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## **Development of Process Controls For Surimi Production**

Canpolar Inc.  
**PART I**



Fisheries Development Division  
Fisheries and Habitat Management  
Newfoundland Region  
P.O. Box 5667  
St. John's, Newfoundland  
A1C 5X1

March 1988

**Canadian Industry Report of  
Fisheries and Aquatic Sciences  
No. 192**



Fisheries  
and Oceans

Pêches  
et Océans

Canada

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DEVELOPMENT OF PROCESS CONTROLS  
FOR SURIMI PRODUCTION

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FISHERIES AND AQUATIC SCIENCES NO. 192

MARCH 1987

DEVELOPMENT OF PROCESS CONTROLS  
FOR SURIMI PRODUCTS: PART 1

BY

CANPOLAR CONSULTANTS LTD.

FOR

FISHERIES DEVELOPMENT DIVISION  
FISHERIES AND HABITAT MANAGEMENT  
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## ABSTRACT

The objective of this study was to document surimi processing parameters for the development of a process control system. Work was carried out to evaluate a number of sensing technologies for process control during surimi production. Sensors to monitor temperature, pH, dehydration pressure and specific ions were installed on the Marine Institute's pilot surimi line. Data from these sensors was collected during processing of surimi and was correlated with other process and product data.

The results indicated that temperature, salinity, pH and pressure are useful operational parameters for day to day processing. Data obtained from ion monitoring were used to develop a preliminary chemical/physiological model for leaching kinetics. It was found that adjusting pH in the leaching process affected the moisture content and elasticity of the final product.

Based on the preliminary processing model and a knowledge of sensor technology, implementation of a "real time" interactive process controller appears feasible.

The following report is accompanied by a document which contains the appendices referenced and all additional information. The report is available upon request from the Fisheries Development Division, Fisheries and Oceans.

## PREFACE

This project was sponsored by the Fisheries Development Division, Fisheries and Habitat Management, Department of Fisheries and Oceans, St. John's, Newfoundland under DSS File No. FP001-6-2102/01-SC.

The Scientific Authority for this project was:

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## 1.0 INTRODUCTION

### 1.1 History

The production of refined minced fish (surimi) products has been common practice in Japan for more than 500 years. The Japanese have been successful in producing a variety of "Neriseihin" products using a simple kitchen process of mincing and washing fish flesh. The majority of these products are variations of "Kamaboko" (Table 1.1). They also include fish sausage and ham. The surimi base in all these products imparts a consistent, elastic texture capable of being shaped, extruded and flavoured.

TABLE 1.1

#### KAMABOKO PRODUCTS

<u>SHAPES</u>	<u>COOKING METHODS</u>	<u>INGREDIENTS</u>
Loaf (Itatsuki)	Steamed	Starch
Tubular (Chikuwa)	Steamed and boiled	Vegetables
Ball, bar (age)	Broiled	Seaweed
Leaf (Sasa)	Boiled (hampen) Fried (tempura, Satsumage)	Egg yolk
Rolled (datemaki)		Ham
Chipped (Kezuri)		Shrimp Squid

Although surimi products have been eaten in Japan for many centuries, large-scale production did not commence until the 1950's and 60's. Commercialization resulted from two factors: (1) a resource shortage for the traditional kamaboko and fish sausage industries forced producers to examine the potential for processing a plentiful, but underutilized Alaskan pollock resource and (2) fish sausage producers discovered that the addition of sugar to surimi permitted effective (extended or longer) frozen storage without loss of textural characteristics. By 1960, 250 tonnes of frozen pollock surimi were produced in four processing plants located at Hokkaido. Production increased in the mid 1970's to about 300,000 metric tonnes, over half of which was produced at sea. Between 1970 and 1984, production reached a plateau, partly because of greater availability of pollock; much of that resource is owned by the U.S., which is now producing surimi in several plants in Alaska. Currently, surimi is produced in at least 20 countries including Canada, New Zealand, Korea, Iceland and the U.S.S.R. In all cases processing is based on Japanese technology and, for the most part, the plants are Japanese-owned or have some Japanese involvement. The technology and equipment utilized in the surimi industry has remained essentially the same since the early 1960's (Figure 1.1). The process has been proven for relatively fresh Alaskan pollock and must be adapted and controlled to be compatible

with other raw materials such as those found in Atlantic Canada. It is known that groundfish such as cod and flounder produce surimi comparable to pollock surimi (Chandra, 1986) but the current market values for these species make them unattractive as starting material for a surimi industry. A viable industry will likely require utilization of mixture of resources, e.g. silver hake, capelin and groundfish frame wastes. The development of flexible process control systems is necessary if an industry is to be based on a variable resource. Existing technology and equipment are not amenable to such an industry.

## 1.2 Industrial Biochemistry

Unlike most fish processing operations, surimi production involves a differential extraction of protein rather than just mechanical manipulation of fish portions, e.g. filleting, mincing. Although there is a certain degree of mechanical processing necessary, the main objective of a surimi operation is to concentrate myofibrillar protein to produce a functional, elastic gel. The basic steps in a surimi process are shown in Figure 1.2. After the meat has been mechanically deboned and minced it is washed liberally with fresh water. The main function of this process is to eliminate water soluble protein and certain undesirable

compounds such as blood, fat, flavors, trimethylamine-n-oxide (TMAO) and degradative enzymes. The overall objective is to selectively retain salt soluble (myofibrillar) protein. In both the refiner and the screw press operations, residual particles and water are removed.

Since the overall process can be explained in terms of protein biochemistry, the requirements for process controls and handling procedures can be readily understood. As a general rule, proteins behave optimally or exhibit certain properties like gel forming ability under specific conditions of storage, pH, temperature, ionic and chemical environment and mechanical stress. These parameters must be monitored and optimized for effective control of the process. Effective process controls will optimize the process so that a predictable product can be produced regardless of the initial raw material used.

### 1.3 Industrial Application

In addition to controlling the surimi process, a major consideration in effectively implementing a system is plant compatibility. The harsh environments of fish processing plants place major restraints on the types of sensors, actuators and control systems that can be used. Equipment must be robust, capable of withstanding temperature and

moisture extremes as well as simple to clean. Sensors must also be self calibrating and maintenance free. Instruments requiring frequent adjustments and scrupulous cleaning become non-functional and unsuitable for processing. The system used for process controls should be interactive and consistently useful to the operator. Information such as time, pH, temperature and pressure require close scrutiny during processing. Finally, it is very likely that process algorithms generated from theory and laboratory are not completely comparable with real-time processing. Algorithms will have to be tested and modified to accommodate variations introduced through scaled-up operations.

The overall success of the surimi industry appears to be dependent on the availability of useable starting material. Existing markets for surimi-based products require lean, white fleshed fish and the general market demand for fillets from these species is high. This market demand has increased the value of conventional surimi feedstock, even pollock, to a point where surimi production is less attractive. There appear to be two options available: (1) create a new North American market for surimi based products from dark-fleshed, underutilized species



(e.g. herring) and (2) introduce technologies to accommodate less valuable species and waste portions from groundfish. The creation of additional products from surimi, other than shellfish analogues, appears to be needed, along with the development of surimi technology. However, better utilization of the available materials for an existing market appears to be an immediate requirement.

Traditional Japanese dogma stipulates that an absolute requirement for the best grade of surimi is freshness. Part of the grading requirement for super-class surimi is that it be produced at sea (Suzuki, 1982). Recent studies conducted at the Marine Institute (Chandra, 1986) have determined that functional surimi can be produced from 9-10 day old commercially handled cod. As of yet, this product has not been produced on a consistent and predictable basis. This is partly because processing is carried out on a "rule" or "recipe" basis (10 day old fish is processed identically to one day old fish product). Results are therefore variable. A more effective processing method is to adapt the process to the starting material. Raw material handling as well as certain physical and chemical characteristics of the fish will affect optimum processing conditions. The role of an

effective process controller is to integrate the starting material cues, evaluate the behaviour of the material as it passes through the process and optimally modify the conditions in real time. For example, an older fish sample may show an extremely high pH during leaching, and experience has shown that these conditions produce an extremely wet mince. This material is difficult to dewater in the screw press. The operator has the option of lowering the pH in the wash tank or adding additional salt during a saline wash. After appropriate adjustments have been made, and if the moisture analysis of meat exiting the refiner indicates that the mince is too dry, further adjustments can then be made to the process to optimize the moisture content.

#### **1.4 Project Objective**

The primary objective of this study was to collect "cause-and-effect" information during surimi processing as part of a long-term project to develop surimi process controls. The first step toward this goal was the development of a process model that included physiological, chemical and thermi-mechanical parameters pertinent to the performance of a surimi processing plant.

The secondary objective was to evaluate the operational performance of specific pieces of process monitoring equipment that might be incorporated into a control system.

The project objectives were addressed by installing a process monitoring system on the Bibun pilot line, monitoring processing parameters and machine performance during operation, and developing a process model on the basis of the information collected.

This report includes (1) a description of the installed processing monitoring equipment (Section 2.0 and Appendix B,C), (2) complete documentation of process data (Section 3.1 and Appendix A), (3) an evaluation of the process sensors (Section 3.3), (4) the development of a preliminary process model (Section 3.2) and (5) discussion and recommendations for further work.

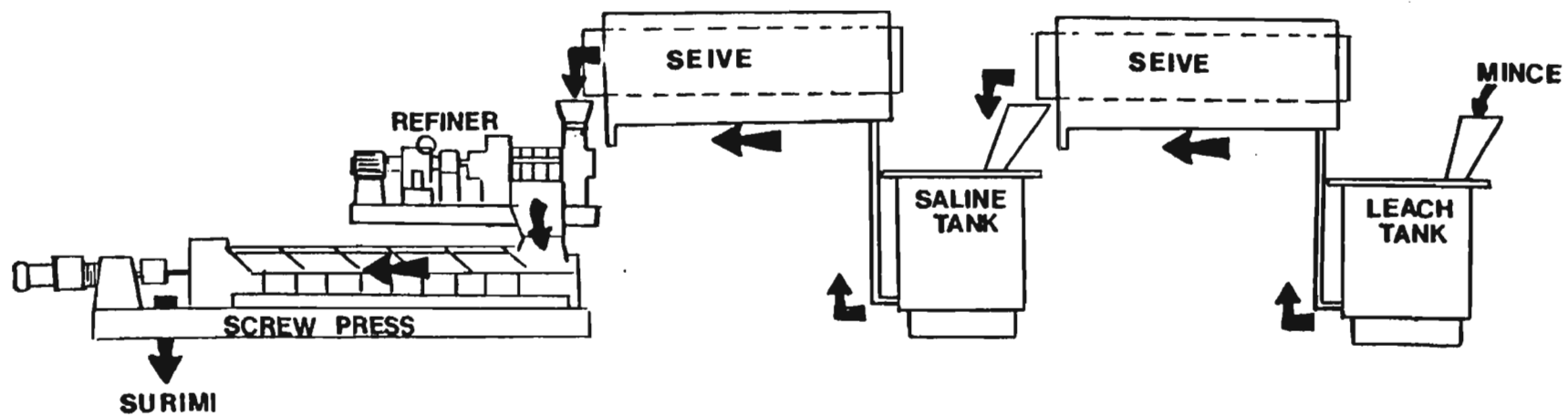
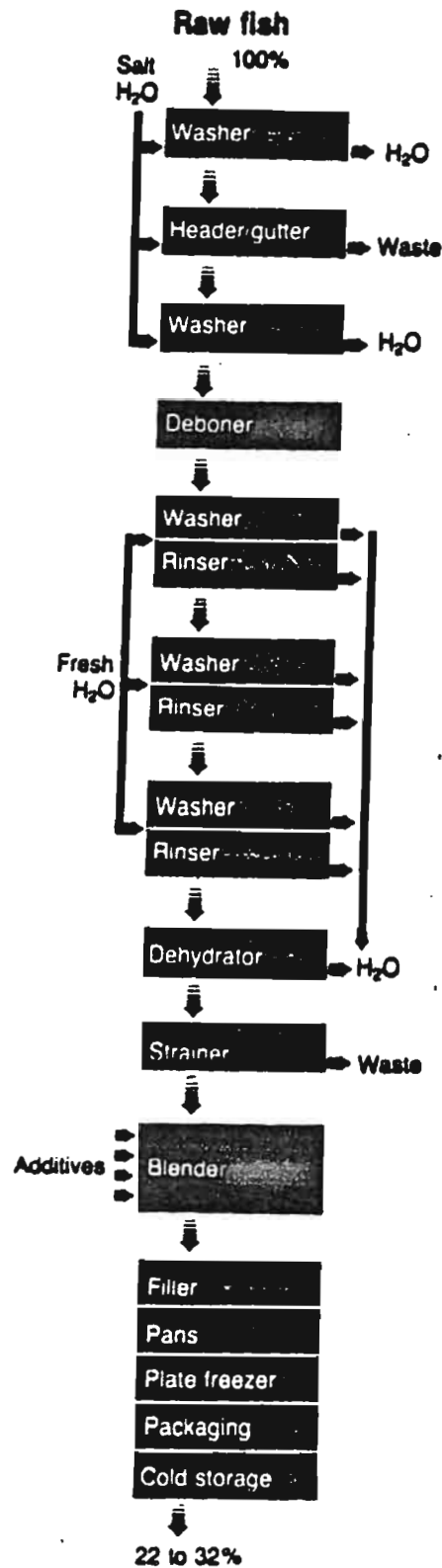


FIGURE 1.1 SURIMI PROCESSING EQUIPMENT



FROM LEE, 1984

FIGURE 1.2 STEPS IN SURIMI PROCESSING

## 2.0 TECHNOLOGY AND HARDWARE

The process monitoring and data logging system installed on the Marine Institute surimi pilot line is shown schematically in Figure 2.1. The sensor system consists of specific ion and pH electrodes, thermocouples and a pressure transducer. Data was collected from each of these sensors through a HP Data Acquisition and Control Unit 3421A/HP 110 Computer Interface. During each pilot run, data was automatically collected at one minute intervals. In order to avoid contamination and physical abuse, the specific ion and pH electrodes were mounted at a remote location from the surimi line. A vacuum flow system was designed to siphon samples of process fluid from both the leach tank and saline tank. Backflush cleaning water (maximum pressure of 80 psi) was also supplied to the electrode system.

