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Title   FOAM SEPARATION OF ORGANIC AND TOXIC MATERIALS

IN KRAFT MILL EFFLUENTS

Abstract approved : _Fred Merryfield_ .
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Because of the organic nature and the natural foaming charac-

teristics of kraft mill effluents, it was decided to investigate the

feasibility of using foam separation as a method of treatment. The

treatment efficiency was evaluated by BOD and COD reductions as

well as the decrease in toxicity to marine life.

Grab samples of the whole mill effluent obtained from a kraft

pulp and paper mill were foamed in a column by sparging air through

the sample. The effect of adding nonionic, anionic, and cationic

surfactants was evaluated. Samples were foamed at 25° C and 40° C

to assess the effect of temperature.

It was observed that a stable foam would not always be formed,

and that the addition of a surface active agent may sometimes be

necessary for foam stability. BOD reductions from 15. 8 to 35. 2

percent and COD reductions from 7. 9 to 20. 2 percent were obtained.

The addition of surface active agents did not materially increase BOD

and COD reduction.

The bay mussel (Mytilus edulis Linnaeus) was used as the test organism for the toxicity tests. TLm's of 1.8 to 3.7 percent concentration were observed on the untreated waste. TLm's up to 8.4 percent were obtained after foaming. The toxicity reduction factor (ratio of TLm of waste after foaming to TLm of waste before foaming) was used as the measure of toxicity reduction. Reduction factors up to 2.3 were obtained when foamed without the addition of a surfactant and when foamed with Krystallamide LA, a nonionic surfactant. Lower reduction factors were observed when using ionic surfactants.

Increasing the temperature did not affect BOD, COD, or toxicity reduction. However, a larger volume of foam was usually generated at the higher temperature.

FOAM SEPARATION OF ORGANIC AND TOXIC MATERIALS
IN KRAFT MILL EFFLUENTS

by

JAMES LEWIS BLAZIER
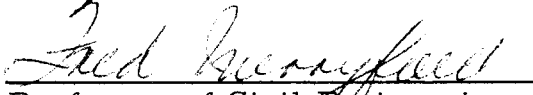
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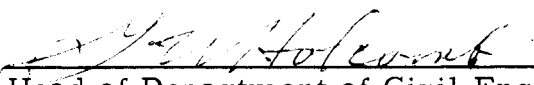the requirements for the
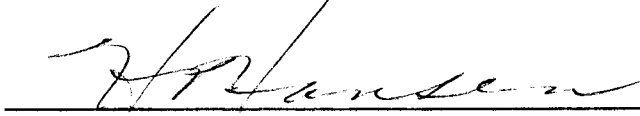degree of

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IN KRAFT MILL EFFLUENTS

INTRODUCTION

The kraft paper manufacturing process generates large quantities

of liquid wastes of varying strengths. Disposal methods for these

wastes have received a large amount of attention in recent years, but

to date no generally accepted economical method of treatment has

been devised.

The manufacturing of kraft paper can be divided into two phases:

pulping of the wood and manufacturing of the finished product. The

pulping process produces the largest volume and most concentrated

waste. Evaporator condensates make up the bulk of the waste from

this process, but excess rinse waters and leakage can also contri-

bute significantly to the waste flow. An average kraft pulping mill

using water conservation measures will use 20,000 gallons of water

per ton of pulp produced with over 90 percent eventually being dis-

charged in the mill effluent. Biochemical Oxygen Demand (BOD)

averages 30 pounds, total solids averages 250 pounds, and suspended

solids averages 20 pounds per ton of pulp produced (4). The waste

contains calcium, sodium, sulfide and sulfate which are used in the

process, as well as the byproducts of the digestion and chemical re-

covery phases. From 30 to 50 different compounds have been found

in the evaporator condensates in large and in trace quantities (18).

Some of the identified products include lignin, sugars, resin and fatty acid soaps, and methyl mercaptans.

The paper manufacturing process produces a smaller volume and less concentrated waste than the pulping process. The BOD averages five pounds per ton of pulp processed, and the suspended solids averages five pounds per ton of pulp. The majority of the suspended solids are fiber losses from the paper machine.

From the above figures, an average pulp and paper mill producing 500 tons of paper per day has a waste flow of 15 million gallons per day, with a BOD of 112 mg/l, and a suspended solids concentration of 80 mg/l. The pH varies from 7.5 to 9.0 (4).

Work done by Warren and Marvell (18) indicates that the toxic components of the waste originate in the pulping phase of the process. The paper machine water was considered to be relatively nontoxic to fish.

Because of the organic nature and the natural foaming characteristics of kraft mill effluents, it was decided to investigate the feasibility of using foam separation as a method of treatment.

Purpose and Scope

The purpose of this thesis is to determine the effectiveness of foam separation of kraft mill effluents. The treatment efficiency will be evaluated by Biochemical Oxygen Demand (BOD) and Chemical

Oxygen Demand (COD) reductions. The treatment efficiency will also be assessed by the decrease in toxicity to marine life.

FOAM SEPARATION

Introduction

When a surface active agent (surfactant) is present in a solution, the concentration of the surfactant is greater at a gas-liquid interface than in the bulk of the solution. Foaming of such a solution gives a large gas-liquid interface at which the surfactants concentrate and provides a convenient means for collecting the surfactants. If the foam is collected and collapsed, the resulting liquid (foamate) will have a higher concentration of surfactants than the remaining bulk liquid. This is the essence of foam separation.

Surface Activity

Surface active molecules have a separated polar and non-polar group. The polar group has a high affinity for other polar molecules and the non-polar group has a low affinity for other polar molecules. In a solution of a surfactant and water, the polar end of the surfactant is attracted to the polar water molecule, and the non-polar end of the surfactant is rejected by the water molecule. The polar end of the surfactant has sufficient affinity for the solvent to bring the entire surfactant molecule into solution. If the forces rejecting the non-polar end of the surfactant molecule are sufficiently strong, the surfactant will concentrate at the gas-liquid interface so that part of

the surfactant molecule is not in contact with the water molecules.

The surfactant molecules at the gas-liquid interface are positioned with the polar groups directed toward the solvent and the non-polar groups directed outwardly. With this orientation, the surface of the liquid will exhibit a minimum free energy. Therefore, the addition of a surfactant to water will decrease the free energy which is reflected by a decrease of the surface tension of the solution. Highly surface active materials will cause the greatest reduction of surface tension.

Adsorption

The concentration of a constituent of a solution at a surface is called adsorption. Positive adsorption is an increase in the concentration of the constituent at the surface; whereas, negative adsorption is the decrease in the concentration of the constituent at the surface. Positive adsorption is characterized by a decrease in the surface tension of a solution, while negative adsorption is characterized by an increase in the surface tension of the solution. If the addition of a solute causes an increase in the surface tension of the solution, the solute is considered to be surface inactive.

The fundamental equation for adsorption was developed by Gibbs (6). At equilibrium with constant temperature, pressure, surface area, and composition, the Gibbs adsorption equation is:

$$d\gamma + \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2 + \ldots \Gamma_i d\mu_i = 0$$

where: γ = surface tension of solution, dynes/cm.

μ = chemical potention of the components in the bulk phase, dyne cm. /gm. -mole

Γ = excess surface concentration of components, gm. -moles/cm^2

In a system containing one solvent and one solute, equating the surface excess of the solvent, Γ_1, equal to zero, the equation becomes:

$$d\gamma + \Gamma_2 d\mu_2 = 0 \quad \text{or} \quad \Gamma_2 = \frac{d\gamma}{d\mu_2}$$

since $\mu_i = \mu_i^o + RT \ln a_i$

where: μ_i^o = chemical potential of component in a standard state, dyne cm. /gm. -mole

a_i = activity of the component, gm. -moles/cm^3

R = universal gas constant, dyne cm. /gm. -mole $^\circ$K

T = absolute temperature, $^\circ$K

then $\Gamma_2 = -\dfrac{1}{RT} \dfrac{d\gamma}{d\ln a_2}$

For a dilute solution, 'a' approaches 'c'

where: c = concentration of solute in the bulk phase, gm. -moles/cm^3

then $\Gamma_2 = -\dfrac{1}{RT} \dfrac{d\gamma}{d\ln c} = -\dfrac{c}{RT} \dfrac{d\gamma}{dc}$

While the Gibbs adsorption equation has limited application in foam separation, useful information can be obtained about the characteristics of surface active agents. The Gibbs adsorption equation

indicates that the surface excess of a solute depends on $d\gamma/d\ln c$.

Therefore solutes that have large negative values of $d\gamma/d\ln c$ will

have high concentrations at the gas-liquid interface.

Foam Formation

Foams are considered to be a dispersion of a gas phase in a

liquid phase. The gas phase is separated by a thin liquid film or

lamella. Foulk (8) maintains that a liquid film results when two

previously formed surfaces approach each other in the liquid phase.

A mechanical force acting to bring these surfaces together is opposed

by a resistance arising from the difference in concentration in the

surface layers and the bulk of the solution. A film is formed when

these two opposing forces become equal.

Foam Stability

The most important factor affecting foam stability is the ability

of the film to resist excessive localized thinning of the lamella while

a controlled general thinning proceeds. Foams possess a special

form of elasticity such that any applied stresses which tend towards

local thinning of the lamella are rapidly opposed and counterbalanced

by restoring forces generated during the initial displacement of the

material.

Gibbs defined this ability of the film to resist excessive thinning

as elasticity and is characterized by the equation

$$E = 2A \ \frac{d\gamma}{dA}$$

where: E = elasticity, dynes/cm.

A = area of the liquid film, cm^2.

If a film contains an adsorbed surfactant, stretching of the film by an external force will cause a decrease in concentration of the surfactant and the surface tension will increase. This increased surface tension counteracts the forces extending the film, tending to restore the film to its original condition. Conversely, if the film is contracted, the surfactant concentration increases, which decreases the surface tension of the film, which tends to extend the film. A stable foam will be one whose liquid films have surface tensions capable of fairly rapid local variations.

A second condition for good foam stability is an abnormal superficial (non-Newtonian) viscosity at the gas-liquid interface. Newtonian fluids do not form stable foams. Non-Newtonian fluids form stable foams as long as the applied stress remains below some minimum yield stress. Kraft black liquor foam exemplifies this behavior (11).

Foam Drainage

Foam drainage is the thinning of the lamellae as the inner layers of the liquid drains from the lamellae. The process of drainage of

the layers of the lamellae leaves the foam more concentrated with the solute since the film layer(s) next to the gas liquid interface are more concentrated with the surfactant. In stable foams, the process of drainage of liquid from between the bubbles eventually stops and the foam would persist indefinitely if protected from disturbing influences. After certain drainage time, the lamellae remain unchanged in thickness. Unstable foams rupture before the process of drainage is complete.

Factors Affecting Foam Separation

The purpose of foam separation is to reduce the concentration of the solute in the bulk liquid to a minimum. For economical processing of the undesirable foamate, it is necessary to maintain its volume to a minimum. Therefore, the ratio of the concentration of the solute in the foamate to the concentration of the solute in the bulk liquid (enrichment ratio) must be large. Gas flow rate, column dimensions, and the addition of chemicals are other factors to be considered.

Rubin and Gaden (16) and Bikerman (3) have made extensive studies of the factors affecting foam separation and their effect. These factors are summarized below:

1. Type of material: Surface active materials will concentrate at the gas-liquid interface and can be easily separated from the solution

providing a stable or moderately stable foam is produced. Surfactants producing unstable foams can be concentrated in the upper layers of a stripping column where they could conceivably be removed (7). Non-surface active materials require the addition of a material to form a surface active complex, chelate or other compound. Surfactants are most commonly used for this purpose. Non-surface active materials may also be electrostatically attracted to the surface (foam) by an oppositely charged surfactant.

2. Concentration: For a single solute, there is an ideal concentration where the most stable foam will be formed. At lower and higher concentrations, the stability will be decreased. For multicomponent solutions, stability may increase and decrease with varying concentrations, or it may vary inversely with concentration.

3. Temperature: From the Gibbs adsorption equation it can be seen that increasing the temperature will decrease the surface excess, thereby decreasing enrichment. Increased temperatures will decrease viscosity and will increase the drainage rate; however, the stability of the foam may be decreased. Higher temperatures may cause preferential evaporation within the film. If the solvent is evaporated, the concentration of the solute may be increased until the bubble collapses. There is a critical temperature for a particular solute above which it is unable to foam.

