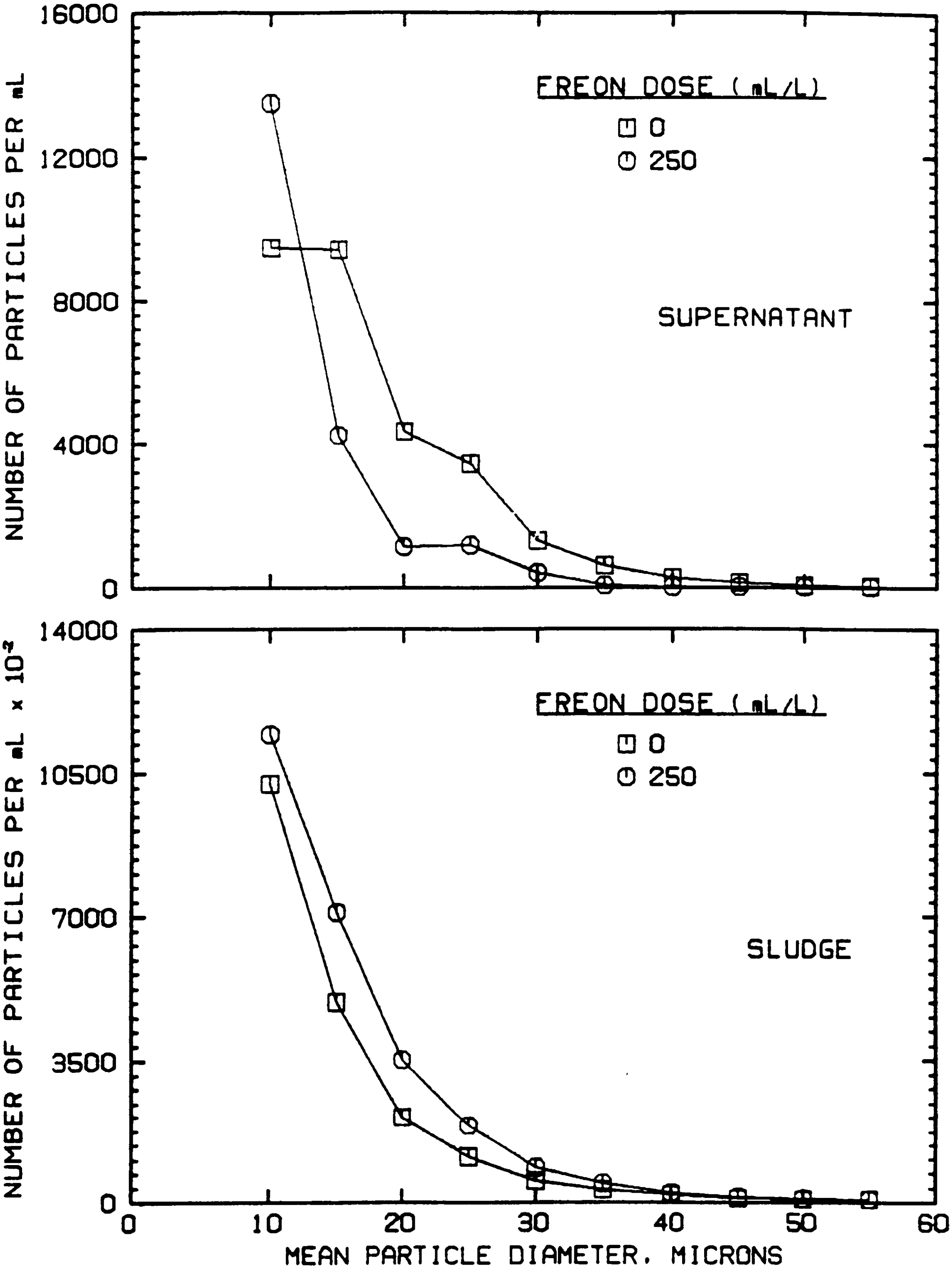


FIGURE 30. PARTICLE SIZE DISTRIBUTIONS, DILUTED, FREON-CONDITIONED ALUM SLUDGE (CONTINUOUS EXPERIMENTS)

was double that of any other sample.

Floc density increased slightly for batch conditioned samples. Supernatant TOC increased with conditioning from 10 mg/L for the unconditioned sample up to 38 mg/L for conditioned samples, with no trend. The pH of batch-conditioned samples decreased with Freon dose, from 8.4 for the unconditioned sample to 7.4 for the sample from the 3-stage experiment, while there were only slight variations in pH for continuously conditioned samples.

The major effect of Freon conditioning on the dewatering characteristics of diluted alum sludge was a substantial increase in vacuum-filtered solids concentration for batch experiments, a change that was not noted for continuously conditioned samples. Vacuum-filtered dry solids concentration increased for all batch-conditioned samples, from 23 percent solids for the unconditioned sample to 27 to 28 percent solids for conditioned samples. This change represented 17 to 22 percent increases in solids concentration. There were only slight variations in final cake solids concentration for continuously conditioned samples, which ranged from 23 to 24 percent, as did the final cake solids concentration for unconditioned samples.