The following discussion outlines the specifications of the sensor system, data housing unit and digital interfacing.

### 2.1 Specific Ion and pH Electrodes

Sodium, calcium and potassium ion specific electrodes as well as a pH electrode were employed to gather information regarding the kinetics of the surimi washing process. A Corning <sup>tm</sup> glass sodium electrode was used to measure the activity of sodium ions in solution. Corning <sup>tm</sup> calcium and

potassium electrodes consisted of a chemically inert body with a detachable PVC membrane. A Corning <sup>tm</sup> reference electrode was used together with the specific ion electrodes to produce stable reference potentials. The pH electrode used on the process monitoring package was a Canlab polymer body, sealed reference combination electrode.

Accurate specific ion measurements are dependent on the ionic strength of the sample. This is generally compensated by the addition of an ionic-strength adjustment buffer (ISAB). This procedure is not practical in a continuous sampling/monitoring system. Sodium is the dominant ion controlling the ionic strength of the surimi leach water. An approximation of the ionic strength of the solution was based on the sodium concentration. Using this ionic strength, the activity coefficient for each individual specific ion was calculated. The apparent concentration measured for sodium, calcium and potassium was then corrected using the previously calculated activity coefficients. Appendix B provides additional information regarding the specific ion calculation. It should be noted that the measurement procedure outlined above provided an "order of magnitude" measure of ionic concentration. The method was useful to determine trends in the concentrations of various ions present. Without the addition of ISAB to individual samples the technique cannot be used on an analytical basis.

### **2.1.1 Continuous Sampling System**

In order to minimize the chemical and mechanical breakdown of the specific ion and pH membranes, the electrodes were mounted and fully enclosed at a remote location from the surimi pilot line. Leach water was drawn from the pilot line to the electrode unit by a vacuum system.

Electrodes were rigidly mounted in 1/2" NPT Parker stainless steel manifolds and samples of wash fluid were drawn through this manifold using a Chapman vacuum pump. The specific ion electrodes were mounted separately from the pH electrode. The configuration of the specific ion electrode manifold is shown in Figure 2.2. Note the presence of the O-ring seal.

A schematic of the continuous sampling system is shown in Figure 2.3. For approximately the first 10 minutes of a surimi pilot line run, samples of leach tank fluid were siphoned for testing by fully opening the main 80 psi faucet, the vacuum valve and the leach tank valve. Wash fluid was drawn in to the pH manifold first and then into the specific ion manifold at a flow rate of 1.5 l/min. The wash fluid was discharged to the drainage area. At approximately 11 minutes, the contents of the leach tank were pumped to the second wash or saline tank. At this point the leach tank valve was closed and the saline valve was opened to facilitate testing of the saline wash water.



At the completion of the pilot run, the vacuum valve was closed and the backflush valve was opened to provide up to 80 psi of cleaning water. All of the valves mentioned are flow adjustable 1/4" NPT brass ball valves except for the 80 psi faucet which is a standard 3/8" NPT female gate valve. The piping network main line consists of 1/4" I.D. tygon and stainless steel tubing. All connectors are 1/4" NPT stainless steel and brass, except for the manifold which is 1/2" NPT stainless steel with fittings bored to appropriate dimensions to accommodate the electrodes.

#### **2.1.2 Electrode Buffer**

An instrument for measurement with specific ion and pH electrodes must be capable of accepting an input voltage between -900mV and +600mV with a source resistance anywhere between  $10^9$  ohms and  $10^{12}$  ohms. The Hewlett Packard Data Acquisition and Control Unit 3421A, chosen as the instrument to measure the specific ion and pH input voltages, is rated for input impedances at greater than  $10^{10}$  ohms. During the course of the project, it was determined that the HP 3421A unit could not measure the input voltage of the specific ion and pH electrodes due to their higher impedances. The circuit shown in Figure 2.4 was designed to alleviate this problem. This circuit acted as an impedance buffer between the high impedance electrodes and the data acquisition and

control unit This electrode buffer includes RCA CA3140AE integrated - circuit operational amplifier with very high input impedance ( $1.5 \times 10^{12}$  ohms) and very low input current (10pA @  $\pm 15V$ ). Note that one amplifier is used per electrode but that the specific ion buffer circuit is separate from the pH circuit since the specific ion electrodes are referenced to a common ground, the Corning <sup>tm</sup> reference electrode. The pH electrode has its own internal reference.

## 2.2 Thermocouples/Pressure Transducer

Thermocouples were used to measure temperature at various locations on the surimi pilot line (Figure 2.5). Thermocouples were OMEGA J type, 1/4" and 1/8" chromel-alumel, with 304 stainless steel sheath. The thermocouples were mounted using standard 1/2" NPT and 1/4" NPT connectors mated with PVC junction boxes to seal the 2 wire electrical connections. All wire leads were encased in 1" and 1/2" watertight flexible conduit. The thermocouples were connected to the HP 3421A data acquisition and control unit as shown in Figure 2.6. The pressure sensor mounted on the press was a sensometrics model SP65 pressure transducer. The transducer was flush mounted with a braze to the exterior surface of the screw press dehydration screen. The transducer has an operating range of 0-125 psia and requires

an input excitation voltage of 10VDC. The electrical connections for this sensor are shown in Figure 2.6 and they are encased in 1/4" watertight flexible conduit. (Refer to Appendix B for pressure transducer calibration information).

### **2.3 Data Acquisition System**

The HP 3421A data acquisition and control unit consists of a built-in 5 1/2 digit voltmeter, a 10 KHz counter, and an HP=IL controller interface. The HP3421A is configured with two 10 channel multiplexers located in slots 0 and 1 at the rear of the unit. Table 2.1 outlines the channel addressing sequence for the various sensors installed on the surimi pilot line.

The fully programmable HP3421A is interfaced to a HP110 portable computer via the standard HP-IL (Hewlett Packard Interface Loop) connections. Communications between the HP3421A and the HP110 were achieved only through macro assembler language software, specifically designed to interface these two devices. A copy of the assembly language routine is given in Appendix C. The sample program was designed to send a DC voltage command from the HP110 portable to channel 3 of the HP3421A through MS DOS<sup>tm</sup> or GW Basic<sup>tm</sup> and store the desired voltage in a file called 3.DAT. This voltage was then read by the normal input communications commands of GW Basic<sup>tm</sup> or MS DOS<sup>tm</sup>. The supplied GW Basic<sup>tm</sup> software accessed the assembly language

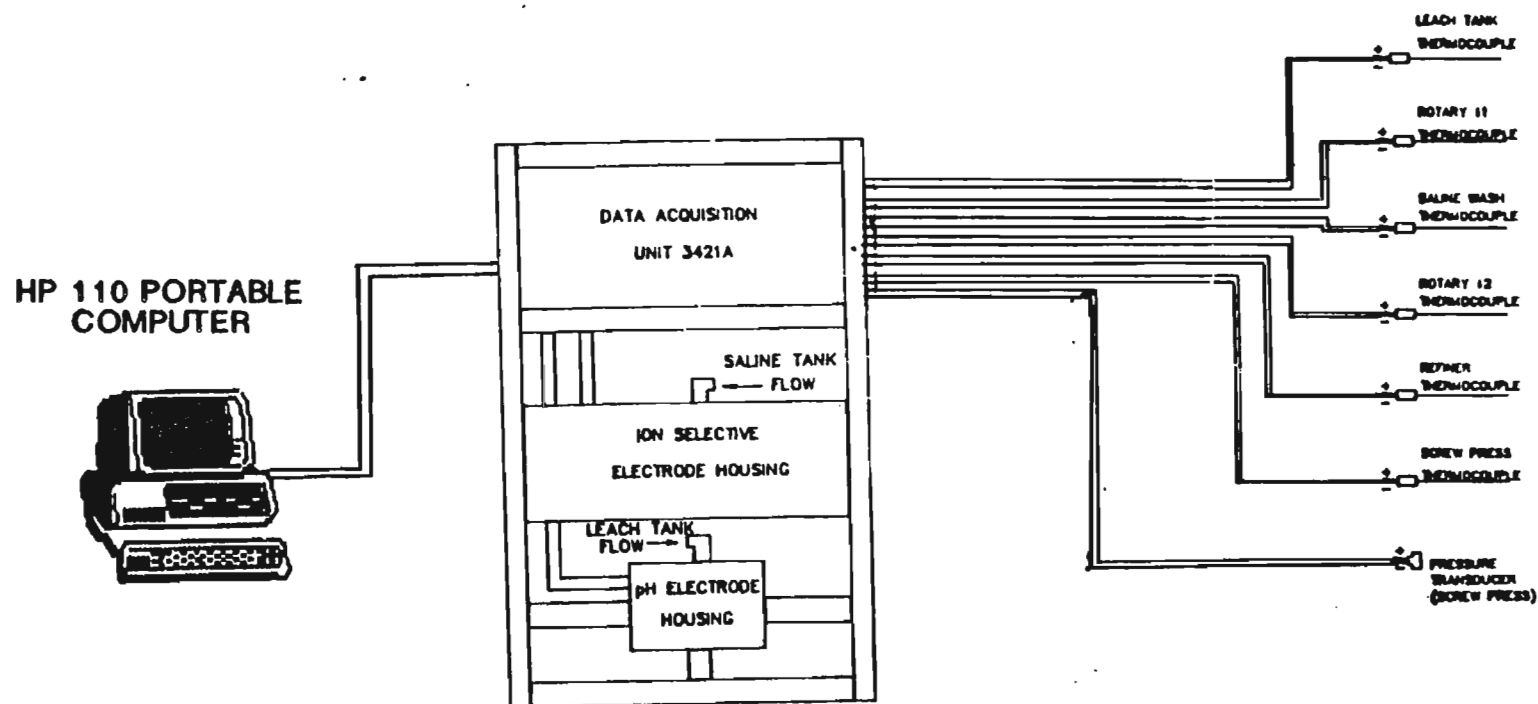
routines through the "Shell" command and thus permitted direct interfacing between the HP3421A and the HP110. Note that for every command sent to the HP3421A unit an appropriate assembler language routine must exist to correspond to that command. Each channel of the HP3421A that must be accessed for information requires a DOS command such as 3.Com for Channel 3 or 14.Com for Channel 14.

#### **2.4 Data Collection Control Panel**

The wet corrosive environment of a fish plant required a watertight housing for all the digital process monitoring equipment and the specific ion/pH electrodes. As well, the data collection housing unit, shown schematically in Figure 2.7, served as a control panel for monitoring the surimi pilot line process. The housing unit consisted of 1" square cross sectional hollow aluminum frame work that measured 30" x 22" x 54". The HP3421A data acquisition and control unit was housed in a 23" x 10" x 20" fiberglass box with a transparent hinged cover to provide quick and easy access.

The specific ion electrode manifold was housed in an 18" x 12" x 6" fiberglass box with a hinged cover. The pH electrode manifold was housed in a 12" x 12" x 4" PVC junction box. Flow between the surimi pilot line and the manifolds was controlled by valves attached to the frame work of the housing unit.

FIGURE 2.1 PROCESS MONITORING AND DATA LOGGING SYSTEM - SURIMI PILOT LINE



CANPOLAR CONSULTANTS  
SURIMI PROJECT 1048

PROCESS MONITORING  
SYSTEM

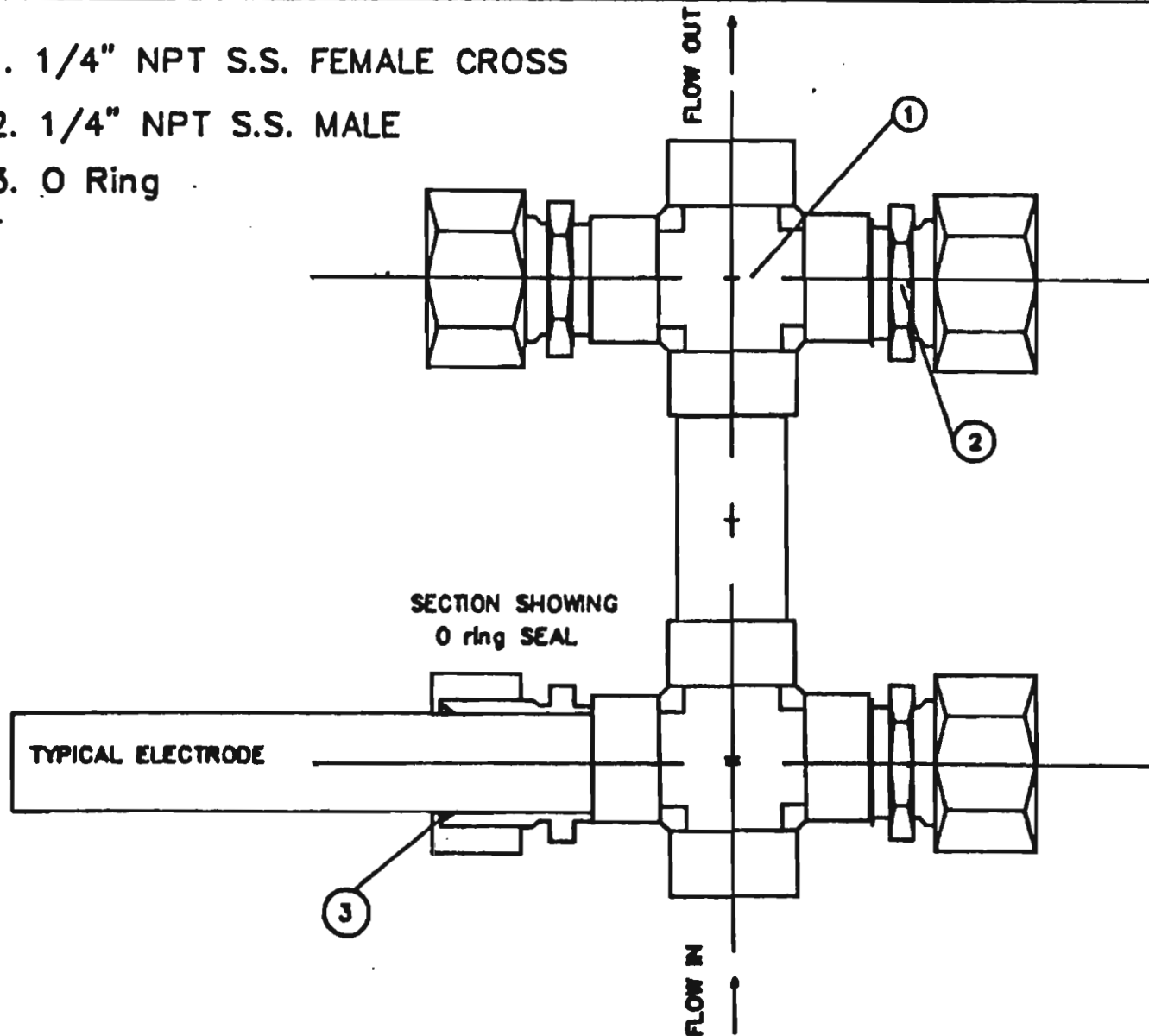
SCALE:

DATE:  
03/17/87

DRWN:

CHK:

1. 1/4" NPT S.S. FEMALE CROSS
2. 1/4" NPT S.S. MALE
3. O Ring



CANPOLAR CONSULTANTS

SURIMI PROJECT 1048

ELECTRODE  
MANIFOLD

SCALE:  
NTS

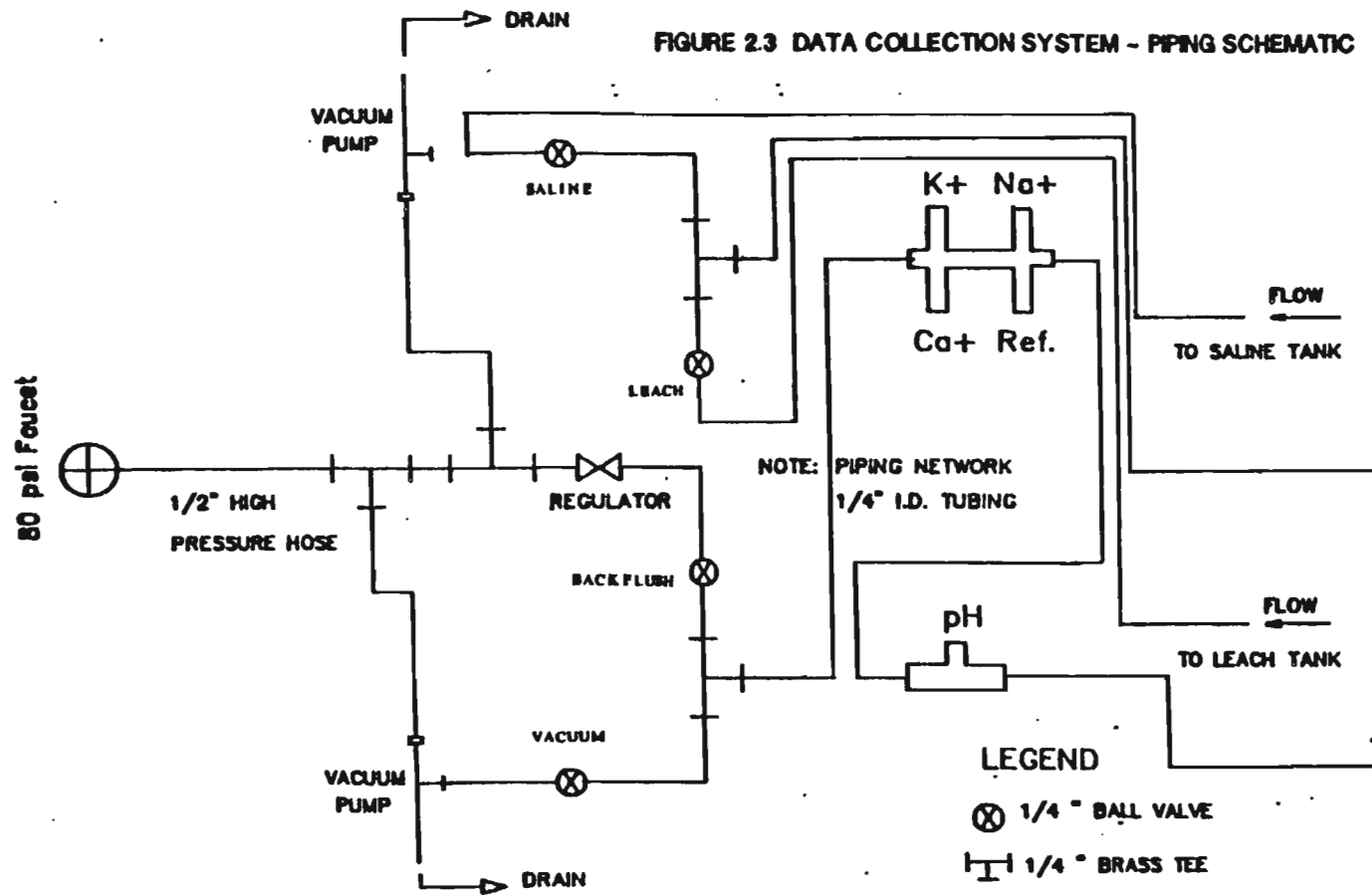
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FIGURE 2.3 DATA COLLECTION SYSTEM - PIPING SCHEMATIC



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SURIMI PROJECT 104B

DATA COLLECTION  
PIPING SCHEMATIC

SCALE:  
NTS

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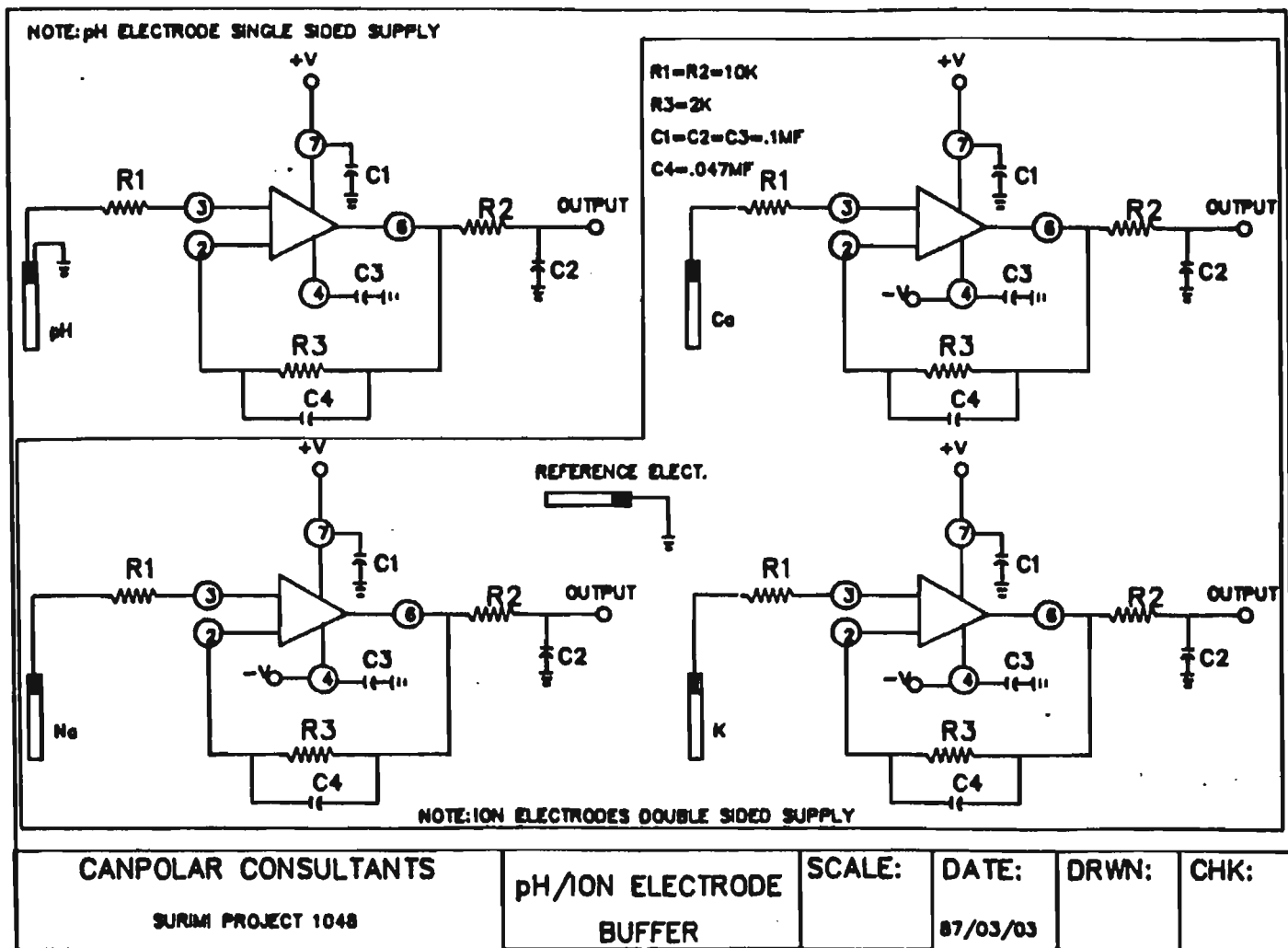
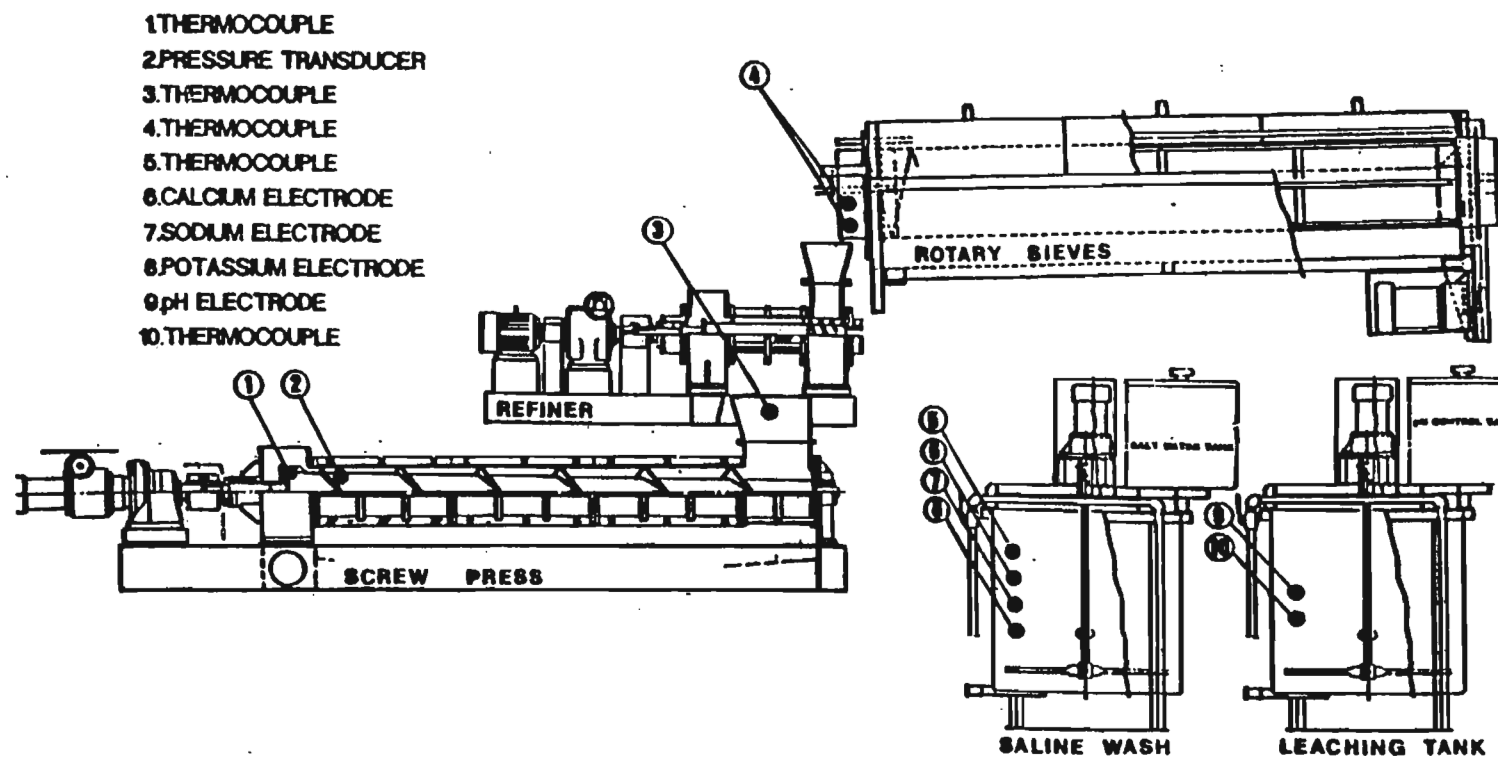