4. Bubble size: Since interfacial area increases with decreasing bubble diameter, more surface active material can be collected per unit volume of gas with smaller bubbles. Decreasing bubble size will increase stability, but may also cause excessive entrainment of the bulk liquid.

5. Surface tension: In a solution with a single solute, the surface excess will be the greatest when the change in surface tension with the change in concentration is the largest (dt/dc maximum). This usually occurs at lower concentrations.

6. pH: This affects the solubility of the surfactant and surface tension of the solution. It has been shown that protein foams are generally most stable when foamed at the isoelectric pH, which is also the point of minimum solubility.

7. Viscosity: High viscosities reduce the drainage rate and may reduce enrichment if foam is removed quickly. However, slow drainage will increase the stability of unstable foams. High viscosities will allow the gas bubble to remain in contact with the bulk liquid longer, and will allow more time for the surfactant to migrate to the gas-liquid interface.

8. Gas flow rate: Increasing the gas flow rate permits more entrainment and reduces enrichment. Unstable foams may collapse in the column at low gas flow rates.

9. Foam stability: Unstable foams must be removed as they are formed, thereby decreasing drainage and enrichment. Moderately stable foams may break and provide internal reflux which increases enrichment. Stable foams require external reflux to increase enrichment.

10. Column dimensions: Holding all other factors equal, increasing column dimensions will allow more residence time and should increase enrichment.

APPLICATION TO KRAFT MILL WASTE

Foam separation of kraft mill effluents has not been investigated to any great extent. A study by Green and Leaf (10) was conducted to determine the cause of the excessive foaming encountered in the grinding of green Jack-Pine wood. Hot water extraction was used to isolate the substance responsible for the foaming. After extraction, the solution was concentrated by foam fractionation. The three main constituents of the extract were carbohydrates, lignin and pitch. Lignin and pitch were colloidally dispersed in the foam. The carbohydrates did not contribute to the foaming phenomenon. By foam fractionation of the extract, approximately 50 percent of the lignin and pitch were removed from the bulk liquid. An increase in concentration of the carbohydrates in the bulk liquid was observed due to the volume reduction.

McCormick (13) did some preliminary work on BOD reduction at a Southern kraft mill. Samples were taken from three sources within the plant and foamed in a crude column by sparging nitrogen through the sample. The BOD varied from an increase of 13.7 percent to a reduction of 29.4 percent. Enrichment ratios of 1.33 to 4.06 were observed. Formation of a voluminous foam was observed in the whole plant effluent. Tests of the foam and effluent indicated BOD reductions of 3.66 to 4.90 percent and enrichment ratios of 1.79 to 1.92.

McCormick made further studies in an effort to remove color from the mill effluent. Because lignins are the primary constituent of the color of kraft effluents, tests were conducted using a solution of Indulin A, a pine lignin derivative. Tests at low gas flow rates gave a small volume of broken foam. The lignin and COD concentration was greater in the foam than in the bulk liquid, but there was no significant removal of lignin. Increasing gas flow rates caused excessive entrainment and gave no appreciable enrichment. Non-ionic surfactants added to increase foam stability increased COD enrichment but did not affect color enrichment. The increased COD enrichment was attributed to the concentration of the surfactant in the foam. Low pH favored enrichment. This was attributed to flotation rather than foam separation because the solubility of lignins decreases with decreasing pH.

An attempt was made to use cationic surfactants to complex or electrostatically attract the anionic lignin. Approximately 30 surfactants were tried and all but Ammonyx LDA precipitated the lignin. Ammonyx LDA is a 30 percent solution of active lauryl dimethyl amine oxide. Maximum color reduction of 35 percent was obtained using a bulk solution of 800 mg/l. However, the quantity of Ammonyx LDA required and the volume of foam produced made this method impractical.

Harding and Hendrickson (11) studied the removal of tall oil soaps from kraft black liquor by foam separation. Tall oil soaps form stable foams and are the major cause of foaming in black liquors. Over 90 percent of the tall oil soap could be removed on one-fourth of the tests and over 80 percent could be removed on one-half of the tests. No correlation could be obtained between the quantity of tall oil removed per liter of air and the concentration of the tall oil in the feed liquor. The two most important variables were column diameter and temperature. Decreasing either variable will tend to increase yield. The average and maximum enrichment ratios were 12 and 40, respectively. Enrichment was most affected by variation in column diameter.

METHOD OF STUDY

The whole mill effluent was selected as the waste stream to be studied. The study was conducted in three phases: (1) without the addition of a surfactant, (2) with the addition of a nonionic surfactant, and (3) with the addition of ionic surfactants. The degree of treatment obtained was analyzed by the reduction in BOD, COD and toxicity.

The tests conducted and their purpose are as follows:

1. A whole waste sample was foamed without the use of a surface active additive to evaluate the natural foam separation potential.

2. A nonionic surfactant, Krystallamide LA, was used to increase the foam stability. Krystallamide LA is a 63-67 percent solution of lauric acid diethanolamide. The effect of gas flow rate was also evaluated using this surfactant.

3. A cationic surfactant, Ammonyx LO, was used to evaluate the feasibility of using a surfactant to complex or electrostatically attract the anionic weakly surface active and non-surface active materials in the waste. The cationic surfactant was evaluated at two concentrations. Ammonyx LO is a 30 percent solution of lauryl dimethyl amine oxide.

4. An anionic surfactant, sodium lauryl sulfate, was used to evaluate the feasibility of using a surfactant to complex or electrostatically

attract the cationic weakly surface active and non-surface active materials in the waste. The anionic surfactant was evaluated at two concentrations.

5. The anionic and cationic surfactants were foamed in tandem to determine if different materials were being removed by the surfactants. This test was conducted at an elevated temperature to appraise its effect.

6. The anionic and cationic surfactants were each foamed in tandem with the nonionic surfactant. The nonionic surfactant was used to give foam stability in order to remove the bulk of the remaining ionic surfactants which were thought to be significantly contributing to the toxicity of the treated waste. The effect of elevated temperature was also evaluated.

APPARATUS

Batch foaming tests were conducted using a one liter sample in a foaming column pictured in Figure 1. A schematic diagram is shown in Figure 2. Compressed air was drawn from the laboratory supply lines and the pressure was reduced to 15 psi by a pressure regulator. The air was filtered and the flow was manually controlled through a needle valve. The air flow rate was measured by a Roger Gilmont instrument flowmeter. The air entered the column through a medium porosity, fritted glass filtering tube fitted in a movable rubber stopper which was used to plug the bottom of the column. A mercurial thermometer was positioned in the rubber stopper.

The foaming column was constructed from a five foot length of 1.5 inch diameter glass pipe. The foam exited from the top of the column through a removable 90 degree elbow. A variac controlled heating tape was wrapped around the column to maintain the desired liquid temperature during the tests. The height of the liquid was varied by the movable rubber stopper in the bottom of the column in order to allow the residence time of the foam to be approximately equal at varying flow rates. After leaving the top of the column, the foam was broken in a centrifugal foam breaker and collected in a beaker.

Figure 1. Foaming column.

1. air supply
2. pressure regulator
3. control valve
4. filter
5. surge chamber
6. needle valve
7. flow meter
8. by-pass valve
9. gas sparger
10. thermometer
11. foaming column
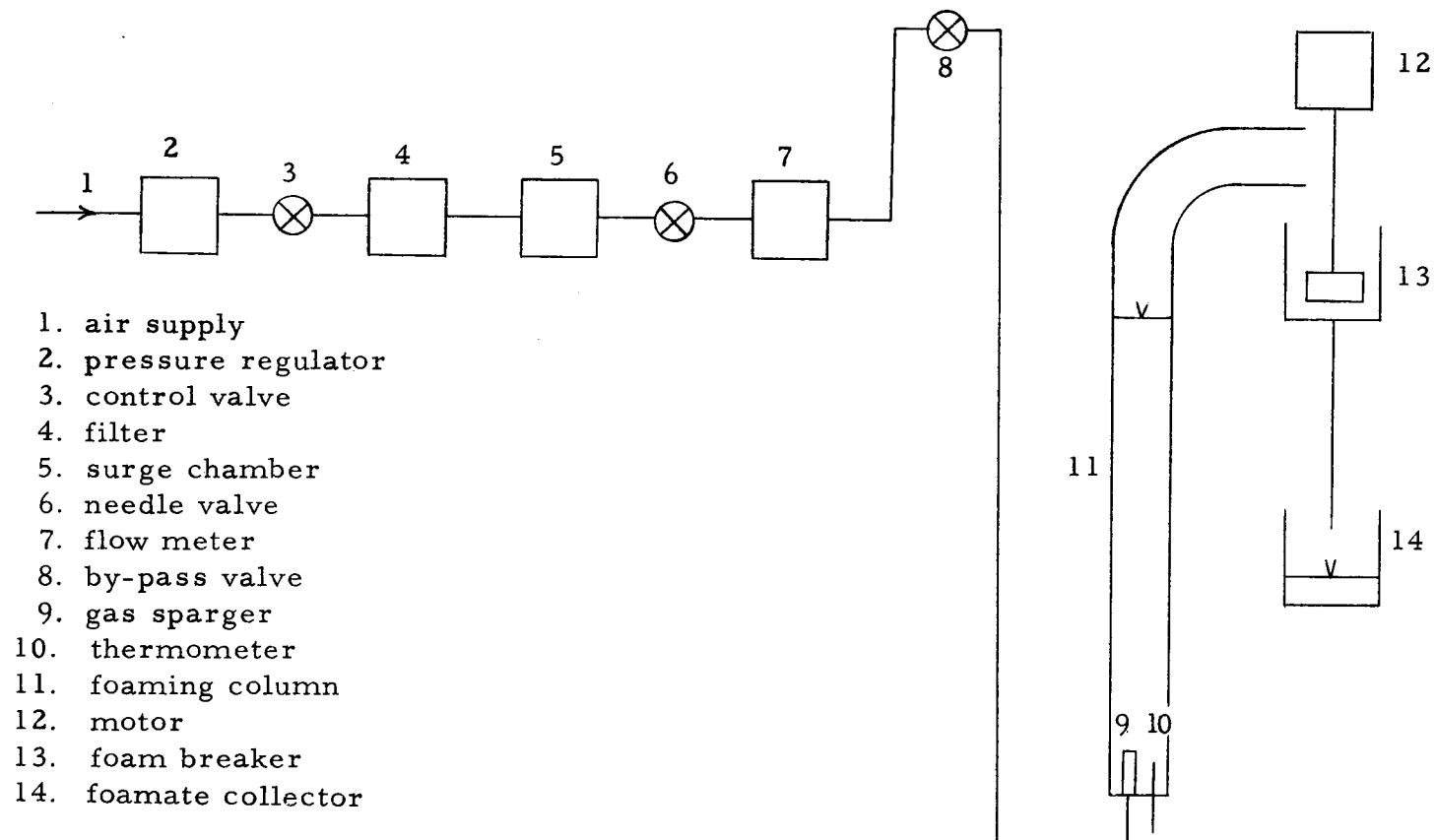12. motor
13. foam breaker
14. foamate collector

Figure 2.   Schematic of experimental apparatus.

EXPERIMENTAL PROCEDURE

Grab samples of the whole mill effluent were obtained from the Western Kraft paper mill located at Albany, Oregon. Samples were stored at 4° C in a stoppered glass container until the tests were conducted.

The foaming operation consisted of bringing a premeasured one liter sample of the waste to the test temperature in a water bath. The column was charged from the top with the sample and the proper air flow was adjusted by means of a needle valve. The sample was foamed at a constant flow rate (± 10 percent) and a constant temperature ($\pm 2^{o}$ C) until the foam broke and no more foam would exit from the top of the column. The remaining foam in the column was allowed to drain momentarily. Then the bulk liquid was drained from the column through a tygon tube fitted in a rubber stopper at the bottom of the column. The foam remaining in the column was allowed to collapse and was then drained from the column and combined with the foamate. This method approximates the conditions that would be found if a continuous flow model had been used.

BOD and COD tests were conducted within 24 hours of foaming, and pH was measured immediately after foaming. Toxicity tests were conducted at the Oregon State University Marine Science Laboratory located at Newport, Oregon. The difficulties in

transportation of samples and scheduling, resulted in some delays in performing the toxicity tests. All samples were stored at 4° C in stoppered glass bottles until the tests were conducted.