Whereas there were only slight variations in specific resistance values of batch-conditioned samples, there was a clear upward trend in specific resistance values with increasing contact time for continuously conditioned samples, as shown in Figure 31. Specific resistance values increased from 100 to 140 x 10^{11} m/kg for

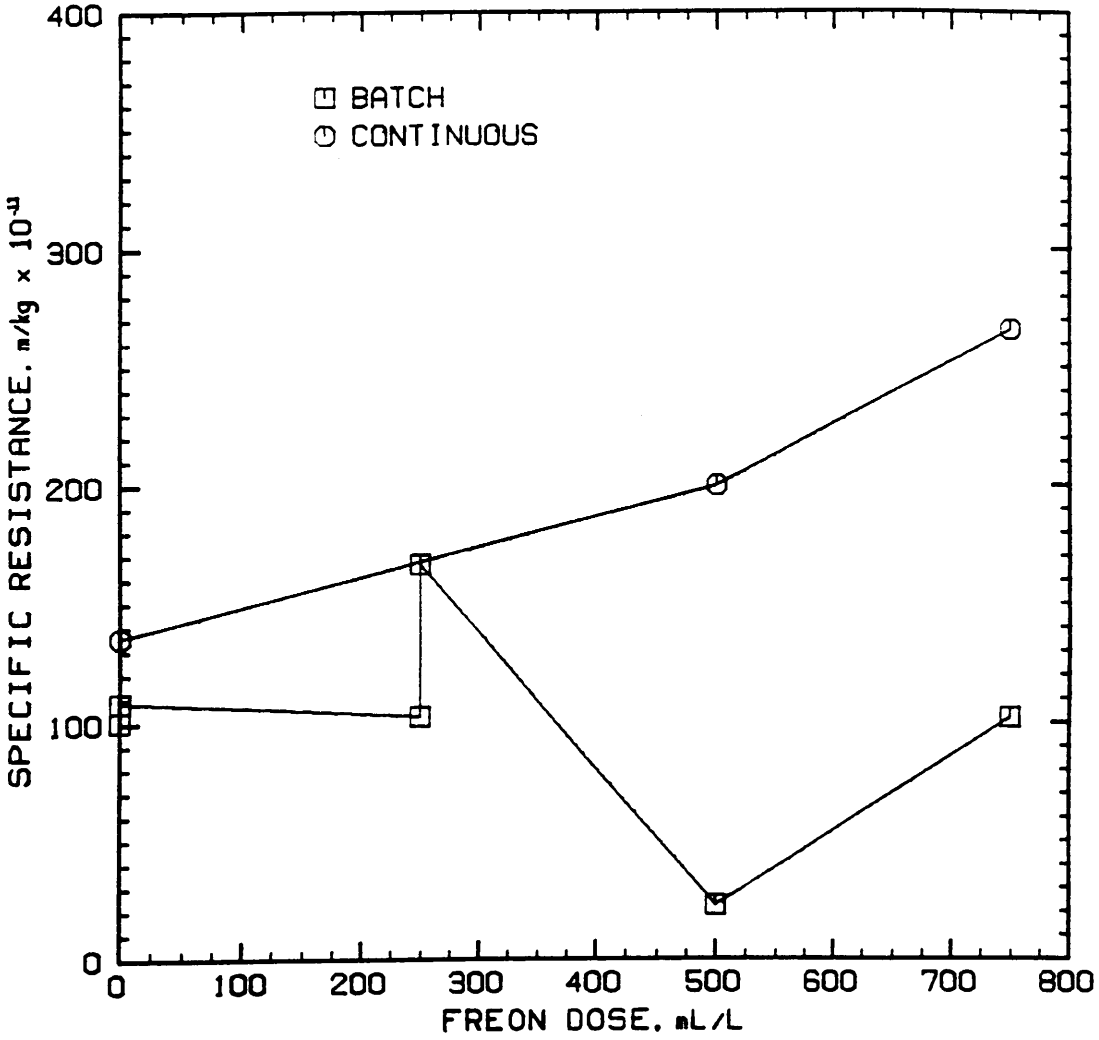


FIGURE 31. SPECIFIC RESISTANCE VS FREON DOSE.
DILUTED FREON-CONDITIONED ALUM SLUDGE.

unconditioned samples, to 270 x 10^{11} m/kg for the sample semicontinuously conditioned with 750 mL Freon. This sample had very poor supernatant quality.

Dewatering characteristics of undiluted sludge had generally deteriorated for samples freeze-thaw conditioned with Freon. More promising results were obtained for diluted sludge, particularly for those conditioned in batch operation.

V. DISCUSSION

The purpose of this study was to develop and evaluate direct-contact, freeze-thaw processes for conditioning wastewater and water treatment sludges in the context of conventional conditioning methods and to develop a theoretical model for the freeze-thaw process. This chapter presents the following:

- a proposed mechanism for conditioning effects achieved during freeze-thaw processes, based upon the results of indirect-contact, freeze-thaw experiments;

- a comparative evaluation of direct-contact, freeze-thaw conditioning; indirect-contact, freeze-thaw conditioning; and polymer conditioning; and

- a comparison of the results of the current investigation with other studies and a discussion of process viability.