FIGURE 2.4 SPECIFIC ION/pH ELECTRODE BUFFER



FIGURE 2.5 SENSOR LOCATIONS ON THE PILOT LINE



Revision 1.0 12/16/86

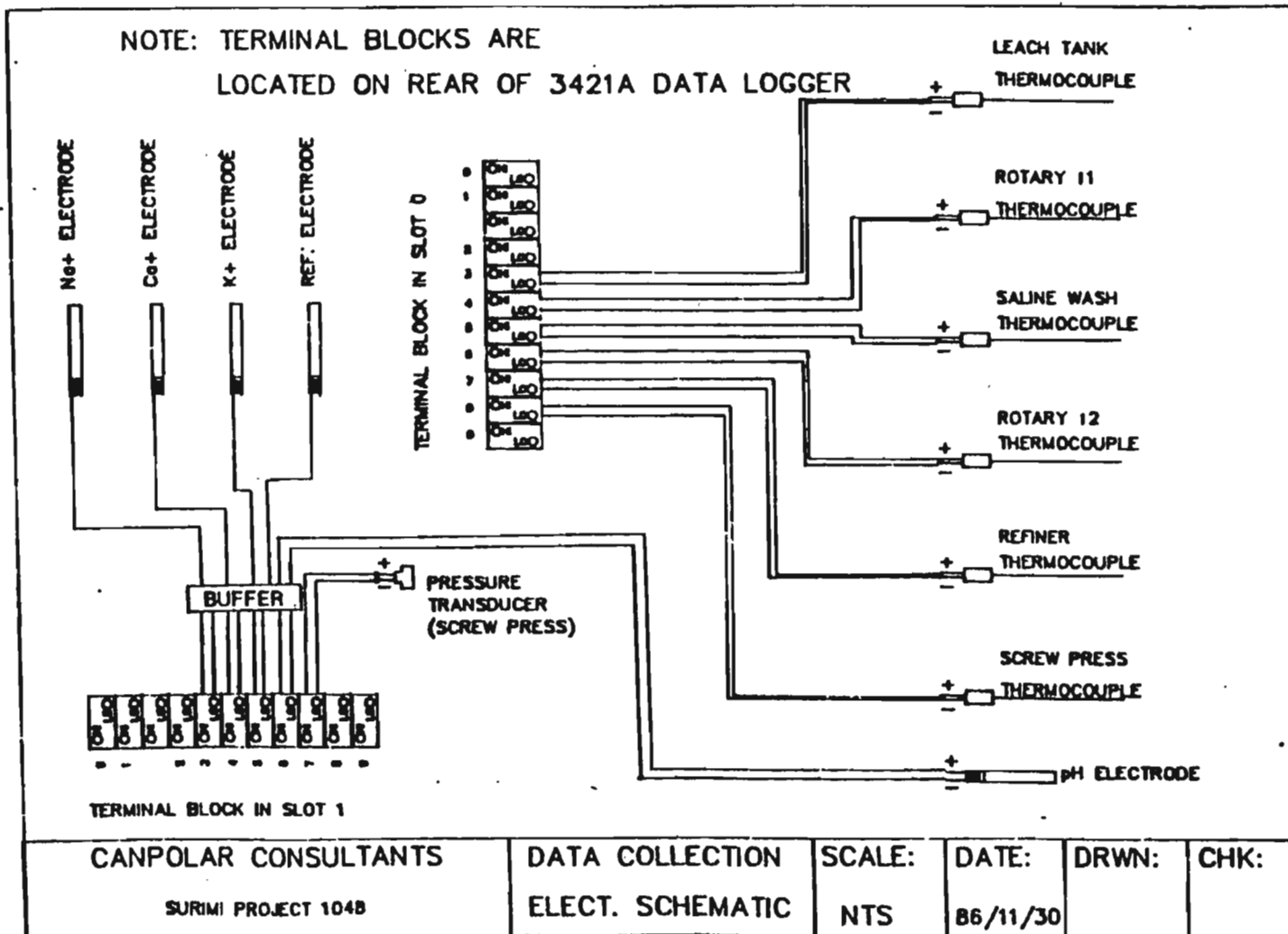


FIGURE 2.6 SENSOR ELECTRICAL SCHEMATIC

SENSOR	SLOT #	CHANNEL TERMINAL BLOCK	ADDRESS	# ON OMEGA PANEL
LEACH T TEMP.	0	3	03	1
ROTARY #1 TEMP.	0	4	04	7
SALINE T TEMP	0	5	05	3
ROTARY #2 TEMP	0	6	06	8
REFINER TEMP	0	7	07	5
SCREW P. TEMP	0	8	08	6
Na+	1	3	13	
Ca+	1	4	14	
K+	1	5	15	
pH	1	6	16	
SCREW P. TRANS.	1	7	17	
TRANS. INPUT VOLT.	1	8	18	

NOTE: THE REFERENCE ELECTRODE IS CONNECTED  
TO THE LO SIDE OF CHANNEL ADDRESS 13

TABLE 2.1 CHANNEL ADDRESS SEQUENCE - DATA ACQUISITION UNIT

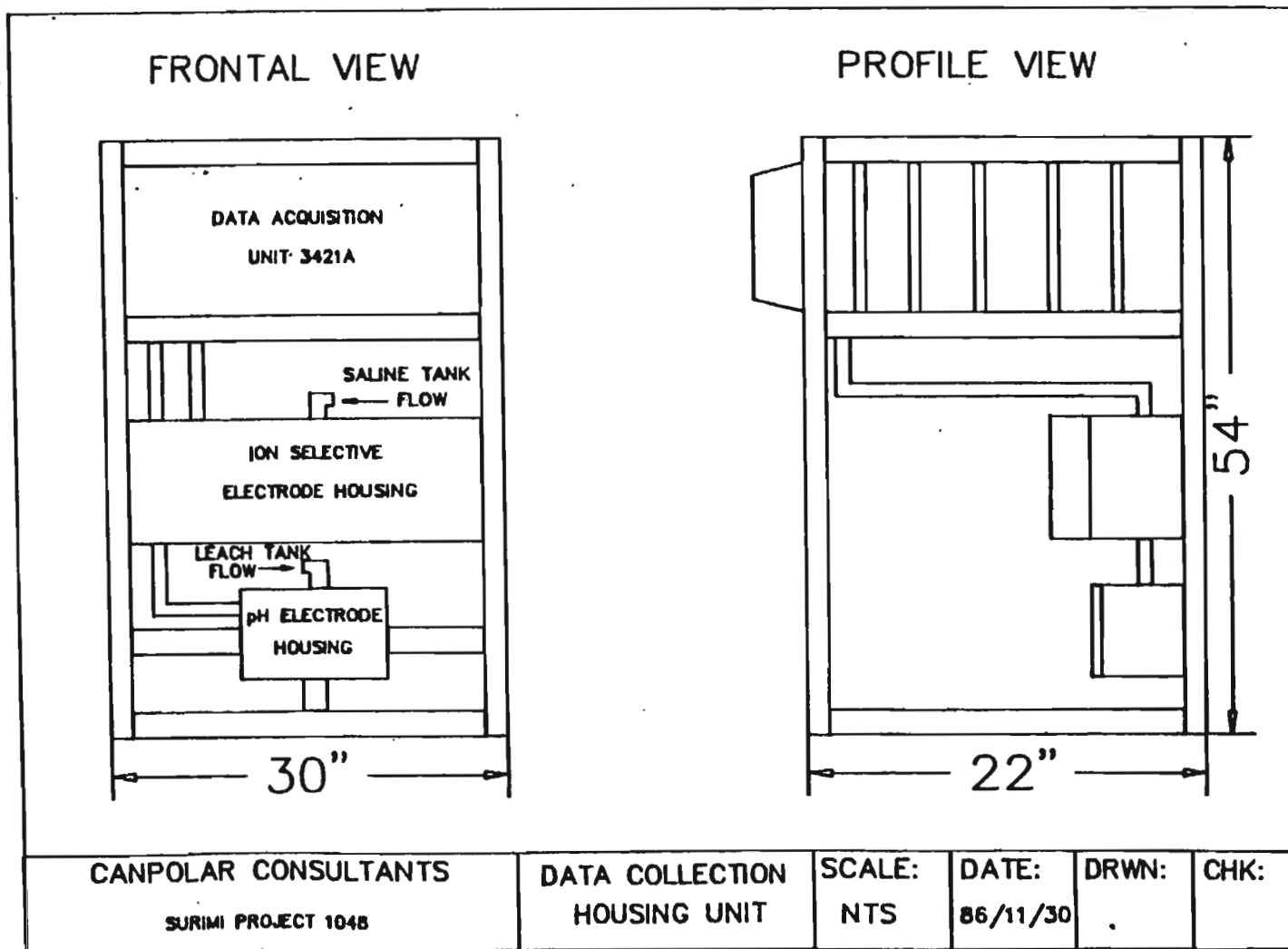


FIGURE 2.7 DATA COLLECTION HOUSING UNIT

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Processing Data

As described in section 2, pH, specific ions, temperature, time and pressure data were collected at one minute intervals during the pilot-scale processing of surimi. A total of 23 pilot scale runs was carried out. Continuous ion and pH data were collected for 13 runs. The data are represented graphically in Figure 3.1 to 3.23. Raw data are included in Appendix A. Because of many variables associated with the raw materials, e.g. frames vs. fillets/ whole fish, days postharvest, frozen vs. fresh species, etc., comparisons of process parameters with product and product quality are limited with the available data.

##### 3.1.1 Temperature

Processing temperatures generally fluctuated between 5 and 12°C from the beginning to the end of each experiment. Temperatures in the leach and saline tank, because of the ambient water temperatures, were lower than the remainder of the processing line. Mince leaving the saline wash was usually 7°C or less, after which the temperature rose steadily through the rotary screen, refiner and screw press. Exceptions to this observation are shown in Figures 3.8 and 3.9 where temperatures in the saline tank were 1°C and 0.3°C respectively. Absolute temperature requirements for the surimi process have not been established, although 10°C has

been adopted by the industry (Okado and Tamoto, 1986). Ten degrees centigrade appears to be a temperature that works for Alaskan pollock. Each species is likely to have a temperature optimum based on the habitat temperature of the fish (Arai et al. 1974). Northern cod is likely to be lower than 10°C, while tropical fish may be processed at a higher temperature. There is also some indication that the older the postharvest age, the greater the sensitivity to thermal denaturation (Haard, 1986).

One of the major effects of water temperature involves the ability to dewater mince. Figure 3.24 from Sonu (1986) shows that as the temperature of the processing water is increased so is the ability to dewater. Clearly, a compromise must be reached between optimum temperatures for maintaining protein integrity and maximizing dewatering. Dr. C. Ho of Terra Nova Fisheries has had to increase water temperature in the final wash to facilitate dewatering (personal communication 1987).

### **3.1.2 Processing Times**

Pilot runs took approximately 60 minutes. Leaching times of 10 minutes each were used for all experiments. Sieving and refining operations took approximately five minutes, depending on the size of the batch being processed. The single most time consuming operation in producing surimi is dewatering. On average, 35 percent of processing time was spent in dewatering. Depending on the batch size, the

screw press operation took up to 30 minutes and close to 50 percent of the entire processing time. As was discussed in Section 3.1, the temperature of the meat in the screw press was also highest during the overall process. The combination of time and temperature will determine the relative losses of protein functionality. The effects of temperature on the properties of muscle enzyme systems such as ATPase (Johnston et al. 1973) and k-value (Nishimoto and Miki 1979) have been evaluated using Arrhenius-type relationships. Extrapolation of these relationships to our situation indicates that exposures of one hour at 10°C would produce minimal effects on functionality whereas a similar exposure at 25°C might reduce functional properties by 30%. This relationship is especially important during the summer when processing temperatures may reach 15-20°C.

### **3.1.3 Pressure**

Pressures in the screw press were generally less than 7-8 psi. Normally, the pressures were about 3 psi. The results indicated that there is a relationship between final moisture content and maximum pressure (figure 3.25). From this graph it is apparent that more efficient dewatering is achieved when higher pressures are achieved. It is not clear why high pressures are reached on some batches of fish and not others. Screw press theory dictates that the efficiency of the press is contingent on the nature of the material being dewatered (Perry, 1984). It was observed that

when the pH of the processing water was reduced to 6.1, the moisture content fell to 73% and pressures rose to 13 psi (Figure 3.14). Protein theory states that when pH is a +, the isoelectric point (5.5 for myofibrillar protein), the protein has a minimum hydration. Presumably, when the pH of the process water was reduced to 6.1, it naturally lost water. A moisture analysis of the meat entering the screw press was not performed but the mince had a drier textural appearance. Possibly this dry texture altered the operating characteristics of the press, thus producing higher pressures and even lower moisture contents.

#### 3.1.4 pH

One of the major parameters which affect the behaviour of muscle proteins is pH. Extremes in pH have been directly implicated in myofibrillar protein disorders such as dark cutting beef, pale soft exudate (PSE) in pork and "yakeniku" in red meat fish such as tuna (Hultin, 1986). When fish are slaughtered, the flesh also experiences extremes of pH starting at a relatively neutral pH, going through rigor and arriving at an ultimate pH of 6.2 to 6.6 for lean fish and 5.5 for red-meat fish (Hultin, 1985). With bacterial spoilage, the pH will rise to 7.0 or higher. In some cases the ultimate pH for lean fish is extremely low (6.0) and results in a condition known as gaping, which is commonly found in fish that are feeding heavily after a period of starvation.



Because of the large amounts of constituent amino acids, muscle proteins can act as important buffering agents. Since Newfoundland water has no buffering capacity, the pH of the overall process will be determined by the muscle itself. With the exception of run no. 13 to 19 where the pH was adjusted, the pH of processing water was determined by the mince. Generally pH was between 6.7 and 7.0; on one occasion the pH of the process was greater than 7.0 (Figure 3.19). In this case, the cod frames which were used as starting material were stored in plastic bags for two days prior to processing. Frame material is extremely susceptible to bacterial spoilage and hence increases in pH.

The effect that pH has on the surimi process stems from the properties of the constituent proteins. Proteins prefer a relatively narrow pH range. For myofibrillar protein this is thought to be about pH 6.5. pH will affect the protein's ability to bind water. Figure 3.26 shows the effect of pH on the water binding capacity of fish meat. Maximum dewatering efficiency is observed at pH 5.5 of the isoelectric point (the pH at which the protein has no net charge). For the purposes of processing surimi, it would be desirable to maximize the ability to dewater. Many of the surimi processing problems are associated with the screw dehydration. However, dropping the pH to 5.5 will have the effect of denaturing or "cooking" the protein, rendering the surimi nonfunctional. Another consideration in lowering pH

might be an increase in the potential for the loss of "fines" in the refiner and screw press, probably caused by hydrolysis of labile aldimine linkages in the connective tissue. Mohn (1987) suggests, however, that the cell envelope collagen is acid stable and mince disruption would be minimal. Clearly a compromise must be struck between dewatering and functionality.