Initial tests using the nonionic surfactant in untreated waste encountered several difficulties. Fibers present in the waste settled to the bottom of the column, adhered to the column walls, and some were carried over in the foam. Results obtained from the COD tests were erratic due to the uneven distribution of the fibers. Several pretreatment methods were tried in order to eliminate the fiber problem. Among these were, homogenization, centrifuging, filtration through glass wool, and sedimentation. Sedimentation gave the most consistent results. On all subsequent work, samples were settled for approximately 12 hours, the supernatant was drawn off and filtered through glass wool prior to foaming.

METHODS OF ANALYSIS

To evaluate the treatment efficiency of foam separation, after foaming in the column, BOD, COD, and toxicity tests were conducted on the whole waste, whole waste with surfactant, bulk liquid, and foamate. BOD and COD were measured in accordance with the practices set forth in Standard Methods for the Examination of Water and Wastewater (1). In the BOD determination, the Alsterberg Modification of the Winkler Method was used to measure dissolved oxygen. Samples were incubated at 20° C ($\pm 2^{\circ}$ C) for five days. In the COD test, the samples were refluxed for two hours using silver sulfate as a catalyst and no chloride corrections were applied. Hydrogen ion concentration was measured by a Leads and Northrup pH meter.

Toxicity tests were conducted using the bay mussel (Mytilus edulis Linnaeus) as the test organism. The procedure normally followed was to make several 100 ml dilutions of the samples in unfiltered sea water adjusted to a salinity of 2.5 percent. A male and female mussel were spawned in separate containers of sea water using potassium chloride as a stimulus. One ml each of the sea water containing the ova and sperm was injected into each dilution and incubated at 21° C ($\pm 2^{\circ}$ C) for 48 hours. The dilutions were then examined under a microscope and the number of mussels having normal shell development were counted. Usually a random sample of 150 mussels was counted to determine the percentage of normal

mussels. The median tolerance limit (TLm) was used as the measure of relative toxicity. Results are expressed in percent concentration by volume.

RESULTS

Test conditions, volumes of bulk liquid and foamate, and foaming time are tabulated in Table I. Results of pH, BOD, and COD analysis are tabulated in Tables II, III, and IV, respectively. Figures 3 through 15 show the results of the toxicity tests.

The characteristics of the kraft mill effluents varied considerably during the course of the tests. pH varied from 9. 0 to 10. 5. BOD varied from 210 to 342 mg/l and COD varied from 577 to 967 mg/l. The range of toxicity was from 1. 8 to 3. 7 percent concentration. For this reason, an accurate comparison between the different test conditions and surfactants cannot be made.

Preliminary investigations on three grab samples taken on different days indicated that erratic results could be expected. One sample formed a moderately stable foam, the second sample formed an unstable foam, and the third sample did not foam. Accordingly, the foaming of the whole waste without the addition of a surfactant was abandoned and the emphasis placed on evaluating the various surface active additives. One successful attempt was made to foam the waste without the addition of a surfactant.

Temperature

Increasing temperature generally increased the volume of foam produced. There was no significant difference in the BOD, COD, and

TABLE I
Test Conditions, Volumes and Foaming Time

Test	Surfactant Type	Conc., mg/l	Air flow rate, cm./min.	Temp., °C	Bulk liquid	Foamate	Foaming time, min.
1	nonionic	50	10	25	730	253	25
2	nonionic	50	20	25	775	222	17
3	cationic	200	10	25	495	500	33
4	cationic	100	10	25	852	140	40
5	anionic	60	10	25	823	175	85
6	anionic	30	10	25	796	200	45
(1) 7a	anionic	30	10	40	758	240	48
(1) 7b	cationic	100	10	40	770	722	24
(1) 8a	anionic	30	10	40	612	385	29
(1) 8b	nonionic	50	10	40	804	195	15
(1) 9a	cationic	100	10	40	670	322	26
(1) 9b	nonionic	50	10	40	827	165	16
10	----	---	20	40	740	258	17

(1) Tests 7a, 7b; 8a, 8b; 9a, 9b were conducted in tandem.

TABLE II

Results of pH Analysis

| Test | pH | | | |
	Whole waste	Whole waste w/surf.	Bulk liquid	Foamate
1	10.3	10.3	10.2	9.6
2	10.3	10.3	10.2	9.9
3	10.5	10.4	10.2	10.0
4	10.5	10.4	10.5	9.5
5	10.0	10.0	9.7	8.8
6	10.0	10.0	9.8	9.2
7a	10.4	10.4	10.2	9.8
7b	10.2	10.2	10.1	9.5
8a	9.0	9.0	8.4	8.7
8b	8.4	8.6	8.0	8.2
9a	9.0	9.0	8.4	8.4
9b	8.4	8.6	8.2	8.2
10	9.0	- - - -	8.4	8.6

TABLE III

Results of BOD Analysis

Test	BOD, mg/1					Percent reduction	Enrichment ratio
	Whole waste	Whole waste w/surf.	Bulk liquid	Foamate	Reduction		
1	274	296	207	420	67	24.4	2.03
2	274	296	200	472	74	27.0	2.36
3	264	295	171	350	93	35.2	2.05
4	264	280	195	500	69	26.1	2.56
5	239	313	184	735	55	23.0	4.00
6	239	297	176	548	63	26.4	3.12
7a	342	392	288	683	54	15.8	2.37
7b	288	303	250	405	38	13.2	1.62
					92 (1)	26.9 (1)	
8a	210	283	156	375	54	25.7	2.40
8b	156	190	152	248	4	2.6	1.63
					58 (1)	27.6 (1)	
9a	210	225	146	239	64	30.4	1.64
9b	146	164	143	240	3	2.1	1.68
					67 (1)	31.8 (1)	
10	210	---	152	254	58	27.6	1.67

(1) Overall reduction

TABLE IV
Results of COD Analysis

| Test	COD, mg/l					Percent reduction	Enrichment ratio
	Whole waste	Whole waste w/surf.	Bulk liquid	Foamate	Reduction		
1	668	757	594	1096	74	11.1	1.84
2	668	757	615	1196	53	7.9	1.94
3	749	820	598	1022	151	20.2	1.71
4	749	839	621	1490	128	17.1	2.40
5	577	699	474	1418	103	17.9	3.00
6	577	637	476	1099	101	17.5	2.31
7a	967	1005	825	1510	142	14.7	1.83
7b	825	886	766	1140	59	7.2	1.49
					201 (1)	20.8 (1)	
8a	578	687	480	846	98	17.0	1.76
8b	480	580	478	719	2	0.4	1.50
					100 (1)	17.3 (1)	
9a	578	651	483	807	95	16.4	1.67
9b	483	574	483	768	0	0	1.59
					95 (1)	16.4 (1)	
10	578	---	472	665	106	18.3	1.41

(1) Overall reduction
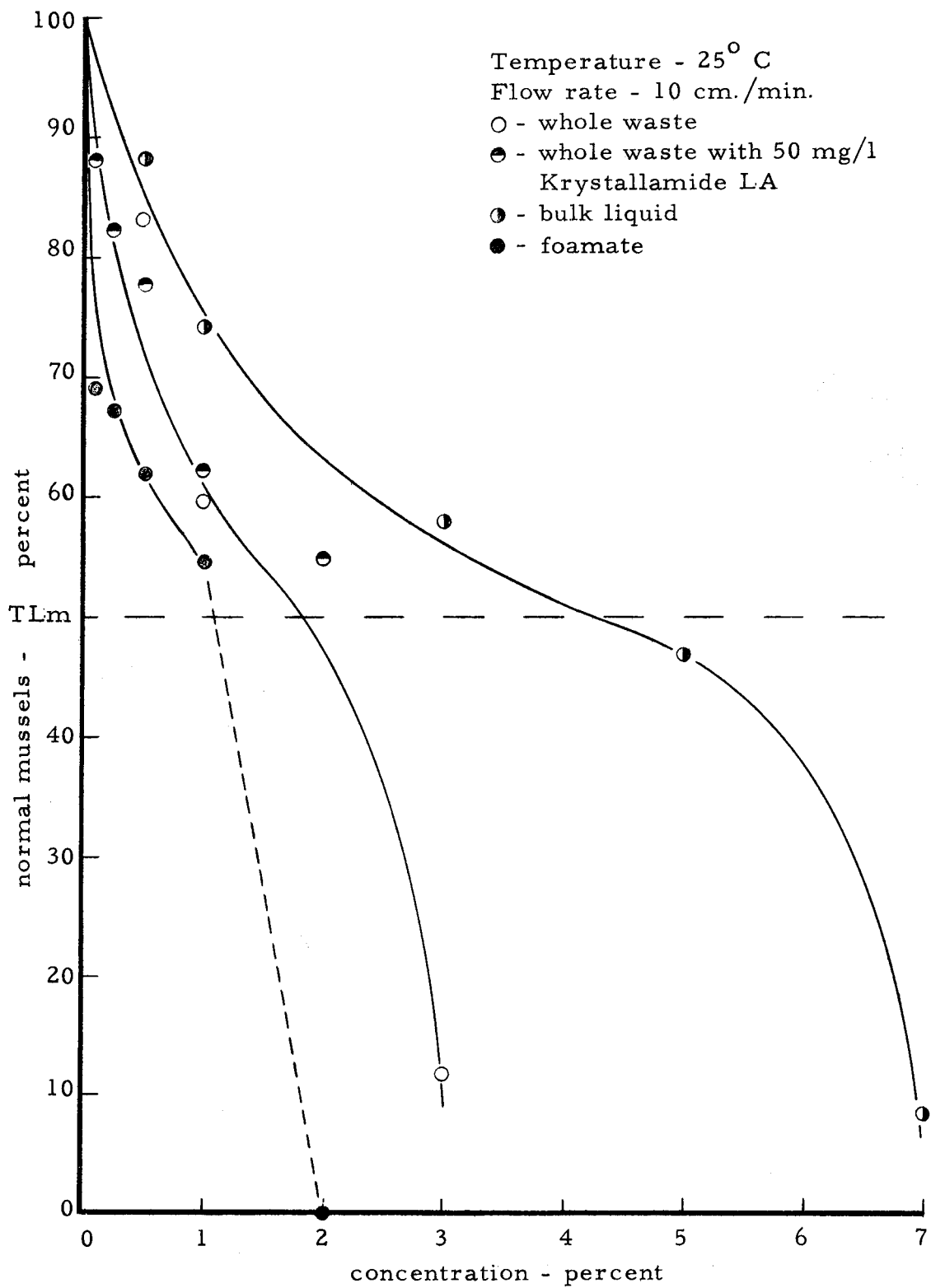
Figure 3. Toxicity results - test 1.

Figure 4.   Toxicity results - test 2.

Figure 5. Toxicity results - test 3.

Figure 6. Toxicity results - test 4.

Figure 7.   Toxicity results - test 5.

Figure 8. Toxicity results - test 6.

Figure 9. Toxicity results - test 7a.

Figure 10.   Toxicity results - test 7b.