PROPOSED MECHANISM FOR FREEZE-THAW CONDITIONING

In reviewing the particle and floc characteristics of sludges treated with direct-contact, freeze-thaw processes, no clear trends were discovered which could be used independently to formulate a mechanistic explanation of freeze-thaw conditioning. Results obtained with indirect-contact, freeze-thaw conditioning of the various sludges used in this study suggested a two-stage mechanism for conditioning: the disruption of both the sludge floc and particle structural components, and the formation of a new sludge floc arrangement. The effects of the freeze-thaw process on dewatering characteristics were dependent upon these sludge-specific changes in particle and floc characteristics.

Disruption of Sludge Structure

The first hypothetical stage in the freeze-thaw process, the disruption of existing flocs and particles, was evidenced in these experiments by changes in floc density ranges, in sludge pH, and in supernatant TOC concentration. The basic conditioning effect of this stage was the release of water previously incorporated in the original floc structure.

Changes in floc density indicated that the freeze-thaw process, at a minimum, altered sludge structure at the floc level. As can be seen from Table 30, freeze-thaw conditioning resulted in wider density ranges for certain sludges and in increased average density for each type of sludge.

The increase in floc density range observed for conditioned samples containing primary sludge included flocs of lesser and greater density than the original range. The appearance of less dense flocs in these samples suggested that the particles

TABLE 30

EFFECT OF INDIRECT-CONTACT, FREEZE-THAW CONDITIONING ON FLOC CHARACTERISTICS

Sludge	Average Floc Density, g/mL Unconditioned	Average Floc Density, g/mL Conditioned	Average Dry Solids Density (g/mL)	Floc Water Content Lost Due To Conditioning (%)
Waste Activated (WA)	1.030	1.055	1.22	53
Primary Sewage (PS)	1.045	1.060	1.4	28
PS/WA Mixture	1.040	1.060	1.3	38
Alum				
Undiluted	1.170	)1.300	2.8	)48
Diluted	1.165	)1.300	2.8	)50

	Floc Density (g/mL)				Floc Density Range, g/mL	
	Unconditioned		Conditioned			
Sludge	Average	Range	Average	Range	Unconditioned	Conditioned
Waste Activated (WA)	1.030	-	1.055	-	-	-
Primary Sewage (PS)	1.045	1.055 - 1.10	1.060	1.03 - 1.11	0.045	0.08
PS/WA Mixture	1.040	-	1.060	1.05 - 1.07	-	0.20
Alum						
Undiluted	-	-	)1.300	-	0.05	-
Diluted	1.165	1.16 - 1.17	)1.300	-	0.01	-

constituting flocs were forced apart from one another during the freeze-thaw process. The observation of this phenomenon only in samples containing primary sludge suggested that primary sludge flocs, characteristically more heterogeneous than either waste activated or alum sludge, were more susceptible to disruption during freezing than the other sludges.

Alternatively, changes in floc density range may actually have occurred in other sludges, but may have been obscured by the limitations of particle analytical methods, i.e.:

1. The amount of water which must be lost or gained to affect a measurable change in floc density depends upon the dry density of the sludge solids. For example, a much larger amount of water loss is required to increase the floc density from 1.02 to 1.03 g/mL for a sludge with a dry density of 1.10 g/mL than for a sludge with a dry density of 2.0 g/mL. Since waste activated sludge dry solids have a low characteristic density, a relatively large change in the amount of water associated with the floc would be necessary to be reflected by changes in measured floc density.

2. The density of indirect-contact, freeze-thaw-conditioned alum sludge flocs was greater than the maximum density that could be achieved via concentration of the Percol media

(maximum density = 1.30 g/mL).

It is also possible that amalgamation of particles in waste activated and alum sludge samples upon thawing may have obscured fundamental changes in particle characteristics induced by freezing.

As shown in Table 30, average floc density increased for all sludges. (Average floc density for each sludge was taken as that density gradient at which the greatest amount of sludge was deposited. If sludge was concentrated more or less equally at more than one gradient, the corresponding densities were averaged to obtain the mean value.) This densification can be attributed to the loss of floc water during the freeze-thaw process. To determine the percentage of floc water hypothetically released, a general mass balance was written around the floc as:

$$p_f = \Phi_{dry}(p_{dry}) + \Phi_w(p_w) \qquad [23]$$

where

Φ_{dry} = fraction of floc volume occupied by dry solids (dimensionless)

Φ_{wet} = fraction of floc volume occupied by water (dimensionless)

p_{dry} = dry solids density (g/mL)

p_{wet} = density of water (1.0 g/mL)

Based upon observed changes in floc density conditions, the percentage of floc water released was calculated as:

$$\% \text{ released} = \frac{[\Phi_{wu} - \Phi_{wc}(\Phi_{dryu}/\Phi_{dryc})](100)}{\Phi_{wu}} \qquad [24]$$

where the notations "u" and "c" denote unconditioned (control) and conditioned volume fractions, respectively.

As can be seen from the data presented in Table 30, the percentage of floc water released by the indirect-contact, freeze-thaw process varied from 28 to over 50 percent.