In an attempt to optimize pH for processing cod, a series of experiments were carried out in which the pH of the process was controlled. Using weak HCL and NaOH a 4:1 mixture of water, meat was titrated to either pH 6.1 or pH 7.0 in the leach and saline tanks. The results are given in Figures 3.13 to 3.18. Results for nine-day old cod are given in Figures 3.13 to 3.15 while the results for four-day old cod are shown in Figure 3.16 to 3.18. Identical procedures were used in both experiments. A number of processing observations are worth noting: (1) four-day old cod was more difficult to titrate to 6.1 after 10 minutes titration pH values of 6.0 could not be obtained (this may be explained, in part, by the differences in the condition of the protein and amino acids which are responsible for the buffering effect). (2) it is more difficult to titrate in the primary leach tank than the saline tank. This suggests that the water soluble protein is mainly responsible for the proteins buffering capacity. When these proteins are leached out in the primary leach, the system's buffering capacity is

reduced. In areas where processing water is subject to fluctuations or extremes in pH, the pH of the saline tank must be monitored and adjusted continuously. When the pH was adjusted to pH 6.2, the visual appearance of the meat entering the refiner was drier and more fibrous than at pH 6.8 or 7.0, where the meat was more hydrated or sloppy.

When product information was correlated with processing data, it was observed that the surimi produced from the pH 6.1 experiment (run No. 14) had a moisture content of 73.9% was opposed to 81.5% for the pH 7.0 run (run No. 15). In addition, this change in moisture content produced gels with entirely different textural properties (see Fig. 3.27). At pH 6.1 the modulus of elasticity was three times that at pH 7.0. Run Numbers 13, 14 and 15 are highlighted on the graph and in the key. The increased modules of elasticity suggest a tougher gel structure whereas the pH 7.0 gel was somewhat rubbery. A similar observation was made by Love (1980) who found that when cod with a low ultimate pH was cooked it had a tougher texture. The unbuffered pH 6.8 mince has intermediate properties. From a processor's viewpoint, pH control offers the opportunity to produce surimi of prescribed gel properties. If a tougher product is required, say for simulated lobster tails, reducing the pH of the process will facilitate dewatering and hence produce a kamaboko with higher stress characteristics. Similarly, products requiring a more rubbery texture should be buffered

to a higher pH.

The manipulation of pH in the surimi process is one which predictive product results can be obtained. The equipment required is technically simple and reliable. Automatic titration systems are available and would effectively accomplish pH control. A processor need only tell the pH controller the gel properties required in the end product and the process will be adjusted accordingly.

### 3.1.5 Specific Ions

Measurements of calcium, potassium and sodium were collected at one minute intervals using an ion selective/double-junction reference electrode system. Continuous ion monitoring was available from run number 11 onward. Monitoring ions by this technique demanded constant attention and adjustment. Electrodes (with the exception of the pH electrode) were continuously cleaned and refilled. Results, especially for the sodium electrode, were inconsistent. For unknown reasons, the potassium electrode produced more consistent results than the sodium or calcium electrodes. Where consistent data was available, it was summarized graphically in Figures 3.11 to 3.22. Otherwise, all raw data is given in Appendix A. It should be noted that measurement of ions using electrode technology is generally carried out under laboratory conditions with the use of an ionic strength adjustment buffer. Ion selective electrodes are sensitive to fluctuations in ionic strength. This is

generally compensated by buffer adjustment. This was not practical in the flow-through system. Results may be considered "order of magnitude" concentrations rather than absolute values. For the purpose of establishment of trends of leaching kinetics, an order of magnitude estimation of ion concentration was satisfactory.

It was observed that the concentration of potassium during fresh water and saline leaching reached a maximum in about 3-4 minutes and then stabilized (see eg. Figure 3.15). Measurement of potassium in subsequent washes demonstrated similar kinetics but reached a lower maximum value. The maximum value of potassium in the second wash was usually less than 25 percent of the first wash. The dilution ratio of the leach tank was 25 percent.

To study this phenomenon more carefully specific ions were monitored in a small scale laboratory experiment. Cod mince was stirred with fresh cold tap water (ratio of 5:1, water:meat) and ion measurements were made at one minute intervals for five minutes. The meat was allowed to settle and the water drained off. Three subsequent wash cycles were performed in a similar fashion. Results are summarized in Figure 3.28. Potassium concentration increased rapidly to a limiting value in each wash. The maximum value of potassium decreased with each wash cycle (see Figure 3.29). The concentration of calcium did not show a dramatic increase with time of increased wash cycles, but appeared to

decrease slightly. Sodium on the other hand showed similar kinetics on each wash. Limiting values of approximately 5mm were observed on each wash.

From a processor's perspective there are two main considerations in washing mince for surimi:

1. There must be sufficient washing to remove undesirable compounds such as blood, fat, TMAO, etc. There are essentially two options: (1) wash for long periods of time in a large water/meat ratio and/or (2) increase the number of wash cycles.
2. Water exposure should be minimized to prevent excessive hydration and hence facilitate dewatering.

The question that needs to be answered is, "How much washing is sufficient and can this be determined in real time?" Most recipes call for 3-5 cycles at 3:1 to 5:1 water to meat ratios. To ensure effective dewatering sodium chloride is added to the final wash. Lee (1986) has suggested that 3:1 water:meat over three cycles is sufficient whereas Okada and Tamoto (1986) suggested four cycles at two or 3:1 water to meat ratio. Less water is used for processing at sea. Wash times are reported to vary from 3 to 10 minutes. To optimize washing, a real time monitor is required. The monitor should follow a component that is being leached by the washing process and this parameter should be representative of the entire process.

In our experiments various constituent ions were examined during the leaching process. Physiologically, potassium is in highest concentration intracellularly, i.e. the part of the cell which is expected to contain water soluble protein, TMAO, etc. Sodium is primarily an intercellular ion. Potassium is probably a better representative of the material which needs to be leached. The results seem to indicate two things:

1. For a given wash, the amount of potassium leached is at a maximum after approximately 3-5 minutes;
2. The potassium concentration is reduced by the same ratio as the water:meat volume ratio during the wash (i.e. 1:4).

Both these findings are in agreement with Lee (1987) who observed that little increase in leaching was achieved after five minutes and that 2-3 cycles are sufficient. Since these leaching kinetics may vary with starting material, times and cycles should be adjusted accordingly.

The preliminary results of potassium leaching suggest its usefulness as an indicator of mince washing kinetics. It is simple and can be measured in real time. More baseline data and correlation to other parameters such as water soluble protein and TMAO are required.

### **3.2 Surimi Process Models**

Surimi process controls for improved yield and

consistent quality can be developed providing that the following components have been established:

1. a knowledge of the post mortem biochemistry and physiology of fish muscle;
2. a good working model which integrates post mortem biochemistry/physiology and the various physical/chemical processes involved in surimi production;
3. a workable sensor/controller system capable of modifying the process on the basis of the processing model; and
4. controllable process equipment.

In this current project, CANPOLAR has employed a number of sensor systems to collect various processing information about the surimi process. By integrating experimental data, published information as well as end-product data processing models have been developed. Using these models, together with an understanding of sensor technologies and processing machinery, viable process control systems can be suggested. The following sections discuss the potential of process controllers in terms of processing models, basic biochemistry and physiology, sensor and equipment technology as well as production considerations. The discussion will attempt to integrate theory with practice and also introduce some novel ideas to develop a working model.



### 3.2.1 Primary Leaching

The first objective of the surimi process is to remove intercellular fluid (eg. blood) and various intracellular components such as water soluble protein, enzymes, TMAO, etc. This primary leaching process produces three main effects:

1. Elimination of color and odor of the mince;
2. Concentration of myofibrillar protein, the active gel forming substance
3. Elimination of potential degradative compounds such as those which demethylate TMAO to DMA and formaldehyde and cause storage deterioration.

The mechanism and kinetics of the leaching process will depend on the particle size and physical integrity of the mince. A complete leaching will include at least three processes:

**1. Simple Diffusion:** Intercellular fluids, ions and small biomolecules will diffuse from meat particles into the wash water. For these small molecules, such as potassium ion, this diffusion will reach equilibrium within a few minutes. The diffusion coefficients for small molecules is approximately  $10^{-5} \text{ cm}^2\text{sec}^{-1}$ . If it is assumed that minced particles are spherical in shape and 3mm in diameter (3mm from a perforated mincer), the diffusion rate for potassium in one particle can be described as follows:

$$4 = 4r CD = 1.51 \times 10^{-9} \text{ moles sec}^{-1}$$

Where:

R = radius of the particle (.15cm)

C = conc. gradient ( $5 \times 10^{-6}$  moles. ml<sup>-1</sup>) Geigy 1980

D = diffusion coefficient

R = mass transfer rate.

Assuming that particles are spherical:

the weight of 1 particle can be calculated to be  $1.41 \times 10^{-2}$ g.

based on the volume of a sphere =  $\frac{4}{3} \pi r^3$

The rate of diffusion per gram then becomes

$$\frac{1.41 \times 10^{-9} \text{ moles sec}^{-1}}{1.14 \times 10^{-2} \text{ g}} = 1 \times 10^{-7} \text{ moles sec}^{-1} \text{ g}^{-1}$$

To compare this theoretical diffusion rate to actual measurements of potassium leaching, consider, for example, Figure 3.17. The initial rate of leaching in the primary leach tank was 4.4 moles litre<sup>-1</sup> per 3 min or 0.03 moles l<sup>-1</sup>.sec<sup>-1</sup>. This amount of potassium was derived from 18.5 kg of mince diluted 1:4 with water.

The rate of diffusion per gram of tissue becomes:

$$\begin{aligned} .01 \text{ mmole l}^{-1} \times 4 \times 18.5 &= 2.22 \text{ mmole sec}^{-1} \text{ 18kg}^{-1} \\ &= 1.23 \times 10^{-7} \text{ mole sec}^{-1} \text{ g}^{-1} \end{aligned}$$

This figure compares with that obtained through a theoretical treatment.

From the data presented one can also calculate the total leaching time for small molecules: Assuming the total concentration of potassium in a cell is 75 mmole l<sup>-1</sup> and a diffusion rate of 1.23 x 10<sup>-7</sup> mole sec<sup>-1</sup> g<sup>-1</sup>, the number of moles of potassium per gram will be:

$$\begin{aligned} 75 \text{ mmole l}^{-1} &= 75 \times 10^{-3} \text{ mmole g}^{-1} \\ &= 75 \times 10^{-6} \text{ mole g}^{-1} \end{aligned}$$

then the rate of diffusion will be:

$$\frac{75 \times 10^{-6} \text{ mole g}^{-1}}{1.23 \times 10^{-7} \text{ mole g}^{-1} \text{ s}^{-1}} = 609 \text{ sec} = 10 \text{ min}$$

In reality some of the potassium will not diffuse because it is bound or associated with larger organelles. The effective leaching time will probably be less than 10 minutes. Normal procedures for the surimi process are in the order of three to four washes of a 10-minute duration. Is the excess time necessary?

The model thus far has not mentioned proteins. Water soluble proteins are much larger than potassium, TMAO or sugar molecules. As described earlier, the diffusion of molecules is dependent on the size of the molecule (and hence the diffusion coefficient), concentration gradient and particle size. Proteins vary in size from a molecular weight of 5000 to millions. Diffusion coefficients are in the order of 10<sup>-7</sup> cm<sup>2</sup> sec<sup>-1</sup> (Barrow, 1986). Based on the same

3mm particle, this would indicate that the diffusion rate would increase approximately by a factor of 100, from 10 minutes for potassium to 1000 minutes for protein. If the total time required to leach the water soluble protein is 1000 minutes then either:

1. The surimi process actually washes out very little of the water soluble protein, i.e. the whole theory behind surimi technology is false; or
2. Protein leaching proceeds by a mechanism other than diffusion.

According to Lee (1986), and many others, protein leach kinetics are readily measured in surimi leach water. Yamamoto (1974) states that 50 percent of all water soluble components, including protein, are washed out during the first leach cycle. Clearly, protein is leached out during washing; so a leaching mechanism other than diffusion appears to be reasonable. A potential explanation is osmotic rupture of cells.

**2. Osmotic Rupture:** In a similar fashion to the diffusion of potassium from a cell, isomotic pressures will cause water to enter and presumably rupture the cell. when the cell wall becomes "leaky", larger molecules such as water soluble proteins will be released.

Exactly how much, or which, water soluble protein needs to be leached from the meat is not clear. The surimi process depends on myofibrillar protein forming a three

dimensional protein matrix (Lee, 1984). Intuitively, one might suspect that much of the extraenous material should be washed away to facilitate actomyosin interaction. It has been shown that increased gel strength can be correlated to the number of washing cycles regardless of the relative concentration of actomyosin (Nishioka, 1984). It has also been suggested that increasing the wash ratio improves the frozen storage characteristics (Sonu, 1986). This author also suggests that a total water:meat ratio of 7:1 over a 30-40 minute duration will give adequate leaching. It is suggested that washing be distributed over three wash cycles. However, surimi produced on factory ships undergoes wash ratios of 3:1 and this surimi is considered to be TOP quality. Surimi literature is full of contradictions such as the above. What is clear is that no one really knows what needs to be leached from the meat. If all the water soluble protein needs to be leached, then wash times need to be considerably longer than for small metabolites such as TMAO. When people describe the surimi process they are very quick to describe leaching of deteriorative "enzymes" and "other" proteins. However, there is very little evidence to support deterioration of muscle structure by an enzymic mechanism. There has been some suggestion of a calcium-activated-factor (caf) acting on the disintegration of the myofibrillar disk and of the potential of some catheptic activity (Hultin, 1986) but there is little

evidence that these are degradive mechanisms in surimi production. One of the major texture deteriorating mechanisms in fish is known to be the TMAO systems. It has been found that TMAO undergoes enzymic degradation in the frozen state to form dimethylamine and formaldehyde and the latter has been implicated in protein crosslinking and textural deterioration in frozen fish (eg. Childs, 1973). Since TMAO is a relatively small molecule it would follow similar kinetics as the potassium model. Other taste active compounds are likely to be small peptides and amino acids which will also leach rapidly.