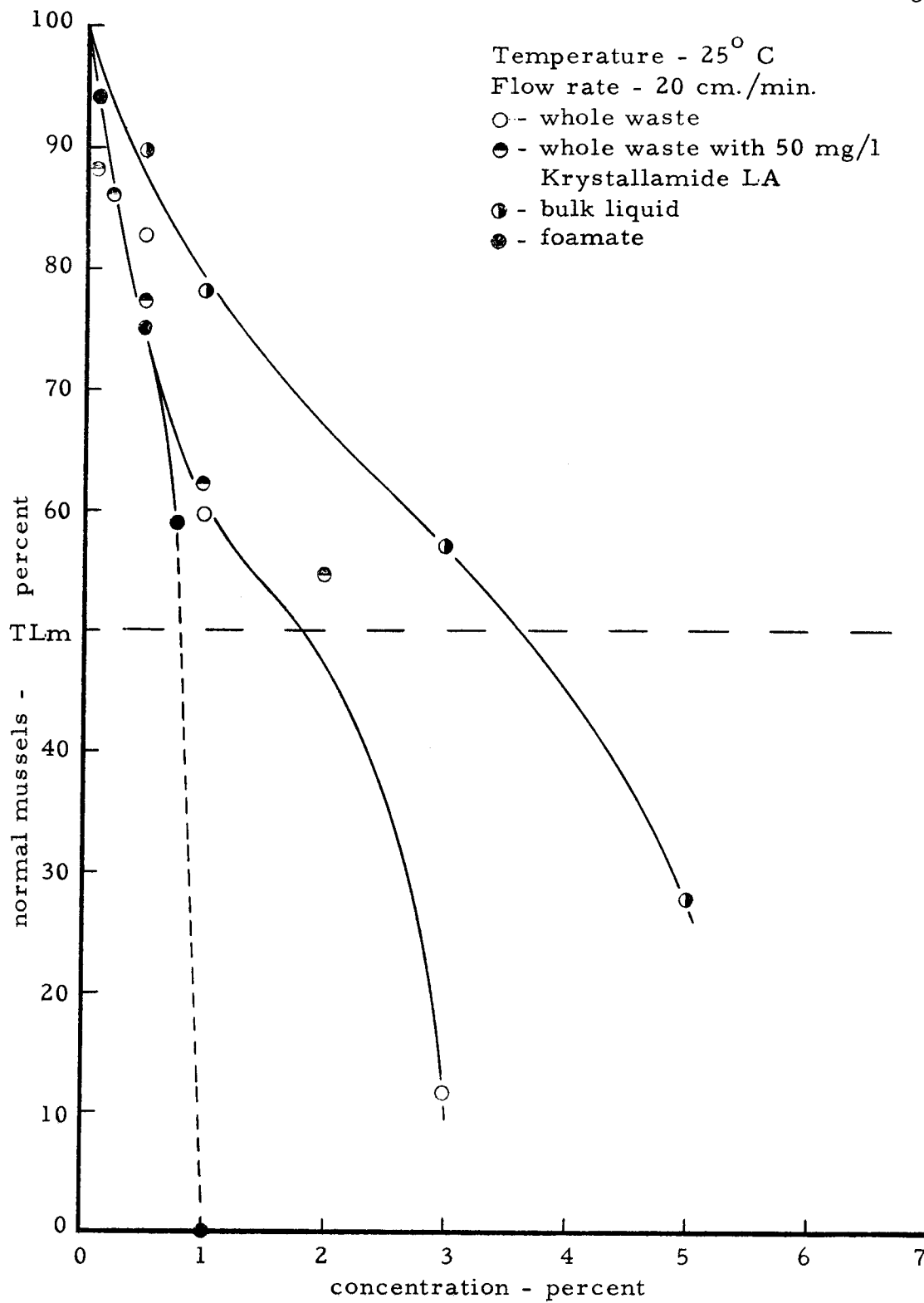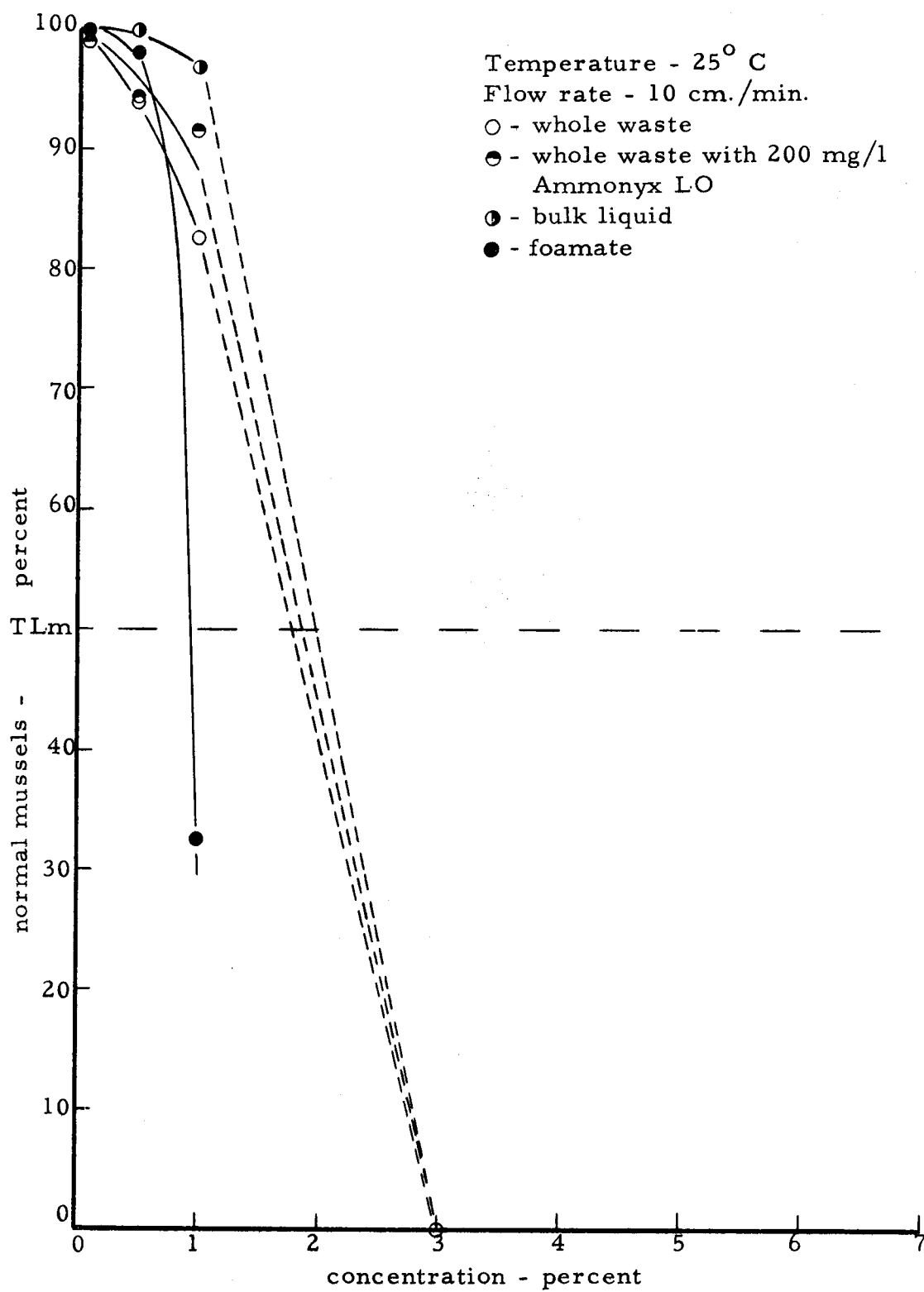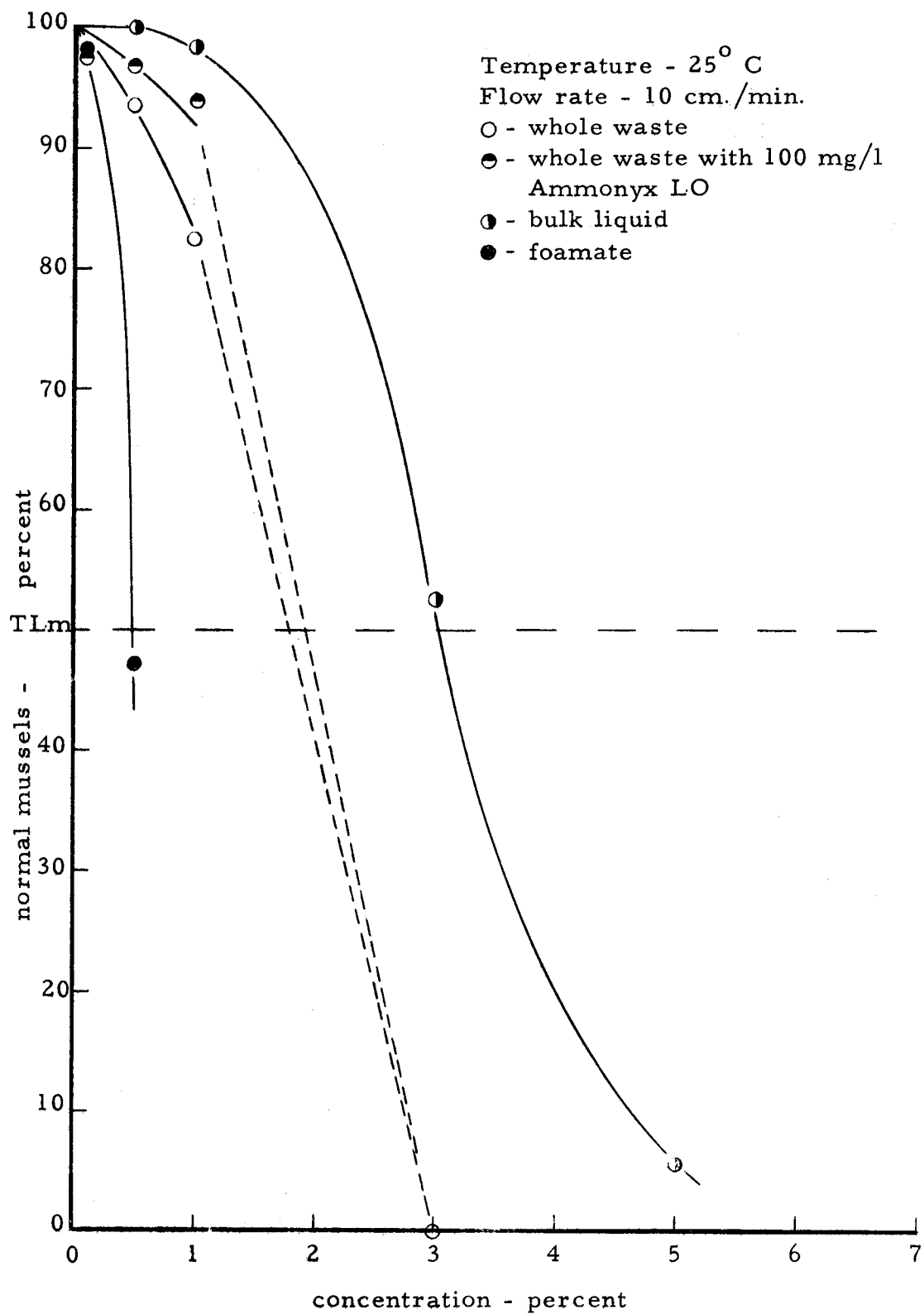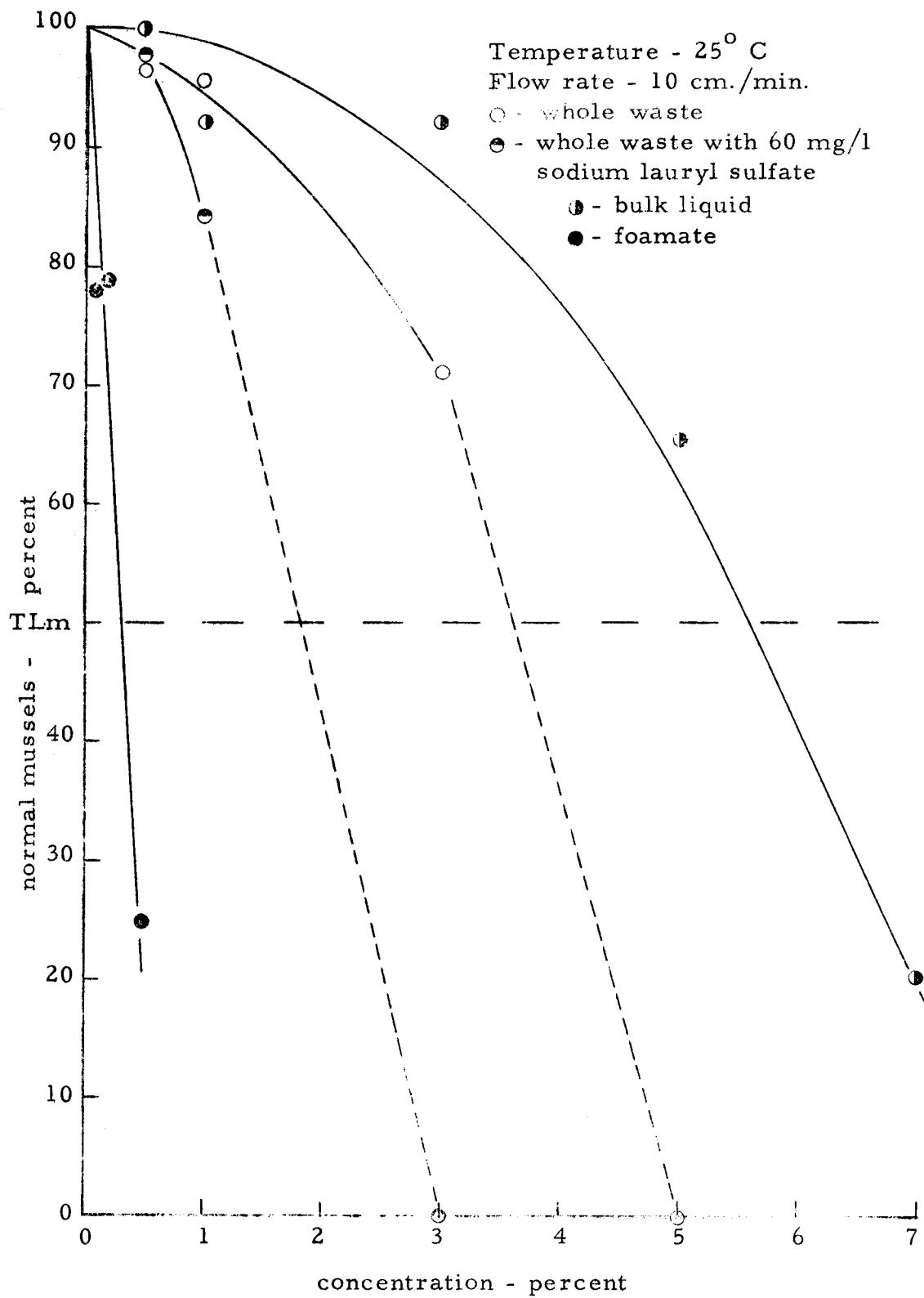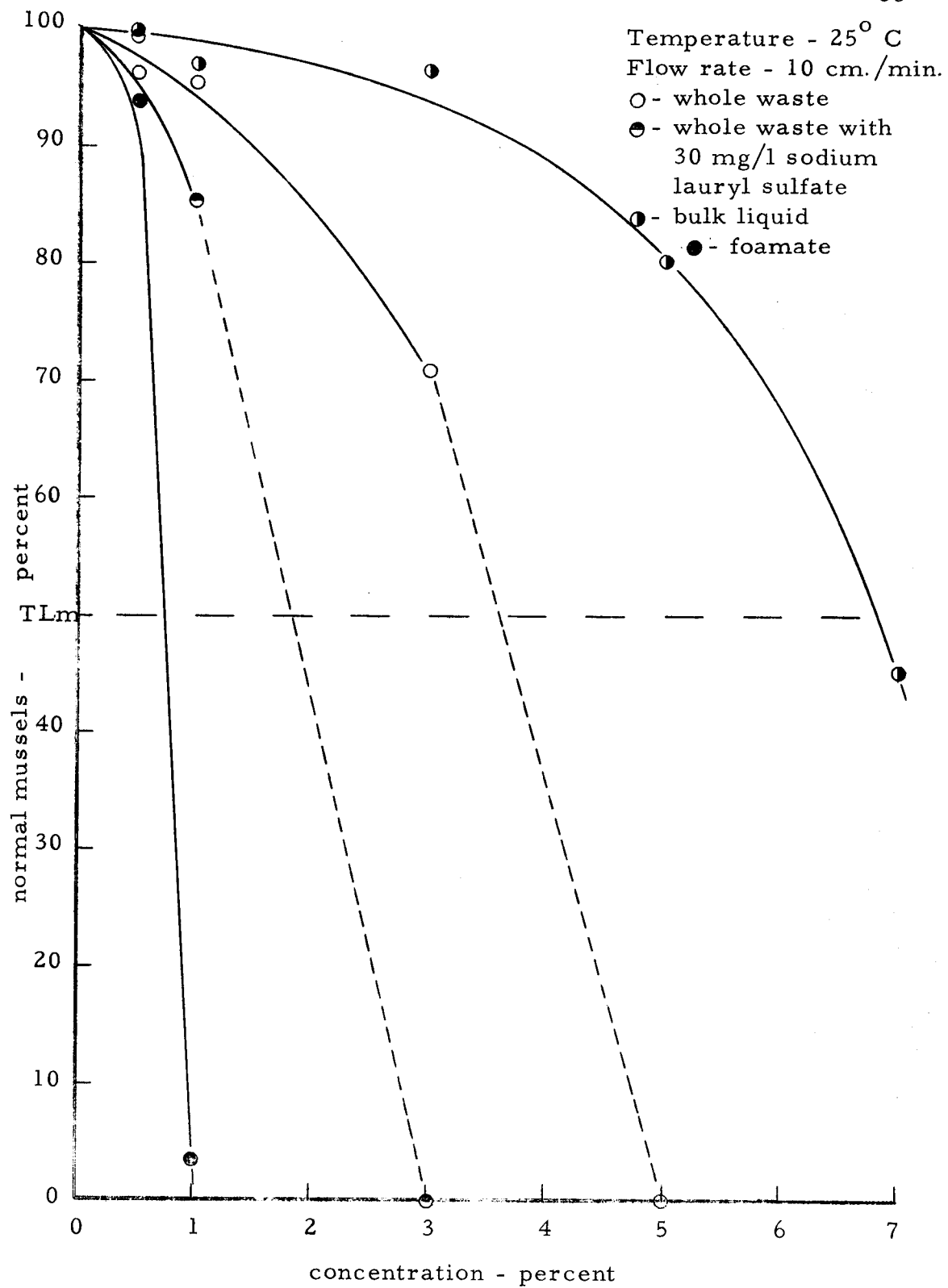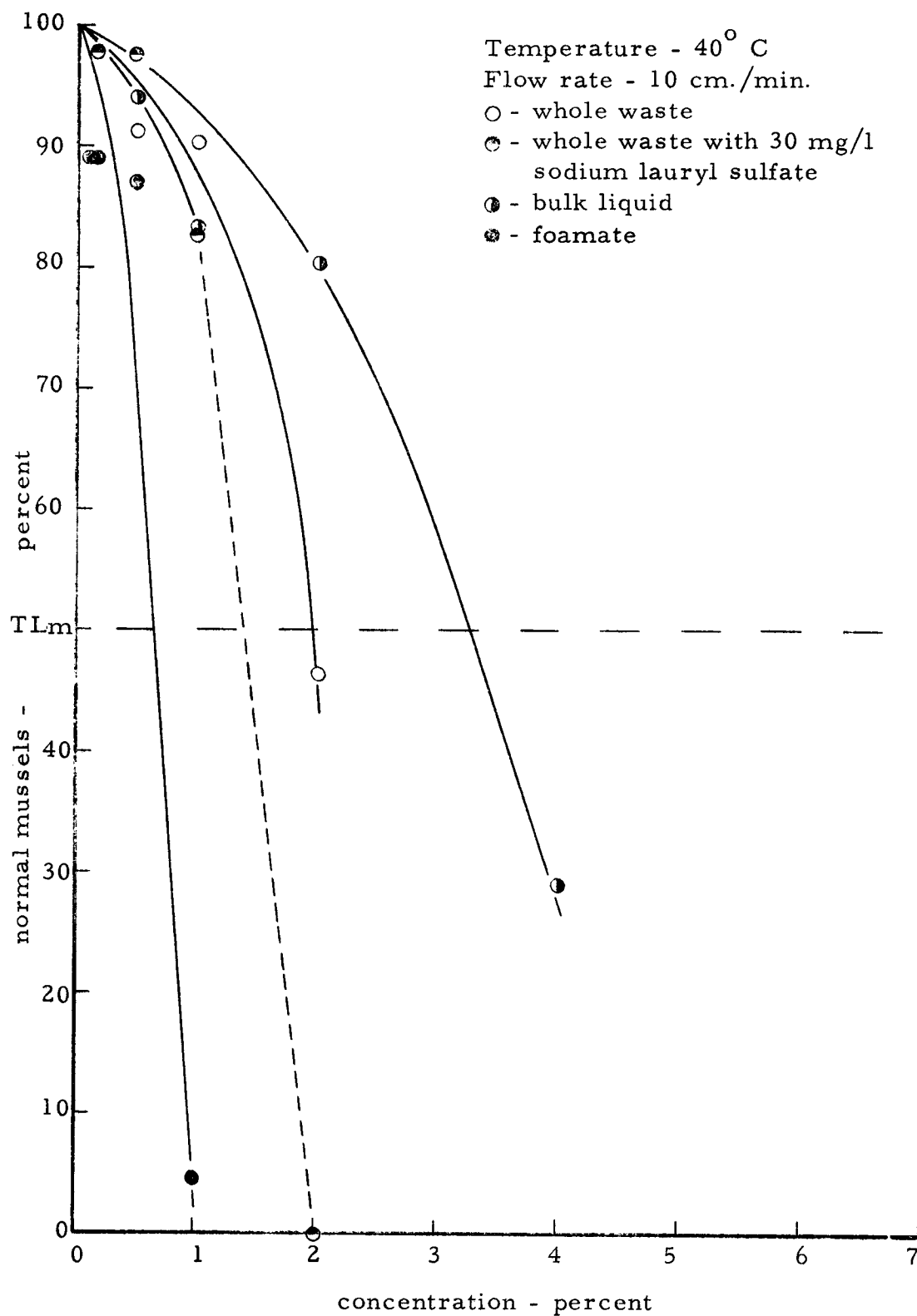