Changes in the fundamental chemical characteristics of conditioned sludges suggested that particles as well as flocs may have been disrupted by the freezing process. As can be seen from the data presented in Table 31, changes in sludge pH and supernatant TOC concentrations were significant. The pH of primary sludge, primary sludge/waste activated sludge mixtures, and alum sludge decreased, while the pH of waste activated sludge increased. Changes in supernatant TOC concentration for primary sludge and for primary sludge/waste activated sludge mixtures were large, with increases of over 100 percent.

Due to the described limitations in particle analyses, the extent and nature of particle disruption is not evident from these observations. There are at least three mechanisms which may singly or together be used to explain the data:

1. <u>Dehydration and Rupture</u> - Mechanical stresses and/or

TABLE 31

EFFECT OF INDIRECT-CONTACT, FREEZE-THAW CONDITIONING ON CHEMICAL CHARACTERISTICS

	Sludge pH		Supernatant TOC, mg/L	
Sludge	Unconditioned	Conditioned	Unconditioned	Conditioned
Waste Activated (WA)	6.9	9.3	-	-
Primary Sewage (PS)	6.9	6.3	56	103
PS/WA Mixture	7.6	6.7	31	152
Alum				
Undiluted	8.2	7.5	13	14
Diluted	7.7	7.3	20	8

physical/chemical imbalances produced during freezing could result in dehydration and rupture of cells and particles. Discussing the results of his study of butane conditioning of waste activated sludges, Khan[30] hypothesized that large mechanical stresses placed on the cell during freezing caused the release of internal water, which subsequently froze outside the cell. Irreversible changes resulted from contact of cellular protein formerly isolated by internal water. Mechanical stress could similarly disrupt non-biological particles.

Silvares[71] found that cells in a slowly freezing solution are immersed in an increasingly saline environment. The resulting concentration gradient across cell boundaries elicits water from the cells, resulting in cellular dehydration. Ice may also form with the cell, which could ultimately lead to the rupture of cells into smaller particles[30,34].

The occurrence of particle/cell dehydration and rupture in the current investigation is supported by the data which indicated increases in floc density range and average floc density and changes in supernatant TOC concentration and sludge pH.

2. Particle Compression - The intense pressures generated during freezing may deform particles without significant

loss of water or destruction of cell boundaries. In freeze-thaw experiments with water treatment sludges, Flint[78] used X-ray diffraction techniques to determine that the size of aluminum hydroxide "crystallites" was actually halved by the process. Flint suggested that the particles were compressed by the expansion of external freezing water. In the current study, compression may have enhanced for the densification of floc observed for all sludges.

3. Change in Particle Surface Charge - Changes in particle surface charge may also occur upon freezing. Flint[78] hypothesized that the readiness with which the aluminum hydroxide "crystallites" produced by freeze-thaw conditioning precipitated was due to reduction of surface charge. The large electric potential which may develop across the ice-water interface may impart a negative charge to the liquid surrounding the particles, thereby neutralizing them. Such changes could also explain in part the increases in average floc density observed for all sludges.

Formation of New Floc Structure

Many of the particle and dewatering data collected in this study support the hypothesis that the second stage in the freeze-thaw process is the formation of new flocs. Whether flocs and particles experienced dehydration and rupture, compression, and/or a change in surface charge, the basic effects of the freeze-thaw process on the sludges in this study were large increases in floc density and particle size. The flocs comprising the conditioned sludge were thus fundamentally different from those originally constituting the unconditioned sludge.

The changes in floc density were previously discussed in the context of floc disruption. Conditioned flocs were, on the average, considerably denser than unconditioned flocs, as can be seen from data in Table 30. Large changes also occurred in particle size distributions for each sludge. Data in Table 32 document the reductions in the number of particles with mean particle diameter less than 250 μm per mg of sludge solids for each sludge. Concentrations of particles (number/mL) were normalized by dividing by initial solids concentration to account for differences in solids content among sludges and between conditioned and unconditioned samples. As can be seen from the data in Table 32, reductions in the number of small particles per unit weight of sludge solids were substantial, ranging from 80 to 96 percent.

Increases in the weight percent of particles greater than 250 μm in size were correspondingly large. For unconditioned samples of waste activated and alum sludges, there was no fraction of particles retained on a 250-μm screen. With conditioning, the weight percent retained on a 250-μm screen increased to 73 percent or greater for each sludge.

TABLE 32

EFFECT OF INDIRECT-CONTACT, FREEZE-THAW CONDITIONING ON PARTICLE CHARACTERISTICS

Sludge	Number of Particles with MPD <250 µm per mg of Sludge Solids ($\times 10^{-6}$) Unconditioned	Number of Particles with MPD <250 µm per mg of Sludge Solids ($\times 10^{-6}$) Conditioned	% Reduction in Particle Concentration (MPD <250 µ)
Waste Activated (WA)	16.5	0.7	96
Primary Sewage (PS)	10.6	1.7	83
PS/WA Mixture	15.8	1.7	89
Alum			
Undiluted	8.6	1.7	80
Diluted	13.3	0.5	96

Sludge	% Sludge Solids Retained on 250 µm Screen Unconditioned	% Sludge Solids Retained on 250 µm Screen Conditioned	% Increase in Particle Concentration (>250 µm)
Waste Activated (WA)	0	76	-
Primary Sewage (PS)	57	87	53
PS/WA Mixture	26	78	200
Alum			
Undiluted	0	73	-
Diluted	0	78	-

Note:

MPD = Mean Particle Diameter (µm)

The increases in floc density and particle size suggest that particles were simply forced together by intense pressure during freezing to form larger ones, squeezing out excess water. Other results suggest a more complex process combining cell disruption, particle compression, and surface charge reduction, as discussed in the previous section.