In summary, leaching kinetics suggest that small molecules such as ions, TMAO, amino acids, peptides and sugars will leach completely in less than 10 minutes. Depending on the size of the protein and the extent of osmotic rupture, water soluble protein may take considerably longer to leach especially in a relatively stagnant system such as the surimi process. To improve or control the process a better knowledge of the exact leach requirements (i.e. what needs to be eliminated) would be useful.

**3. Swelling:** A second type of osmotic swelling will also occur during leaching. The insoluble intracellular protein (actomyosin) will imbibe water due to the net negative charge on the protein at neutral pH. The charged protein complex will swell in fresh water until mechanical forces in the tissue counterbalance the osmotic pressure.

The latter mechanism appears to be the primary cause of meat swelling that results in difficult dewatering later in the process. The use of isotonic wash water would prevent this swelling, but also would prevent osmotic rupture of cell walls thus reducing the efficient removal of intracellular water soluble proteins. Saline wash water is normally only used in the final wash to osmotically shrink the actomyosin gel.

Another means of reducing the swelling of meat is to reduce the pH of the leaching process. As previously discussed proteins have minimum water binding at their isoelectric point (pH at which the protein has no net charge). In the case of myofibrillar protein the isoelectric point is approximately 5.5. Lowering the pH to 5.5 may reduce the excess water binding of the meat but would inevitably destroy the functional properties of the protein. Ideal control of the process will minimize swelling and maximize gel strength.

As part of this current work, a series of preliminary experiments were carried out to investigate the relative merits of adjusting pH. As shown in Figures 3.13, 3.14 and 3.15, reduction of pH to 6.1 decreased the moisture content to 73.9% from 79.3% and increased the shear stress value to 30.0 KPa from 22.5 kg for the unbuffered system. These results indicate that at pH 6.1 the gel properties (and hence the functionality of the protein) were actually

improved by modification of pH. It should be emphasized that these results are preliminary and need to be confirmed and further refined, but interestingly the experiment did concur with theory.

#### **Gel Modification**

From a processor's perspective, the notion of improving gel properties by lowering moisture content via a simple pH modification is attractive. To further investigate this possibility a scattergram, plotting ELASTIC MODULUS (stress/strain) vs SHEAR STRAIN was produced (Figure 3.30). The data is derived from torsion test measurements on cod kamaboko from both the 1985-86 and 1986-87 projects (Chandra, 1986). Letters on the graph refer to processing runs noted in the legend given below. This treatment of data is derived from Lanier (1986). Generally, the graph indicates that a surimi sample with high moisture content has a low elastic modulus. This is a similar observation as that made by Kim et al (1985). These authors also found that the quality of the protein will ultimately affect the shear strain or elasticity of the product. From Figure 3.30, however, a relationship between the age of fish and shear strain is not apparent. It seems that cod has the ability to retain its protein functional properties (quality) over a 10-15 day storage period, certainly much longer than commonly reported for pollock. Depending on the end product required, the processor can modify the process



to produce the required surimi. We have already shown that lowering the pH will reduce the moisture content and produce a more rigid or still gel. This may be a requirement for a lobster analogue. Processing a lower quality starting material (such as poorly handled fish) will produce a surimi, that is less elastic and suitable for sausage products. The processor also has the option of blending two batches of surimi with different gel properties to produce the required result. In addition, certain water-imbibing substances such as milk powder or cellulose will effectively reduce water content and increase the gel's rigidity. (Wu et al. 1985).

#### **Other pH Considerations**

Before recommending the use of pH adjustment in industrial practice, a number of consideration should be investigated:

1. The pH may affect the freezer storage life of the surimi.
2. The pH may affect the functional properties of the surimi. A low pH appears to improve gel strength.
3. Saline wash for the final leach may be unnecessary in a low pH wash and if so the freezer storage life may be improved (see further discussion later).
4. In a multiple wash system, pH titration would require less buffer if carried out during the second wash. The economy in chemicals saved would

have to be balanced off against changes in leaching kinetics

5. The choice of pH modifying chemicals may be important to the storage life and functional properties of surimi. For example, HCl and NaOH introduce sodium and chloride salts into the meat replacing the  $K^+$  and  $PO_4^{3-}$  normal to intracellular fluid.

### **3.2.2 Saline Leaching**

To facilitate dewatering, sodium chloride is commonly included in the final leaching cycle. A minimum water holding capacity for mince has been observed for saline concentrations between 0.03 and 0.6% (ionic strength 0.005 and 0.1). At ionic strengths greater than 0.1 the water holding capacity is actually increased (Okado and Tomoto, 1986). These authors report that the addition of saline salt to the leach water was especially important when processing winter pollock when the level of freshness is extremely high. It is not clear why the freshest fish were particularly susceptible to swelling. The mechanism of lowering water content by addition of saline was explained by Okado and Tamoto (1986) to involve neutralization of the negative charge on the protein by sodium ions. The authors explained this condition as being similar to the protein at its isoelectric point (ie. no net charge).

The removal and replacement of natural salts and pH

buffers during the leaching process may be an important factor in the storage life of surimi in vivo. Potassium and phosphate are the major intracellular ions while intercellular fluids are comprised mainly of sodium chloride. The effect of replacing intracellular  $K^+$  and  $PO_4^{3-}$  with NaCl is unknown but deserves consideration. Two potential areas of concern are:

1. Stability during freezing is likely to be maximized by the creation of an ionic environment capable of buffering fluctuations in pH. NaCl has very little buffering capacity while potassium phosphate is a natural physiological buffer;
2. One of the common mechanisms for freezer damage is thought to involve precipitation of physiological salts.

### **3.2.3 Dewatering**

The meat slurry from the dewatering screens or from the refiner is a loose matrix of fibers, cell debris, and water. Water is held as bound water on protein molecules, as osmotically bound water in a protein gel and as free water held only by Van der Waals and cohesive forces. In the natural state, muscle contains approximately 5% bound water and 95% unbound water. Free water can be easily expressed under mild compression (e.g. 1.5 psi), but water that is held in the protein gel matrix cannot easily be expressed. Thus with water/meat ratio around 75-80%, depending on pH,

relief at the output end of the press. This effectively reduces the compression ratio.

### **3.3 Technical Considerations in Process Control**

A major consideration in the development of a process control system is the availability and reliability of sensors and actuators. In the case of surimi processing, the technologies employed must be sturdy and self-standardizing, requiring a minimum of maintenance and capable of measurement in real time. During this work, a series of sensors were installed on the surimi pilot line with the objectives of (1) monitoring process variables, (2) evaluating their usefulness in process control, and (3) assessing their reliability in a fish processing environment. The following section discusses the various sensor systems as well as the methods of data collection and measurement. Recommendations regarding modifications to existing methodology as well as introduction of new technologies are also outlined.

#### **3.3.1 Thermocouples**

Temperature was measured using robust thermocouples sheathed in stainless steel. These thermocouples operated trouble free and required no maintenance. This technology can be installed at a moderate cost. It can produce data on a continuous basis and can be easily rearranged to accommodate process needs. The data is easily measured and

useful for day-to-day operations particularly in summer when process water temperature may fluctuate.

### **3.3.2 Pressure Transducer**

The pressure transducer mounted on the screw press also provided trouble-free monitoring of dewatering pressure. Again, data is reliable and can be produced in real time on a continuous basis. Pressure data is useful for day-to-day operation of the pilot line. Without the transducer the operator evaluates pressure subjectively by assessing the torque on the machine frame.

Data from processing also indicated that the final moisture content depended on the dewatering pressure. If the screw press compression ration was controllable, real time data would be useful in manipulating the final product.

### **3.3.3 pH and Ion Selective Electrodes**

The data produced from pH and specific ion monitoring were the most useful in understanding and modifying the surimi process. Controlling pH appears to be a possible alternative method to addition of saline as a "dewatering aid." Measurement of pH also gives the operator useful information about the state of the fish protein. In a continuous operation this may assist the operator in modifying the process to accommodate changing raw material. Specific ion electrodes appear to be useful indicators of the leaching kinetics providing processing information about optimal washing times and cycles. In addition, they can be

used as a monitor for ionic strength in the final saline wash.

There are, however, many and varied problems associated with electrode sensing. During this work the majority of day-to-day maintenance was associated with the pH/ion sample collection and measurement. The main problems are listed below:

1. Because ion selective electrodes are affected by ion activity, an adjustment buffer is usually added to all samples to normalize ionic strength. This is not practical for in-plant monitoring so ionic strength assumptions have to be made. The result is an "order of magnitude" rather than a precise measurement.
2. Electrodes require maintenance of filler solution, elimination of surface crystallization and general trouble shooting. The presence of tiny bubbles in the electrodes will affect the results by several orders of magnitude.
3. Two alternatives were considered for continuous monitoring: (i) direct immersion of electrodes in leach tanks, and (ii) removal of sample by vacuum to a remote electrode manifold.

It was decided that the latter alternative was more sensible for this application because electrodes are not robust enough to withstand the constant

abuse of direct immersion. It was found that in the remote system the electrodes remained undamaged, but necessitated an intricate vacuum/manifold system. Problems arose with vacuum leaks. Problems were also experienced with blockages in the filter system.

4. Electrodes require constant calibration, even the more reliable pH electrode.

The pH and ion parameters are useful measures of the surimi process and should be incorporated in process control. It is not likely that electrodes will function successfully in a plant environment (pH electrodes may be an exception). Processors do not have sufficient time or expertise to maintain such a system. Alternatives should be considered. A non-specific conductivity sensor may be useful.

#### **3.3.4 Data Acquisition and Controls**

The data acquisition system that has been installed on the line consists of an I/O interface and a computer/logger. The system is suited to preliminary system development, but is not packaged for use as an inplant control system.

The current system could continue in use as a development tool and could be configured to control some surimi line functions automatically (e.g. salinity, pH). The simplest extension would be provision of real time data to the operator in a "control panel" format.

Ultimately, a control system would be based on an expert system type of controller that could interact with an operator by recommending procedures and/or carrying out procedures at the operators instructions.

### **3.3.5 Software: Surimi Process Models**

Effective process control with a minimum lag requires a predictive model of the surimi process incorporating both biochemical and mechanical factors related to the operation of the various machines used in the process. The foregoing process descriptions constitute the first steps toward a comprehensive process model.