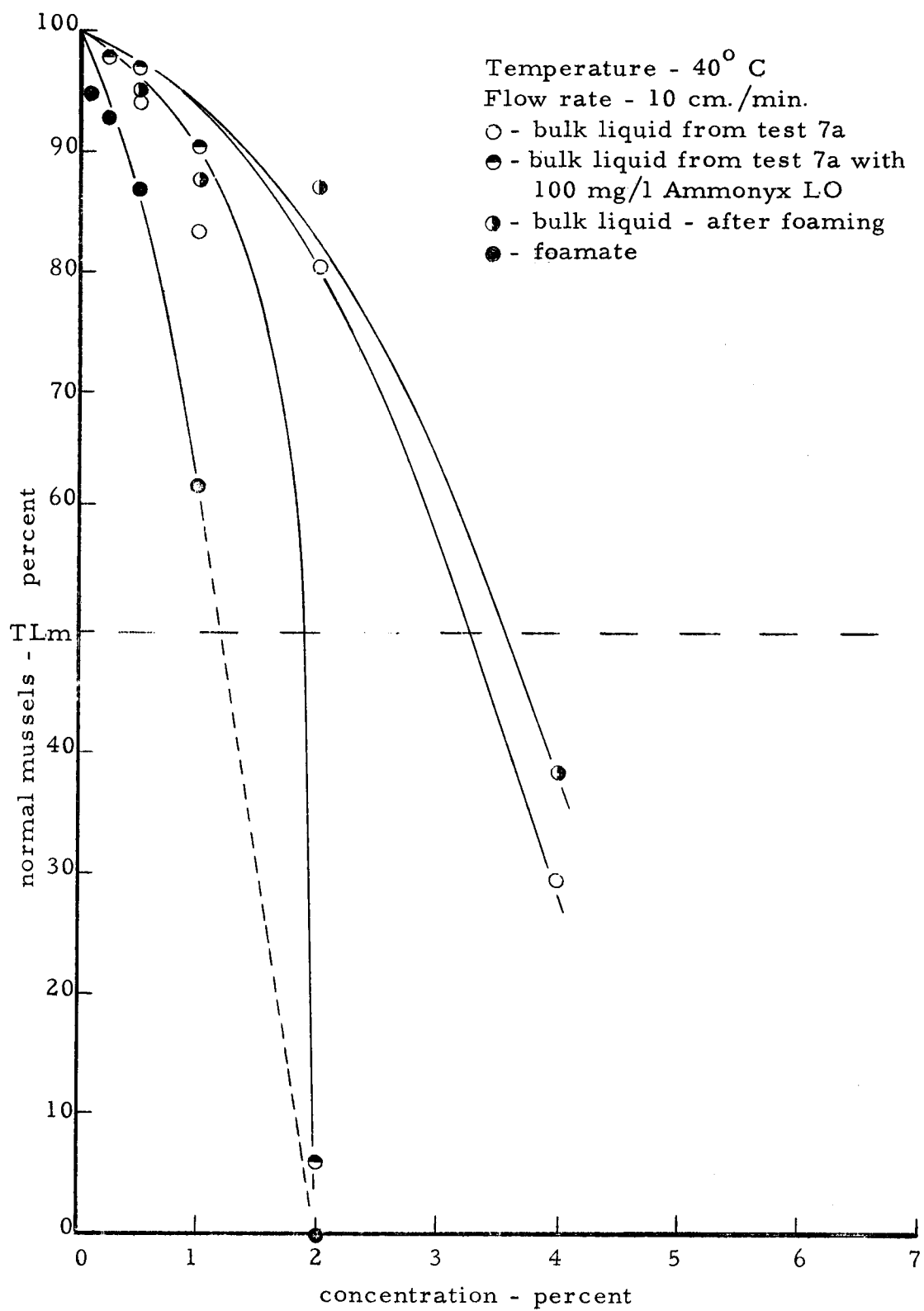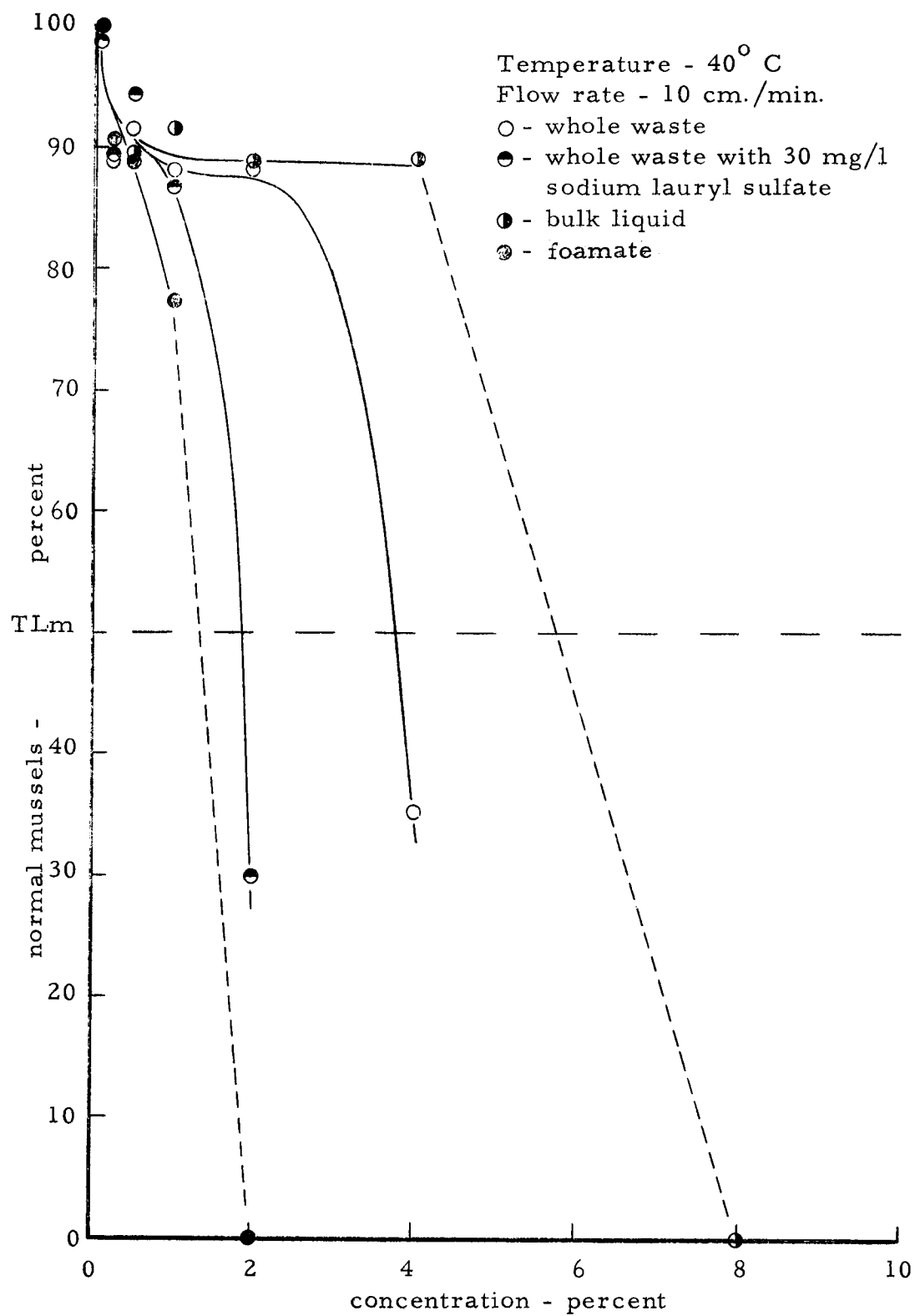Figure 11. Toxicity results - test 8a.
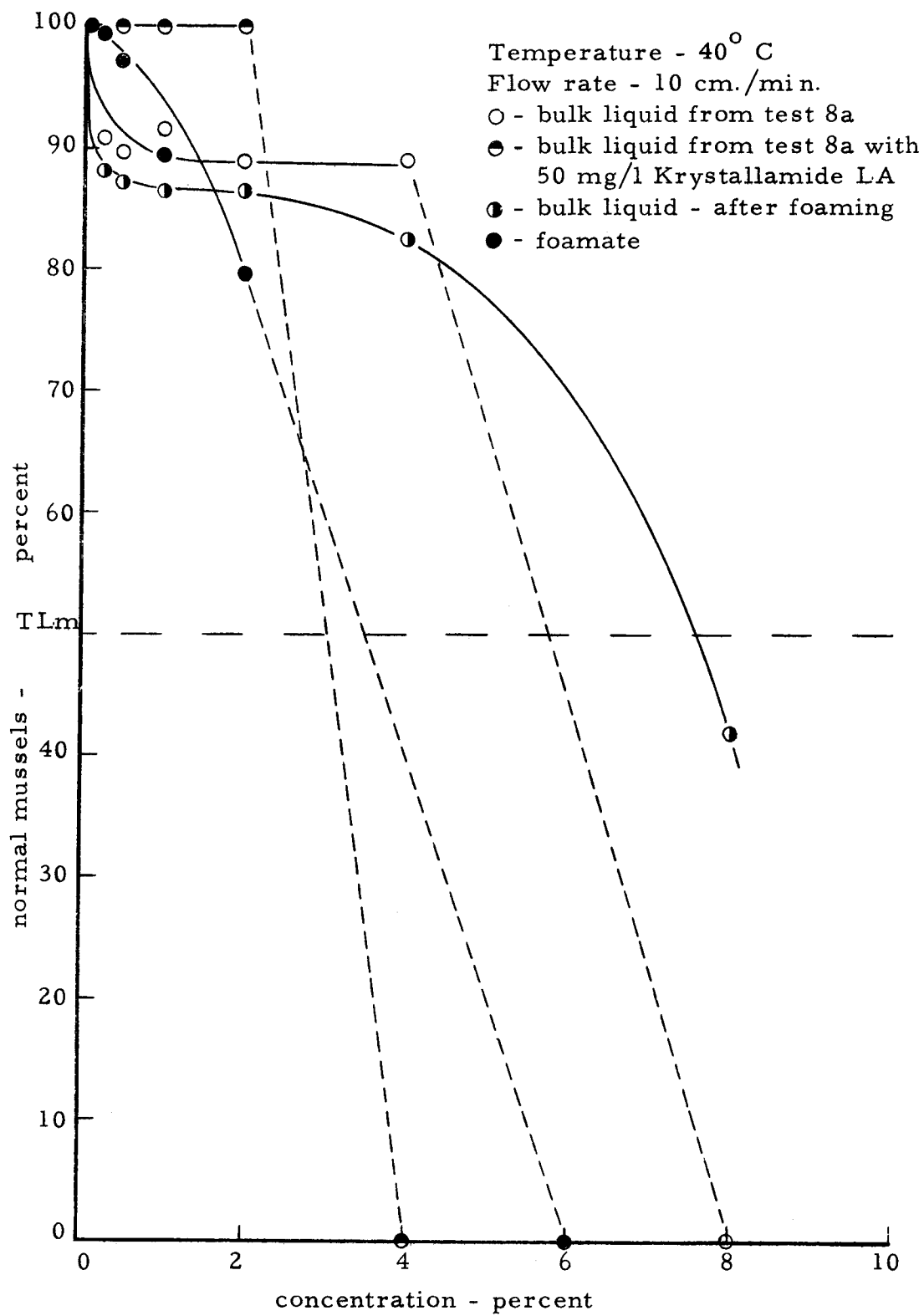
Figure 12. Toxicity results - test 8b.