The general effects of the conditioning-induced changes in particle and floc characteristics were increases in initial and vacuum-filtered solids concentrations, and variable, sludge-specific changes in centrifuged solids and specific resistance. Data included in Table 33 show that the change in initial, gravity-thickened solids concentration with conditioning was substantial, with increases ranging from 62 to 1600 percent. This increase corresponds well with the calculated values for floc water content lost due to conditioning (Table 30). Much of the floc water released by the freeze-thaw process completely dissociated from the floc and was easily drained off as supernatant.

The improvements in dewatered solids concentrations for certain sludges can also be related to the release of previously bound floc water. As can be seen from data in Table 33, the solids obtained following vacuum filtration showed increases of 51 to 90 percent, where measurable. (Primary sludge and primary sludge/waste activated sludge mixtures did not produce cakes before conditioning; thus extent of improvement could not be determined). Indirect freezing showed increases of 15 to 190 percent in the solids concentration

TABLE 33

EFFECT OF INDIRECT-CONTACT, FREEZE-THAW CONDITIONING ON DEWATERING CHARACTERISTICS

Sludge	Vacuum-Filtered Solids Concentration %		% Increase in Solids Concentration	Centrifuged Solids Concentration %		% Increase in Solids Concentration
	Unconditioned	Conditioned		Unconditioned	Conditioned	
Waste Activated (WA)	13.6	20.5	51	8.8	10.1	15
Primary Sewage (PS)	*	*	-	16.9	11.3	-33
PS/WA Mixture	*	24.2	-	13.3	7.9	-40
Alum						
Undiluted	21.0	39.9	90	10.5	25.5	140
Diluted	22.3	41.0	84	9.6	27.9	190

Sludge	Initial Solids Concentration %		% Increase in Solids Concentration	Specific Resistance m/kg x 10^{-11}		% Decrease in Specific Resistance
	Unconditioned	Conditioned		Unconditioned	Conditioned	
Waste Activated (WA)	1.0	4.3	330	49	120	-145
Primary Sewage (PS)	2.1	4.8	130	2,600	500	81
PS/WA Mixture	1.3	2.1	62	1,500	130	91
Alum						
Undiluted	3.2	14.6	350	190	1	99
Diluted	0.9	15.1	1,600	160	3	98

Note:

* No cake produced in 30 minutes of dewatering.

obtained following centrifugation, except for samples containing primary sewage sludge. Conditioned samples comprised by or containing primary sewage showed a decrease in centrifuged solids concentration. This decrease was assumed to result from the change in floc density range, with less dense particles remaining suspended after centrifugation.

Arundel[77] investigated the dewatering behavior of sludges exposed to long-term applications of high pressure. She characterized both the floc density and the dewatered solids concentration obtained following high pressure application. The observed increase in floc density was concluded to be related to floc deformation and the release of internal floc water. This likewise correlated to the generation of significantly greater cake solids concentrations. Likewise, the intense pressures developed during freezing have been suggested as producing similar water release during sludge conditioning[63,78].

Indirect freezing produced a marked improvement in sludge dewatering rate as evidenced by a significant decrease in sludge specific resistance (data in Table 33). This result was predictable based upon the increase in the characteristic particle size distribution observed following conditioning. The only anomaly was with respect to the conditioning of the waste activated sludge sample; in this instance, an increase in specific resistance was observed. The reason for this response was not immediately evident upon analysis of the sludge characterization data collected.

EVALUATION OF DIRECT-CONTACT, FREEZE-THAW CONDITIONING

There are three main advantages of direct-contact, freeze-thaw conditioning processes when compared to indirect-contact processes: (1) reduced energy requirements, (2) flexibility in reactor configuration, and (3) maintenance of a pumpable slurry, thus permitting continuous operation. These advantages must be weighed against the main disadvantage of direct-contact processes, that is, the reduced potential for improvement in dewatering characteristics. The following sections discuss the observed effects of direct-contact freeze-thaw conditioning on particle, chemical, and dewatering characteristics and compare them to the results of the indirect-contact process.

Particle and Chemical Characteristics

The decrease in the number of particles with mean particle diameter (MPD) less than 250 μm per mg of sludge solids, observed for all sludges conditioned with the indirect-contact process, provided evidence of the general increase in particle size and change in floc structure resulting from this freeze-thaw process. In contrast, normalized concentrations of particles present in each sludge sample conditioned with a direct-contact process increased significantly in comparison to the control sample. (Selected data are presented in Table 34.) These values reflected an increase in the number of particles; in fact, most of this increase was due to the production of very fine (<20 μm) size particles.