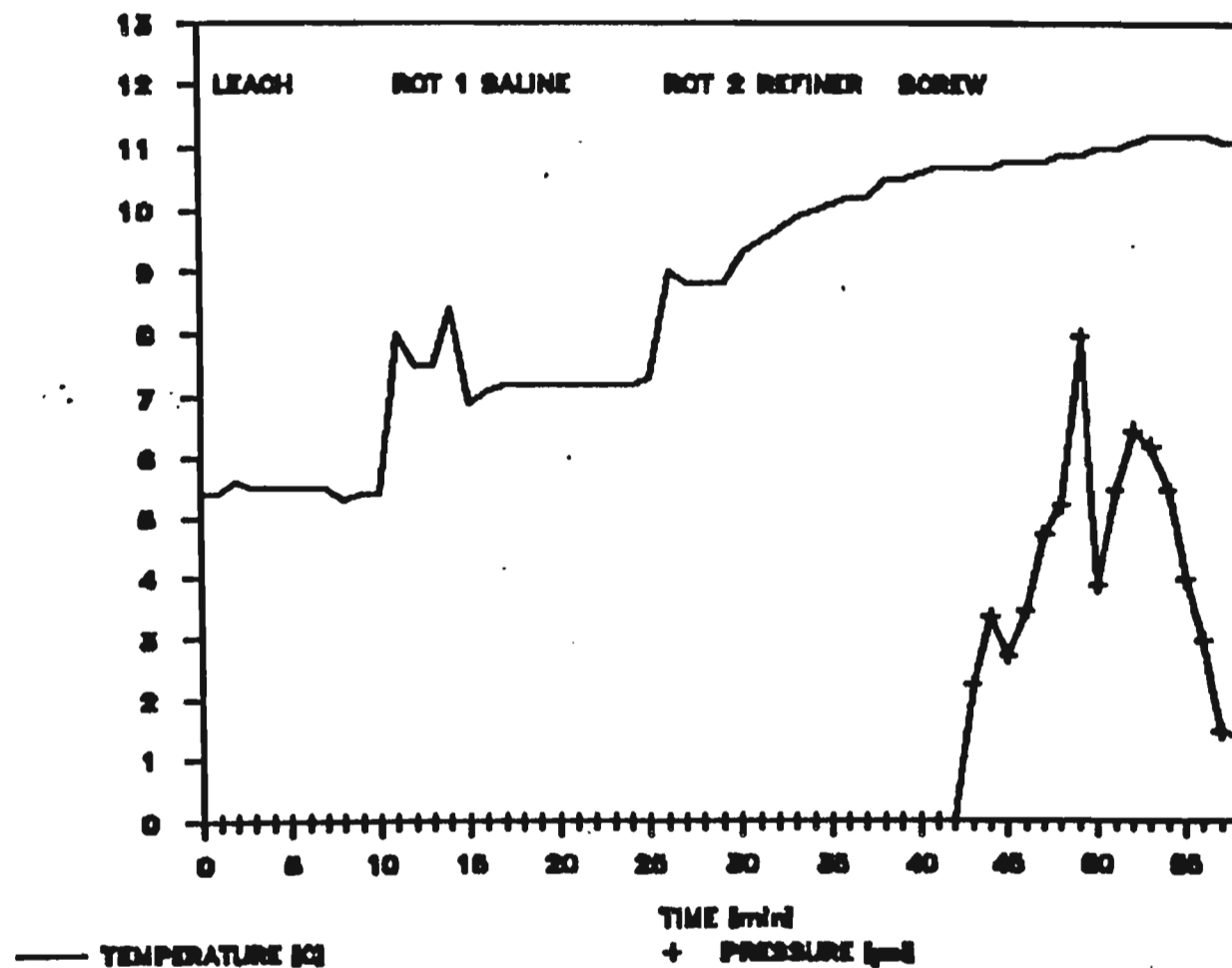


FIGURE 3.1  
SURIMI PROCESS DATA  
OCTOBER 29, 1986 5 DAY OLD COD FILLET

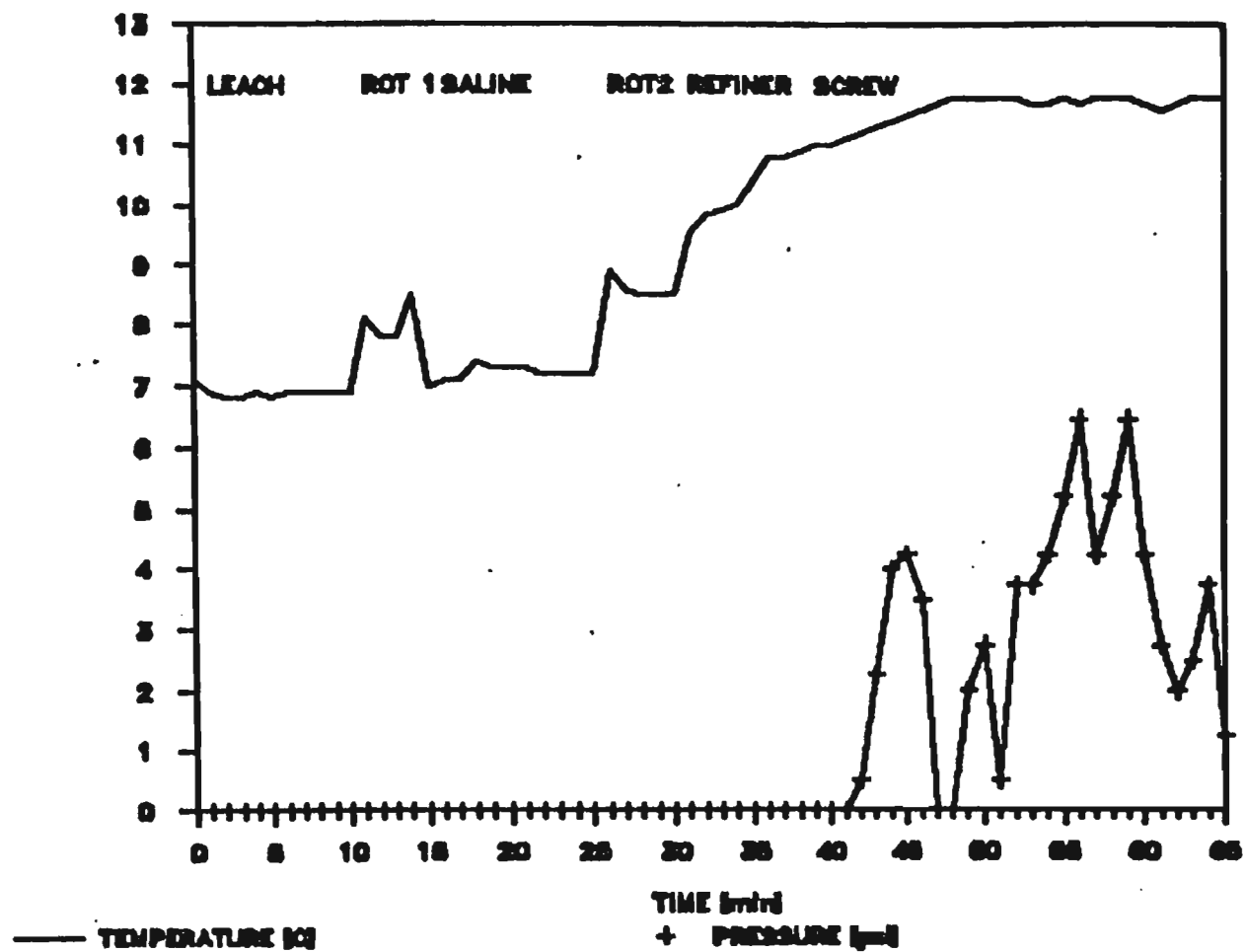


FIGURE 3.2

**SURIMI PROCESS DATA**  
OCTOBER 29, 1986 5 DAY COD FRAMES

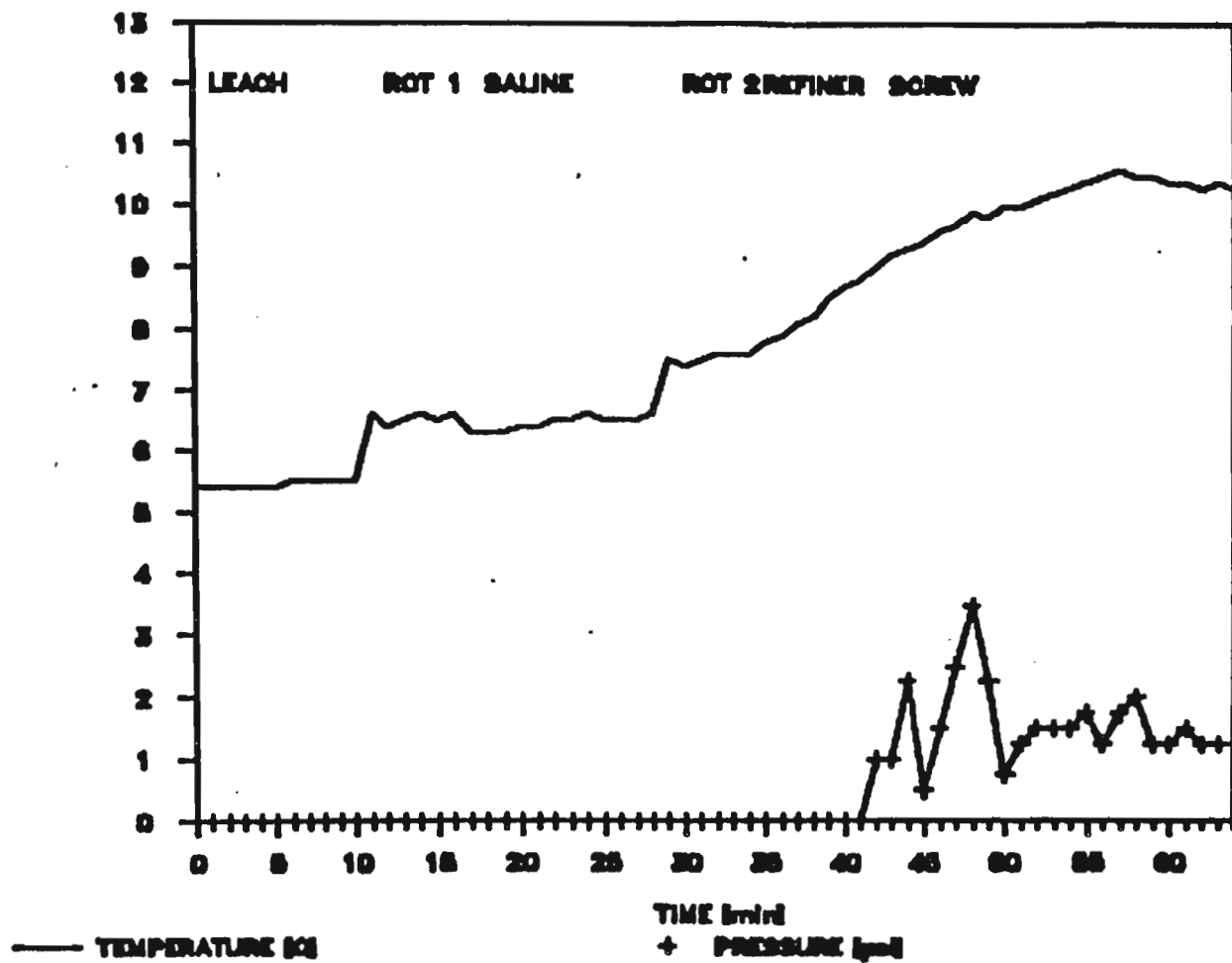


FIGURE 3.3

**SURIMI PROCESS DATA**  
**OCTOBER 30, 1986 5 DAY COD FRAMES**

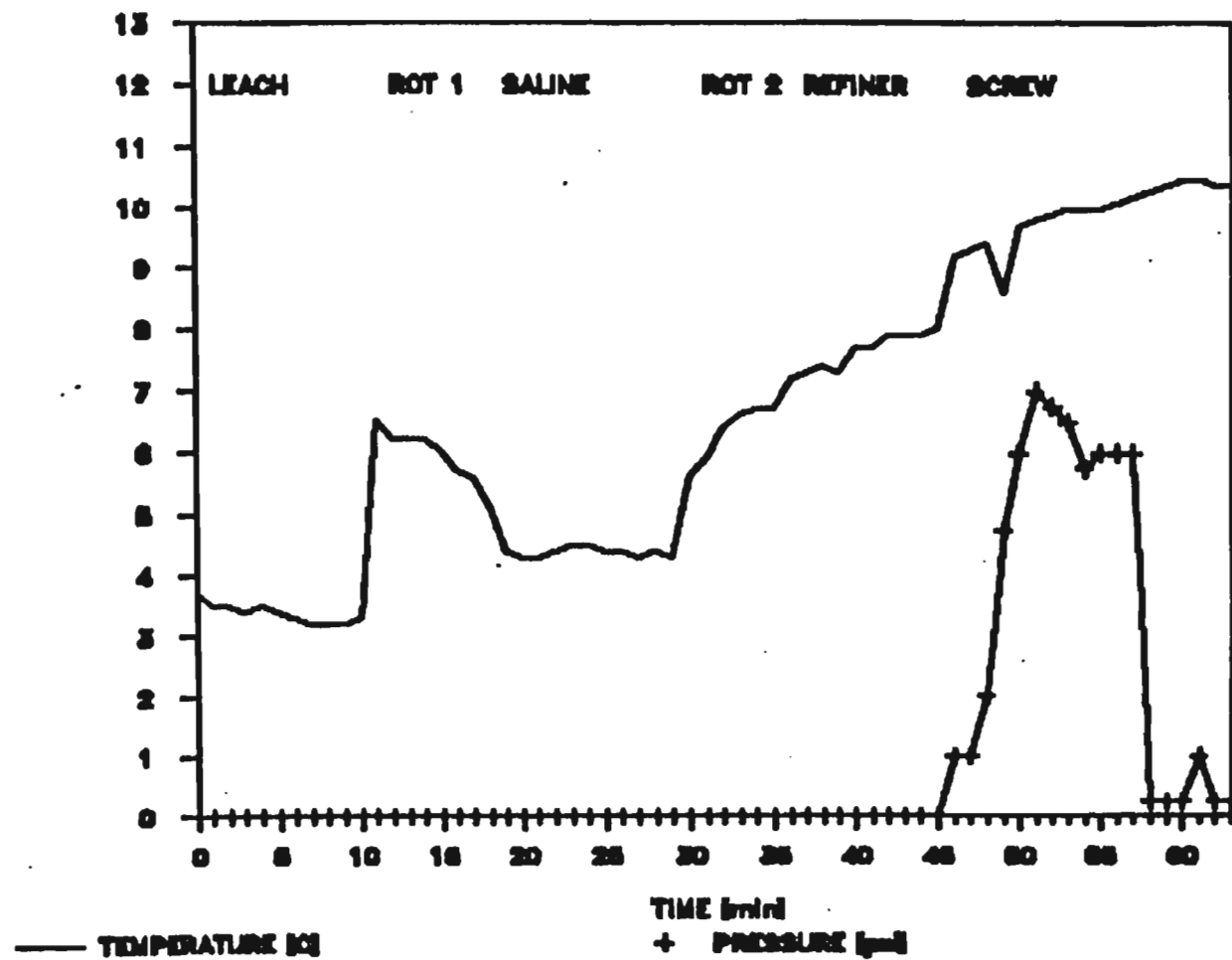


FIGURE 3.4

**SURIMI PROCESS DATA**  
OCTOBER 30, 1986 5 DAY FLOUNDER FRAMES