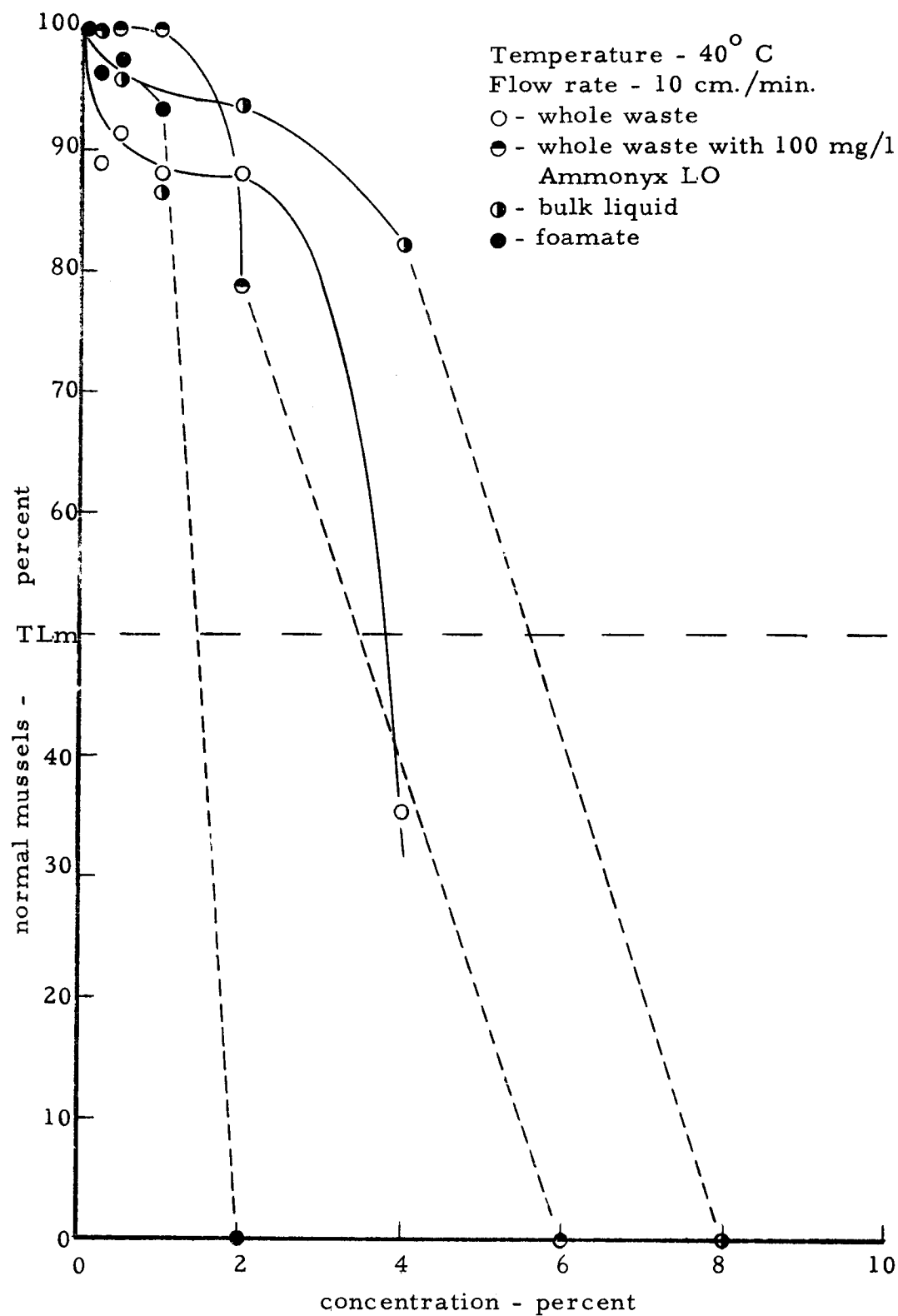
Figure 13.   Toxicity results - test 9a.
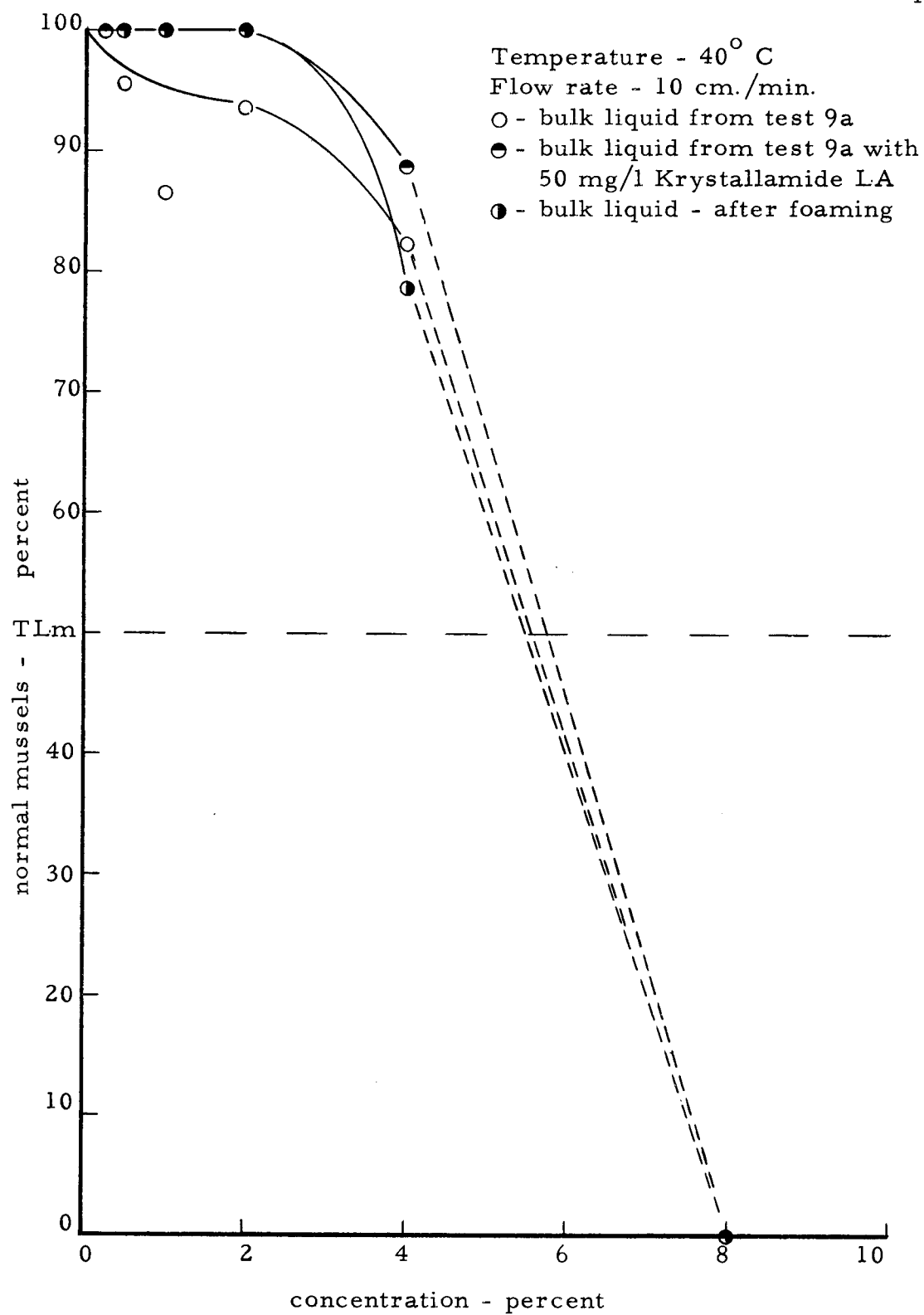
Figure 14.   Toxicity results - test 9b.
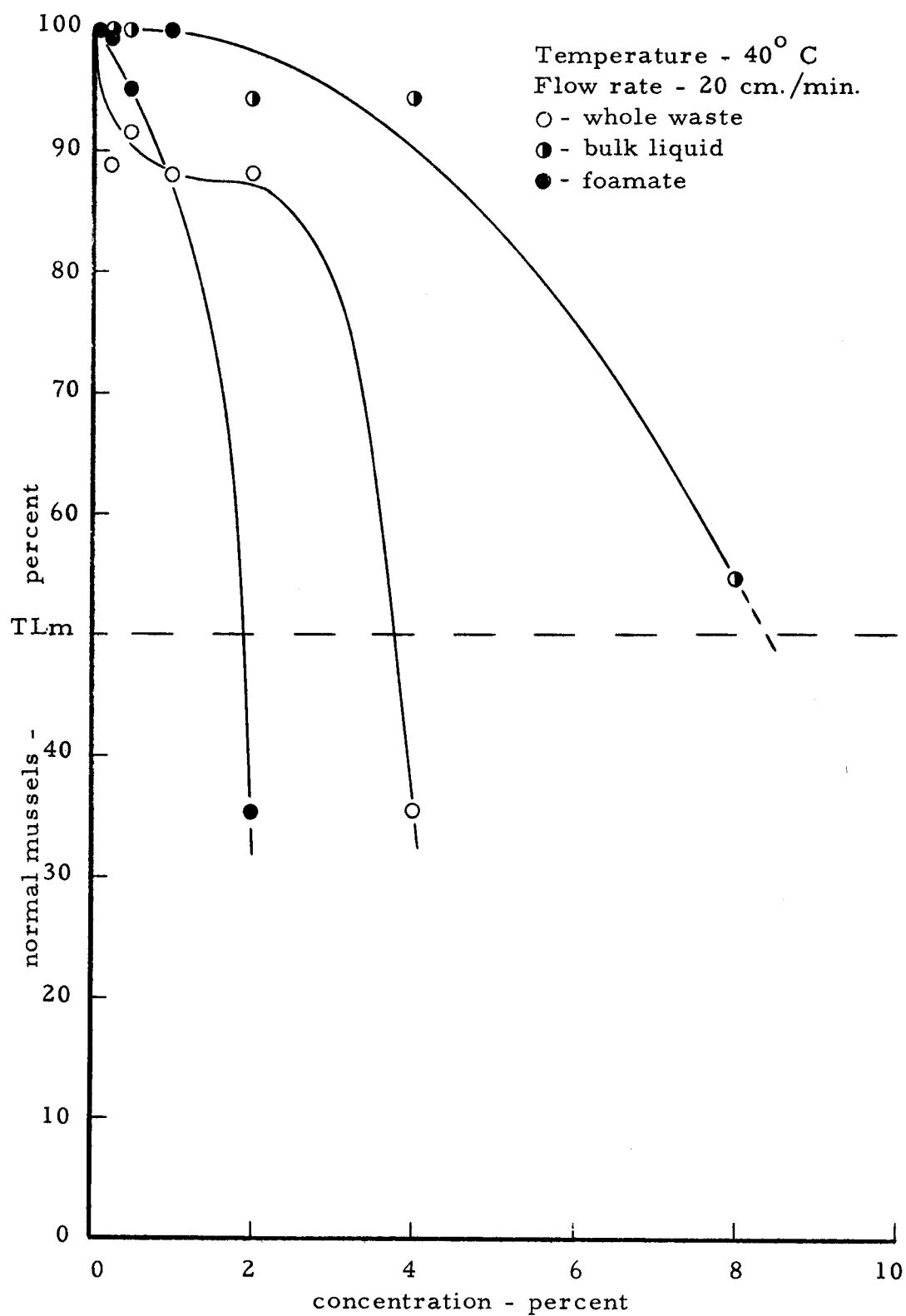
Figure 15. Toxicity results - test 10.