TABLE 34

EFFECT OF DIRECT-CONTACT, FREEZE-THAW CONDITIONING ON PARTICLE CHARACTERISTICS

Sludge	Conditioning Method	No. of Particles With MPD <250 μm per mg of Sludge Solids (x 10^{-6}) Range
Waste Activated (WA)	None (Control)	10.4
	Direct Freeze (Butane)	14.5
	None (Control)	18.6
	Direct Freeze (Freon)	24.3
Primary Sewage (PS)	None (Control)	10.6
	Direct Freeze (Butane)	15.4
	None (Control)	17.8
	Direct Freeze (Freon)	25.7
Alum, Undiluted	None (Control)	17.9
	Direct Freeze (Butane)	28.2
	None (Control)	7.4
	Direct Freeze (Freon)	9.0
Alum, Diluted	None (Control)	17.0
	Direct Freeze (Butane)	18.2
	None (Control)	20.9
	Direct Freeze (Freon)	38.7

The general effect of indirect-contact, freeze-thaw conditioning on measured sludge floc characteristics was an increase in the average sludge floc density. For certain sludges (alum sludge, in particular), this increase was large. In contrast, minimal changes in floc density ranges and averages for both butane- and Freon-conditioned sludges were observed. The direction of change varied, as can be seen from the selected floc density data presented in Table 35. Two trends were noted:

1. Average floc density increased for alum sludge conditioned with Freon, as it had for sludges conditioned with the indirect-contact process.

2. Floc density range increased for all sludges batch-conditioned with Freon, as it had for indirect-contact conditioned samples consisting totally or partially of primary sludge. The latter was interpreted as a sludge-specific phenomenon, as the increase was not observed for other sludges. In this case, the result appeared to be refrigerant-specific.

Changes in sludge pH were observed in sludges conditioned with the indirect-contact process. These changes were interpreted to signal disruption of the sludge at the primary particle level. Similar changes were noted in butane- and Freon-conditioned samples

TABLE 35

EFFECT OF FREON CONDITIONING ON FLOC CHARACTERISTICS

Sludge	Conditioning Method	Floc Density g/mL	
		Average	Range
Waste Activated (WA)	None (Control)	1.035	1.03 - 1.04
	Direct Contact (Freon)	1.02	1.01 - 1.05
Primary Sewage (PS)	None (Control)	1.03	-
	Direct Contact (Freon)	1.03	1.02 - 1.04
WA/PS Mixture	None (Control)	1.04	-
	Direct Contact (Freon)	1.04	1.03 - 1.05
Alum, Undiluted	None (Control)	1.17	1.16 - 1.18
	Direct Contact (Freon)	1.18	1.16 - 1.18
Alum, Diluted	None (Control)	1.17	1.16 - 1.18
	Direct Contact (Freon)	1.18	-

of alum sludge. Minimal change in pH was noted for other sludges.

Moderate changes in supernatant TOC were also observed in sludges conditioned with the indirect-contact process. In general, increases of similar magnitude to these changes occurred for sludges conditioned with the direct-contact process. Two deviations were noted. First, the supernatant TOC concentration of the waste activated sludge conditioned with 400 mL/L butane was several times greater than the supernatant TOC concentration for any other conditioned or unconditioned waste activated sludge sample. Also, the supernatant TOC concentration of certain butane- and Freon-conditioned alum sludge samples increased, whereas there had been no such increase for the samples conditioned with the indirect-contact process.

As suggested in the presentation of results, these increases may have been caused by the suspension of fines in the supernatant as a result of mixing. Butane-conditioned supernatant samples might also have contained significant concentration of dissolved or emulsified butane. For example, based upon butane solubility at experimental temperatures, up to 50 percent of the total increase in TOC concentration noted for the waste activated sludge sample treated with 400 mL/L butane could be attributed to solubilized butane. All or part of the remaining increase could be accounted for by the presence of emulsified butane in the supernatant, which has been reported in amounts up to ten times that of dissolved butane in freeze-thaw process products[26].

Dewatering Characteristics

The indirect-contact, freeze-thaw process generally resulted in higher cake solids concentrations and lower specific resistance values for the sludges studied. As for changes in particle characteristics, the direct-contact processes resulted in variable changes in dewatering characteristics, usually of lesser magnitude.

Initial and vacuum-filtered solids concentrations obtained upon indirect-contact, freeze-thaw conditioning were typically higher than those noted for unconditioned samples. Similar results were noted in solids concentrations of certain sludges conditioned with direct-contact processes. Selected results are presented in Table 36.

Certain samples of butane- and Freon-conditioned alum sludge and butane-conditioned waste activated sludge showed slight increases in initial solids concentration. The dewatered solids concentrations of certain samples of waste activated and diluted alum sludges conditioned with direct-contact processes improved.

Changes in specific resistance with indirect-contact, freeze-thaw conditioning were sludge specific. The specific resistance of alum and primary sewage sludges and of primary sewage/waste activated sludge mixtures greatly improved, while increasing with indirect-contact conditioning for waste activated sludge. In contrast, specific resistance deteriorated for almost every sludge sample conditioned with a direct-contact process. (Selected data are presented in Table 36.) The exceptions were

TABLE 36

EFFECT OF DIRECT-CONTACT, FREEZE-THAW CONDITIONING ON DEWATERING CHARACTERISTICS

Sludge	Conditioning Method	Solids Concentration, % Initial	Solids Concentration, % Vacuum-Filtered	Specific Resistance, m/kg × 10^{11}
Waste Activated (WA)	None (Control)	1.0	12.9	36
	Direct Contact (Butane)	1.2	13.3	290
	None (Control)	0.8	8.3	210
	Direct Contact (Freon)	0.6	13.5	360
Primary Sludge (PS)	None (Control)	2.1	-	4,100
	Direct Contact (Butane)	1.4	-	3,200
	None (Control)	1.5	-	7,100
	Direct Contact (Freon)	1.1	-	23,200
Alum, Undiluted	None (Control)	1.3	24.0	160
	Direct Contact (Butane)	2.8	23.7	290
	None (Control)	3.3	16.1	150
	Direct Contact (Freon)	3.6	13.1	260
Alum, Diluted	None (Control)	1.1	21.3	125
	Direct Contact (Butane)	1.2	23.1	205
	None (Control)	0.8	23.4	110
	Direct Contact (Freon)	0.8	28.0	120

butane-conditioned primary sludge, for which there was an improvement, and Freon-batch-conditioned alum sludge, for which there was virtually no change in specific resistance with conditioning.

The increases in specific resistance, which were very significant in certain instances (for example, the Freon-conditioned primary sludge), were probably due to the production of large numbers of very fine particles during conditioning and to the foam and scum layers typically generated during the direct-contact process.

In summary, the benefits observed from indirect-contact conditioning, such as particle compression, increased floc density, higher cake solids concentrations, and lower specific resistance values, were not generated by the direct-contact processes. A combination of causes is likely responsible for these results, including the rate and extent of freezing and process-specific factors, such as mixing and foaming.

The rate of freezing was relatively rapid in the direct-contact experiments. The detention time for freezing was typically less than 45 minutes, with virtually instantaneous freezing occurring in certain instances (i.e., batch conditioning with Freon). In comparison, in the indirect-contact process, solid freezing occurred over two to four hours.

Other researchers have noted that the rate of freezing affects sludge characteristics. Logsdon and Edgerly[63] found that slow freezing permitted development of elongated, crystalline solids, which drained well upon thawing. Rapid freezing resulted in small ice crystals enveloped by a matrix of dissolved and suspended solids, which drained poorly. Martel and Vesilind[79], subjecting samples of wastewater sludges to variable rates of freezing and different final temperatures, found that dewatering characteristics (as evaluated by capillary suction time) showed the greatest improvement at the slowest rate of freezing. (Although the final freezing temperature also had an effect on dewatering characteristics, with lower temperatures resulting in improved dewatering, the rate of freezing appeared to be the significant factor.)

The direct-contact methods utilized in this study generally resulted in rapid freezing, which appeared to promote cell rupture and the production of fine particles, as evidenced by particle size distribution data. The aggregation and densification noted as a result of the indirect-contact process did not take place in the direct-contact process.

The extent of freezing also differed between the direct-contact and indirect-contact processes. In this study, the direct-contact process was designed and conducted to produce approximately a slurry composed of equal parts of ice and sludge, typical of the mixture produced in salt water desalination. In comparison, sludges conditioned with the indirect-contact process were allowed to freeze solid. From the comparative results, it appears that the higher fractions of ice formation (approaching a near total freeze) achieved with the indirect-contact process may be necessary to achieve significant internal water removal and densification of sludge floc.

COMPARISON WITH OTHER STUDIES AND PROCESS VIABILITY

The purpose of this study was to develop a process model for direct-contact, freeze-thaw processes within the existing context of previous research and to gauge general process viability. The following sections present comparisons of the results of this study with earlier research and discuss the potential of future application of direct-contact freeze-thaw conditioning processes.

Butane Conditioning

Selected results from research conducted by Khan[30] to determine the feasibility of conditioning waste activated sludge with butane in a direct-contact process were previously presented in Table 1. Khan[30] observed substantial reductions in specific resistance and large increases in dewatered solids concentration using high butane doses (up to 1800 mL/L) in batch experiments and long contact times (6 to 36 hours) in continuous experiments. Comparable results were not obtained in the current study for waste activated sludge for any freeze-thaw method, including the indirect-contact process. Several factors may have contributed to this difference:

1. The dewatering characteristics of the unconditioned waste activated sludge used in this study were far superior to those of the unconditioned sludge used in Khan's study. Typical specific resistance values for unconditioned waste activated sludge in Khan's study ranged from 850 to 4700 x

10^{11} m/kg; in the current study, typical specific resistance values for waste activated sludge ranged from 40 to 70 x 10^{11} m/kg. Therefore there was less room for improvement in the current study.

2. Khan's best results from batch experiments were achieved at butane doses that were at least 50 percent greater than those used in this study. His best results from continuous experiments were achieved at butane doses that were almost twice as large as those used in this study and at very long contact times. The extent of freezing achieved was likely greater in Khan's study than in the current investigation, and, in the continuous experiment, the rate of freezing slower. Both of these factors would serve to improve conditioning.

3. Khan limited mixing speeds to 45 rpm or less. This moderate agitation probably minimized foaming, to which a certain part of the deterioration of sludge quality observed in this study has been attributed.