toxicity reductions.

pH

In most cases the addition of a surfactant to the whole waste tended to decrease the pH slightly. This would be expected since the pH of the surfactants was lower than the whole waste. In all but one case, the pH of the bulk liquid was lower than the pH of the whole waste with or without the surfactant added. The reduction in pH could be due either to the removal of some alkaline material from the sample by foam separation and/or evaporation, or it could have been caused by chemical reactions within the sample during aeration. It was observed that the pH of the whole waste would gradually decrease if it was stored unstoppered at room temperature. The pH of the foamate was always lower than the pH of the whole waste with or without the surfactant added. This would be expected when a surfactant was used since it would be concentrated in the foamate. Possibly some acidic materials were concentrated in the foamate.

In test 10, the whole waste was successfully foamed without the addition of a surfactant. This sample also had the lowest pH of the samples tested. Possibly the lower pH increased the foam stability.

Gas Flow Rate

Increasing the gas flow rate when using the nonionic surfactant (tests 1 and 2), decreased the stability of the foam. A smaller

volume of foamate was collected at the increased flow rate, but there was no significant difference in the BOD, COD, and toxicity reductions. A greater enrichment ratio was observed at the higher flow rate.

An unstable foam was produced at a flow rate of 10 cm./min. when the whole waste without a surfactant was foamed (test 10). By increasing the flow rate to 20 cm./min. , a moderately stable foam was produced.

BOD Reduction

BOD reduction ranged from 15. 8 to 35. 2 percent. More significant than the percent reduction is the quantity reduction. Tests 5, 6, 7a, and 8a with the anionic surfactant indicated BOD reductions of 55 mg/l at 60 mg/l surfactant concentration; and 63, 54, and 54 mg/l at 30 mg/l surfactant concentration. Apparently the anionic surfactant combined with materials in the waste only in small quantities or not at all.

With the cationic surfactant, BOD reductions of 93 mg/l at 200 mg/l surfactant concentration; and 69 and 64 mg/l at 100 mg/l surfactant concentration were obtained (tests 3, 4, and 9a). On the basis of prior work by McCormick (13), this surfactant was expected to aid in the removal of lignin from the sample. Lignin is not considered to be readily degradable by biological action and should not

contribute significantly to the oxygen demand in the five day BOD test. It appears that there was some combination of the surfactant with organic material in the waste to give the greater BOD reduction at the higher surfactant concentration. Without some external reflux to reduce the volume of foamate, the use of high concentrations of the cationic surfactant to obtain greater reduction in BOD would not be practical due to the large amount of foamate produced (test 3).

In test 7, the whole waste was first foamed with the anionic surfactant and the bulk liquid was then foamed with the cationic surfactant. An additional BOD removal of 38 mg/l was obtained. This indicates that the cationic and anionic surfactants are probably combining with different materials in the waste.

In tests 1 and 2, with the nonionic surfactant, BOD reductions of 67 and 74 mg/l were obtained. This is slightly higher than the 58 mg/l reduction obtained without the use of a surfactant (test 10). However, the latter waste was less concentrated which could account for the difference in removal.

Tests 8a, 9a, and 10 were conducted on the same waste sample using the ionic surfactants and without a surfactant. There was no appreciable difference in BOD reduction between the three methods.

<center>COD Reduction</center>

COD reductions ranged from 7.9 to 20.2 percent. As in the BOD

test, there was no significant difference between the amount removed

by the two concentrations of the anionic surfactant (tests 5 and 6).

The cationic surfactant removed a larger percentage of COD when

tested at the higher surfactant concentration as would be expected

if the surfactant combined with the lignin (tests 3 and 4).

Using the nonionic surfactant (tests 1 and 2), less COD was re-

moved than without the use of a surfactant (test 10). The opposite

result was obtained in the BOD analysis. Because of the lower pH,

more lignin was probably removed in test 10. During the latter test,

brown colored material was observed in the foam. No appreciable

difference was noted in COD reduction when tests were conducted on

the same waste using the ionic surfactants and without a surfactant.

Toxicity Reduction

The toxicity reduction factor (ratio of TLm of bulk liquid to TLm

of waste before foaming) varied from 1.1 to 2.3. With the cationic

surfactant, reduction factors of 1.1 at 200 mg/l surfactant concen-

tration; and 1.7 and 1.5 at 100 mg/l surfactant concentration were

observed (tests 3, 4, and 9a). With the anionic surfactant, reduc-

tion factors of 1.6 at 60 mg/l surfactant concentration; and 1.9, 1.7,

and 1.5 at 30 mg/l surfactant concentration were observed (tests 5,

6, 7a, and 8a).