Freon Conditioning

Selected results from Molayem and Bardaki's[33] feasibility study utilizing Freon 11 to direct-contact freeze-thaw condition wastewater sludges were presented in Table 3. Large increases in final solids were observed in certain experiments. As noted, however, Freon doses were extremely large and results variable. Gains in solids concentrations observed in the current study, while not as substantial as the best results of Molayem and Bardaki's research, were more consistent.

Process Viability

Although the results of the current study did not warrant development of the experimental apparatus to larger scale or to include refrigerant or heat recovery, several observations may be made with respect to process viability:

1. External factors, e.g., mixing and reactor configuration, appeared to have a significant effect on process results. A viable process must include means of intimate contact between sludge and refrigerant without disturbing floc structure. In this study, mixing resulted in deteriorating sludge quality by reducing particle size and exacerbating refrigerant foaming. Possible alternative solutions exist, such as higher refrigerant doses, application of sludge in thin layers, and longer contact times; however, these options tend to increase the cost of the operation and reduce its potential for full-scale applications.

2. Foaming is more likely to occur when back pressures in feed systems cause partial volatilization[30]; but it also appears to be depend upon the type of sludge. Since it is worst for waste activated sludge, it may be enhanced by biomass-produced surfactants.

3. Refrigerant hazards must be addressed. For example, butane is both toxic and explosive; Freon 12 is toxic at high concentrations and may become obsolete, as its potential as an ozone-destroying agent is better defined.

4. Mechanical and operational complexity must be considered in comparing direct-contact, freeze-thaw processes with other alternatives. Temperature, pressure, mixing, and refrigerant and sludge flowrates must be tightly controlled. To be cost effective, the process must include refrigerant and heat recovery, requiring sophisticated compression and heat exchange systems.

5. Refrigerant and power costs are among the several market-sensitive variables upon which the cost-effectiveness of direct-contact, freeze-thaw processes depend. The economic feasibility of these processes is enhanced by market climates wherein energy costs are low.

VI. CONCLUSIONS

The results obtained in this study indicate that direct-contact, freeze-thaw conditioning processes do not offer a panacea for producing marked improvements in sludge dewatering properties. Long conditioning times at slow rates of freezing may be necessary to produce significant changes in floc size and water content, parameters which ultimately affect the rate and extent of sludge dewatering achieved. The rapid rate of freezing which characterized the direct-contact conditioning investigated in this study produced significant concentrations of fine particles, possibly as a result of floc rupture. In contrast, the slow freezing of sludge to a solid, as occurred in the indirect-contact process utilized in this study (and as achieved by natural freezing colder climatic conditions) resulted in the release of internal floc water and a corresponding aggregation and densification of the floc structure, producing excellent sludge dewatering characteristics.

The following specific conclusions were reached:

1. As evidenced by the results of the indirect-contact process, freeze-thaw conditioning has the potential to greatly increase dewatered solids concentration and reduce specific resistance for both wastewater and water treatment sludges.

2. The conditioning effects of freeze-thaw processes can be explained by a two-stage model in which disruption of sludge structure at the floc and particle level is followed by formation of a new, denser floc structure.

3. Variability in the response of alum sludge, waste activated sludge, primary sewage sludge, and mixtures of waste activated and primary sewage sludges to freeze-thaw conditioning can be attributed to inherent differences in sludge characteristics. Freeze-thaw conditioning was most effective in improving the dewatered solids concentration of alum water treatment sludge.

4. The rapid and incomplete freezing characteristic of direct-contact, freeze-thaw processes was not conducive to significant changes in the particle and dewatering characteristics of treated sludges.

5. The reduced performance of direct-contact, freeze-thaw processes when compared to indirect-contact results may also be attributed in part to the interfering effects of mixing-induced changes in particle size distribution and of refrigerant foaming.

Although significant improvements in dewatering characteristics were not observed for sludge conditioned with direct-contact, freeze-thaw processes, the results obtained in this study should not necessarily be interpreted to show that future investigation of direct-contact, freeze-thaw processes is unwarranted. Many other agents form gas hydrates or clathrates with water; further testing is appropriate with different compounds. The results of this study have indicated which design parameters (e.g., rate of freezing, particle properties) are critical to the potential success of such conditioning methods.

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APPENDIX A

DESIGNATIONS FOR HALOGENATED HYDROCARBONS

Halogenated hydrocarbons used as secondary refrigerants share the general formula $C_aH_bCl_cF_d$, where b+c+d = 2a + 2. These refrigerants are designated by a two- or three-digit number, calculated from the variables above. The first digit equals (a-1), unless this is zero, in which case, it is omitted. The second digit equals (b+1), and the third, d.

If isomers occur, the most symmetrical is assigned the basic designation, while "a" and successive lower case letters are appended to isomers with decreasing symmetry. Brominated compounds are designated by an upper case B, followed by the number of bromine atoms. The identifying number is preceded by either an F or an A (indicating "Freon" or "Arcton") or by an R (for the general term "Refrigerant"), or by the term for which the letter stands. For example, monochlorodifluoroethane (CH_3CClF_2) is marketed as Freon 142b, where a = 2, b= 3, c = 1, d = 2, and a-1 = 1, b+1 = 4, d = 2, and it is the third most symmetric isomer. It can be designated as F-142b or R-142b.

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