Using the nonionic surfactant, reduction factors of 2.3 at the low

flow rate and 2. 0 at the high flow rate were observed (tests 1 and 2).

When foamed without a surfactant, the reduction factor was 2. 3

(test 10). It appears that there is no significant difference between

foaming without a surfactant and with a nonionic surfactant.

It was observed that the nonionic surfactant did not contribute

significantly to the toxicity of the whole waste in the concentrations

used. The anionic surfactant had a significant contribution to the

toxicity. Toxicity tests with the cationic surfactant were not conclu-

sive in this matter. In tests 8 and 9, the ionic surfactants were

foamed in tandem with the nonionic surfactant to remove the bulk of

residual ionic surfactants. No additional decrease in toxicity was

observed over what was obtained with the cationic surfactant (test 9b).

The anionic surfactant's bulk liquid toxicity was reduced to approxi-

mately the same level as the bulk liquid of the foaming test without

a surfactant (test 8b).

CONCLUSIONS

The following conclusions have been derived from the above results:

1. The addition of a surfactant will be necessary in order to form a stable foam during periods of low foaming potential.

2. Lowering of the pH may increase foam stability.

3. Increasing the temperature will increase the volume of foamate.

4. No significant BOD or COD reductions can be obtained.

5. Toxicity reduction factors up to 2.3 can be obtained.

6. The addition of the ionic surfactants did not improve treatment efficiency.

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APPENDIX

APPENDIX

Results of Toxicity Tests

Test	Sample	Sample concentration, %	Number counted	Number normal	Number normal, % Counted	Number normal, % Adjusted
1, 2	Control (ave.)	100. 00	150	119	79. 4	100. 0
1, 2	Whole waste	0. 50	150	99	66. 0	83. 2
		1. 00	150	71	47. 3	59. 6
		3. 00	150	14	9. 3	11. 8
		5. 00	150	0	0	0
1	Whole waste with 50 mg/1 Krystallamide LA	0. 10	150	105	70. 1	88. 3
		0. 25	150	98	65. 3	82. 4
		0. 50	150	92	61. 3	77. 3
		1. 00	150	74	49. 3	62. 1
		2. 00	150	65	43. 3	54. 6
		5. 00	150	0	0	0
1	Bulk liquid	0. 50	150	105	70. 1	88. 3
		1. 00	150	88	58. 7	74. 0
		3. 00	150	69	46. 0	58. 0
		5. 00	150	56	37. 3	47. 1
		7. 00	150	10	6. 7	8. 4
		10. 00	150	0	0	0
1	Foamate	0. 10	150	82	54. 7	68. 9
		0. 25	150	80	53. 3	67. 2
		0. 50	150	74	48. 3	62. 1
		1. 00	150	65	43. 3	54. 6
		2. 00	150	0	0	0
2	Bulk liquid	0. 50	150	107	71. 3	89. 8
		1. 00	150	93	62. 0	78. 2
		3. 00	150	68	45. 3	57. 1
		5. 00	150	33	22. 0	27. 7
		7. 00	150	0	0	0
2	Foamate	0. 10	150	112	74. 7	94. 2
		0. 50	150	89	59. 3	74. 8
		0. 75	150	70	46. 7	58. 8
		1. 00	150	0	0	0
3, 4	Control (ave.)	100. 00	100-150	98-146	96. 6	100. 0

APPENDIX Continued

Test	Sample	Sample concen- tration, %	Number counted	Number normal	Number normal, % Counted	Adjusted
3, 4	Whole waste	0.50	94	85	90.5	93.6
		1.00	108	86	79.6	82.5
		3.00	107	0	0	0
3	Whole waste	0.10	96	91	94.8	99.0
	with 200 mg/l	0.50	110	100	90.9	94.2
	Ammonyx LO	1.00	113	100	88.5	91.7
		3.00	93	0	0	0
3	Bulk liquid	0.50	110	102	97.3	100.0
		1.00	91	85	93.4	96.6
		3.00	109	0	0	0
3	Foamate	0.10	150	145	96.7	100.0
		0.50	150	142	94.7	98.0
		1.00	150	47	31.3	32.4
		3.00	150	0	0	0
4	Whole waste	0.10	150	141	94.0	97.3
	with 100 mg/l	0.50	150	140	93.3	96.6
	Ammonyx LO	1.00	150	136	90.7	93.8
		3.00	150	0	0	0
4	Bulk liquid	0.50	150	145	96.7	100.0
		1.00	150	143	95.3	98.5
		3.00	150	76	51.7	52.4
		5.00	150	8	5.3	5.5
		7.00	150	0	0	0
4	Foamate	0.10	150	143	95.3	98.7
		0.50	150	68	45.3	46.9
		1.00	38	0	0	0
5, 6	Control (ave.)	100.00	150	139	92.7	100.0
5, 6	Whole waste	0.50	150	134	89.4	96.4
		1.00	150	133	88.7	95.7
		3.00	150	99	66.0	71.2
		5.00	150	0	0	0
5	Whole waste	0.50	150	136	90.7	97.8
	with 60 mg/l	1.00	150	117	78.0	84.2
	sodium lauryl sulfate	3.00	150	0	0	0

APPENDIX Continued

Test	Sample	Sample concen-tration, %	Number counted	Number normal	Number normal, % Counted	Adjusted
5	Bulk liquid	0. 50	150	141	94. 0	100. 0
		1. 00	150	128	85. 4	92. 1
		3. 00	150	128	85. 4	92. 1
		5. 00	150	91	60. 7	65. 5
		7. 00	150	28	18. 7	20. 2
5	Foamate	0. 10	150	81	54. 0	77. 8
	(Test conducted	0. 20	150	82	54. 6	78. 8
	separately, con-	0. 50	150	26	17. 3	25. 0
	trol was 69. 7%)	1. 00	150	0	0	0
6	Whole waste with 30 mg/l sodium lauryl sulfate	0. 50	150	138	92. 0	99. 3
		1. 00	150	119	79. 4	85. 7
		3. 00	150	0	0	0
6	Bulk liquid	0. 50	150	139	92. 7	100. 0
		1. 00	150	135	90. 0	97. 1
		3. 00	150	134	89. 4	96. 5
		5. 00	150	112	74. 7	80. 6
		7. 00	150	63	42. 0	45. 3
6		0. 50	150	131	87. 3	94. 2
		1. 00	150	5	3. 3	3. 6
		3. 00	150	0	0	0
7	Control (ave.)	100. 00	150	138	92. 0	100. 0
7	Whole waste	0. 50	150	126	84. 0	91. 3
		1. 00	150	125	83. 3	90. 6
		2. 00	150	64	42. 6	46. 4
		4. 00	150	0	0	0
7a	Whole waste with 30 mg/l sodium lauryl sulfate	0. 25	150	135	90. 0	97. 8
		0. 50	150	135	90. 0	97. 8
		1. 00	150	114	76. 0	82. 6
		2. 00	150	0	0	0
7a	Bulk liquid	0. 50	150	130	86. 7	94. 2
		1. 00	150	115	76. 7	83. 3
		2. 00	150	111	74. 0	80. 4
		4. 00	150	40	26. 7	29. 0
		8. 00	150	0	0	0

APPENDIX Continued

Test	Sample	Sample concen-tration, %	Number counted	Number normal	Number normal, % Counted	Number normal, % Adjusted
7a	Foamate	0.10	150	123	82.0	89.1
		0.25	150	123	82.0	89.1
		0.50	150	120	80.0	87.0
		1.00	150	6	4.0	4.3
		2.00	150	0	0	0
7b	Bulk liquid test 7a with 100 mg/l Ammonyx LO	0.25	150	135	90.0	97.8
		0.50	150	134	89.4	97.1
		1.00	150	125	83.4	90.6
		2.00	150	8	5.4	5.8
		4.00	150	0	0	0
7b	Bulk liquid	0.50	150	131	87.4	94.9
		1.00	150	121	80.7	87.7
		2.00	150	120	80.0	87.0
		4.00	150	53	35.4	38.4
		6.00	150	0	0	0
7b	Foamate	0.10	150	131	87.4	94.9
		0.25	150	128	85.4	92.8
		0.50	150	120	80.0	87.0
		1.00	150	86	57.4	62.3
		2.00	150	0	0	0
8,9, 10	Control (ave.)	100.00	150	141	94.0	100.0
8,9, 10	Whole waste	0.25	150	125	83.4	88.7
		0.50	150	129	86.0	91.5
		1.00	150	124	82.7	88.0
		2.00	150	124	82.7	88.0
		4.00	150	50	33.3	35.4
		8.00	150	0	0	0
8a	Whole waste with 30 mg/l sodium lauryl sulfate	0.10	150	139	92.7	98.6
		0.25	150	126	84.0	89.4
		0.50	150	133	88.7	94.3
		1.00	150	122	81.3	86.5
		2.00	150	42	28.0	29.8
		4.00	150	0	0	
8a	Bulk liquid	0.25	150	128	85.3	90.8
		0.50	150	126	84.0	89.4
		1.00	150	129	86.0	91.5

APPENDIX Continued

Test	Sample	Sample concen- tration, %	Number counted	Number normal	Number normal, % Counted	Adjusted
8a	Bulk liquid	2.00	150	125	83.4	88.7
	Continued	4.00	150	125	83.4	88.7
		8.00	150	0	0	0
8a	Foamate	0.10	150	147	98.0	100.0
		0.25	150	128	85.3	90.8
		0.50	150	125	83.4	88.7
		1.00	150	109	72.7	77.3
		2.00	150	0	0	0
8b	Bulk liquid	0.25	150	>141	---	100.0
	test 8a with	0.50	150	>141	---	100.0
	50 mg/l	1.00	150	>141	---	100.0
	Krystallamide	2.00	150	>141	---	100.0
	LA	4.00	150	0	0	0
8b	Bulk liquid	0.25	150	124	82.7	88.0
		0.50	150	123	82.0	87.2
		1.00	150	122	81.3	86.5
		2.00	150	122	81.3	86.5
		4.00	140	116	77.3	82.3
		8.00	150	59	39.4	41.8
8b	Foamate	0.10	150	141	94.0	100.0
		0.25	150	140	93.4	99.3
		0.50	150	136	90.7	96.5
		1.00	150	126	84.0	89.4
		2.00	150	112	74.7	79.5
		6.00	150	0	0	0
9a	Whole waste	0.10	150	>141	---	100.0
	with 100 mg/l	0.25	150	>141	---	100.0
	Ammonyx LO	0.50	150	>141	---	100.0
		1.00	150	>141	---	100.0
		2.00	150	111	74.0	78.7
		6.00	150	0	0	0
9a	Bulk liquid	0.25	150	146	97.4	100.0
		0.50	150	135	90.0	95.7
		1.00	150	122	81.3	86.5
		2.00	150	132	88.0	93.6
		4.00	150	116	77.4	82.3
		8.00	150	0	0	0

APPENDIX Continued

Test	Sample	Sample concen-tration, %	Number counted	Number normal	Number normal, % Counted	Number normal, % Adjusted
9a	Foamate	0.10	150	142	94.7	100.0
		0.25	150	136	90.7	96.5
		0.50	150	137	91.3	97.2
		1.00	150	132	88.0	93.6
		2.00	150	0	0	0
9b	Bulk liquid	0.25	150	>141	---	100.0
	Test 9a with	0.50	150	>141	---	100.0
	50 mg/l	1.00	150	>141	---	100.0
	Krystallamide	2.00	150	>141	---	100.0
	LA	4.00	150	125	83.4	88.7
		8.00	150	0	0	0
9b	Bulk liquid	0.25	150	>141	---	100.0
		0.50	150	>141	---	100.0
		1.00	150	>141	---	100.0
		2.00	150	>141	---	100.0
		4.00	150	118	78.7	83.7
		8.00	150	0	0	0
9b	Foamate		Not tested			
10	Bulk liquid	0.25	150	>141	---	100.0
		0.50	150	>141	---	100.0
		1.00	150	>141	---	100.0
		2.00	150	133	88.7	94.3
		4.00	150	133	88.7	94.3
		8.00	150	77	51.3	54.6
10	Foamate	0.10	150	145	96.7	100.0
		0.25	150	140	93.4	99.3
		0.50	150	134	89.4	95.0
		1.00	150	143	95.3	100.0
		2.00	150	50	33.3	35.4
		6.00	150	0	0	0