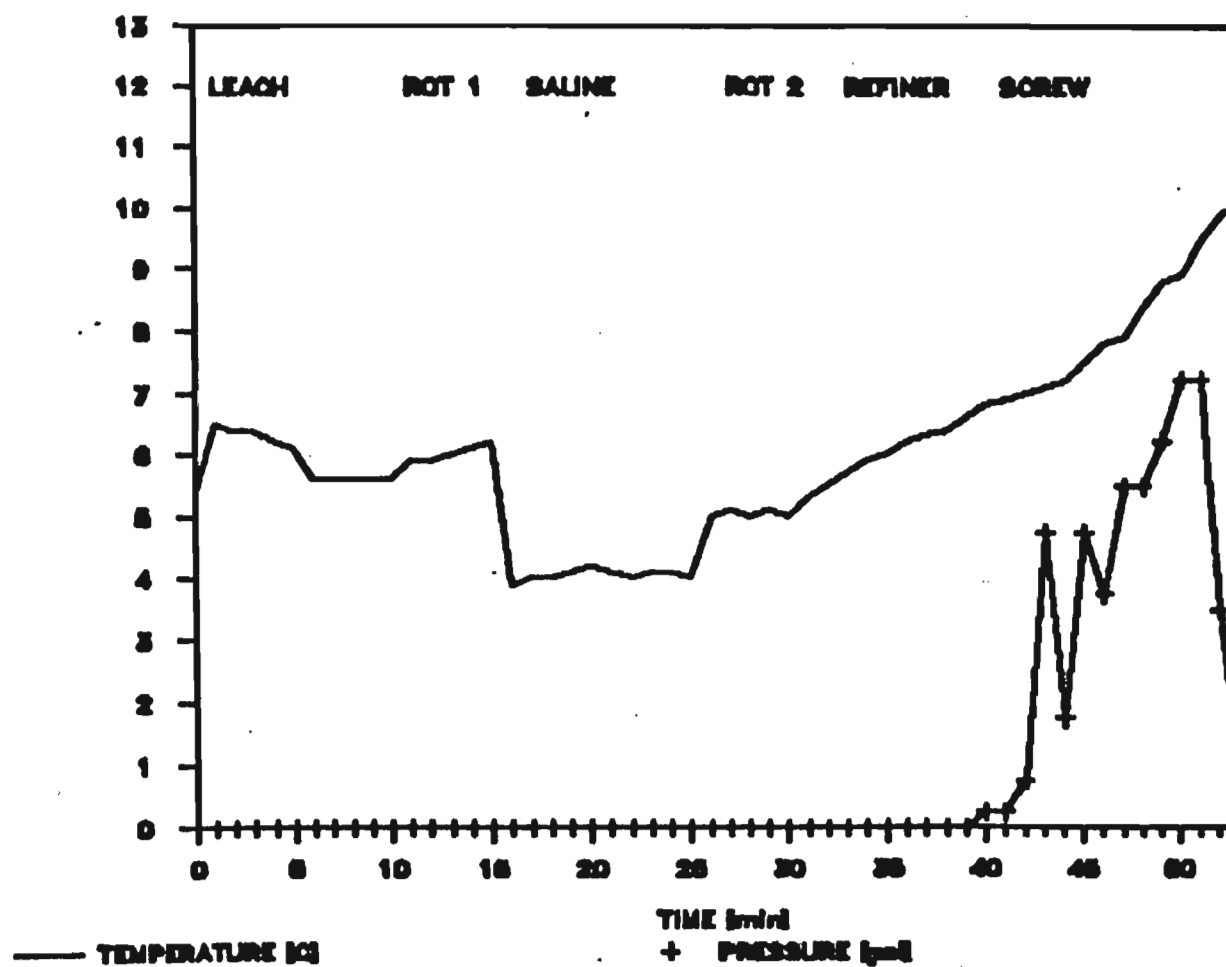


FIGURE 3.5

**SURIMI PROCESS DATA**  
NOVEMBER 13, 1986 6 DAY TRAWLER COD

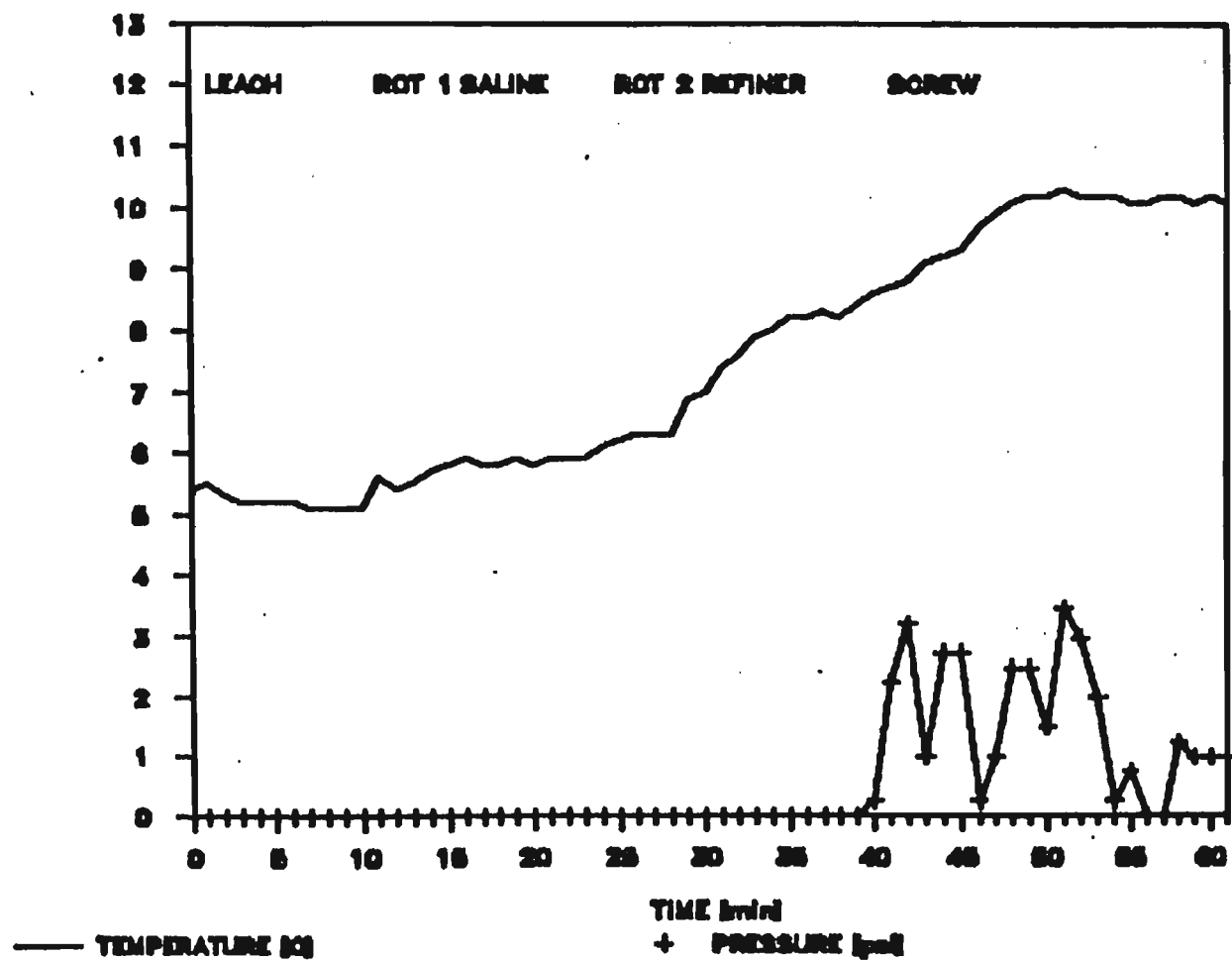


FIGURE 3.6  
 SURIMI PROCESS DATA  
 NOVEMBER 18, 1988 5 DAY TRAWLER COD

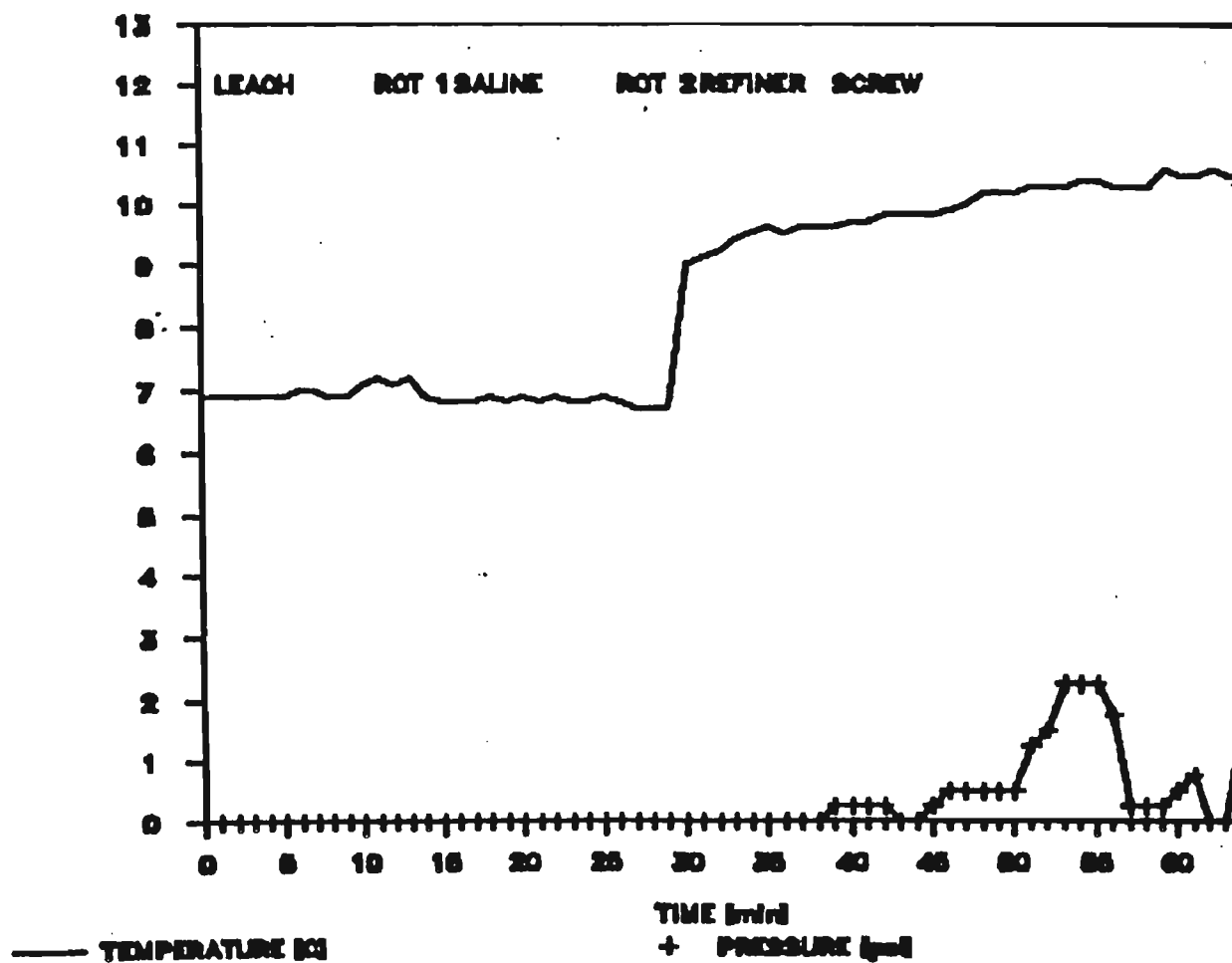


FIGURE 3.7

**SURIMI PROCESS DATA**

NOVEMBER 19, 1986 5 DAY TRAWLER COD

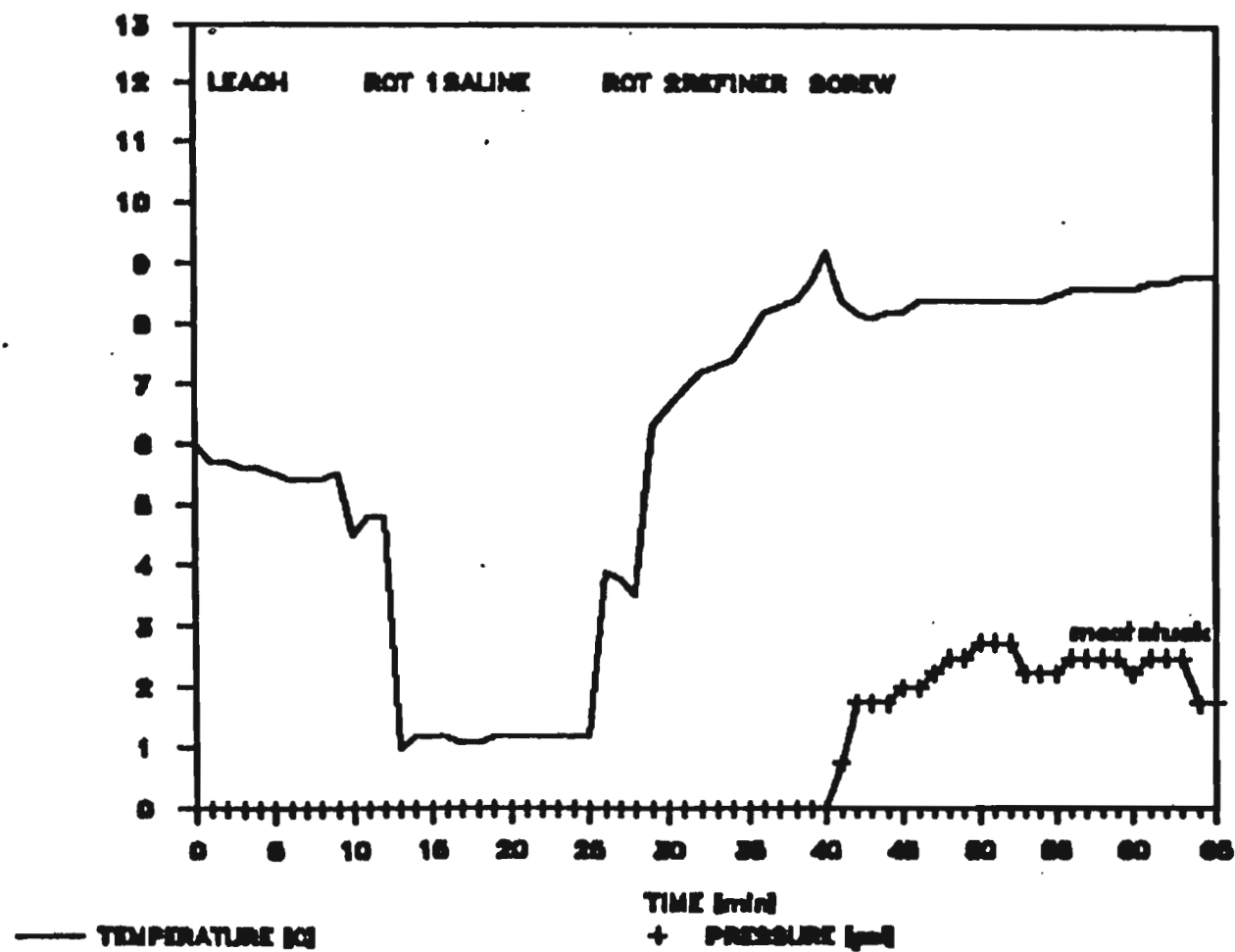


FIGURE 3.8  
**SURIMI PROCESS DATA**  
 NOVEMBER 21, 1986 5 DAY TRAWLER COD



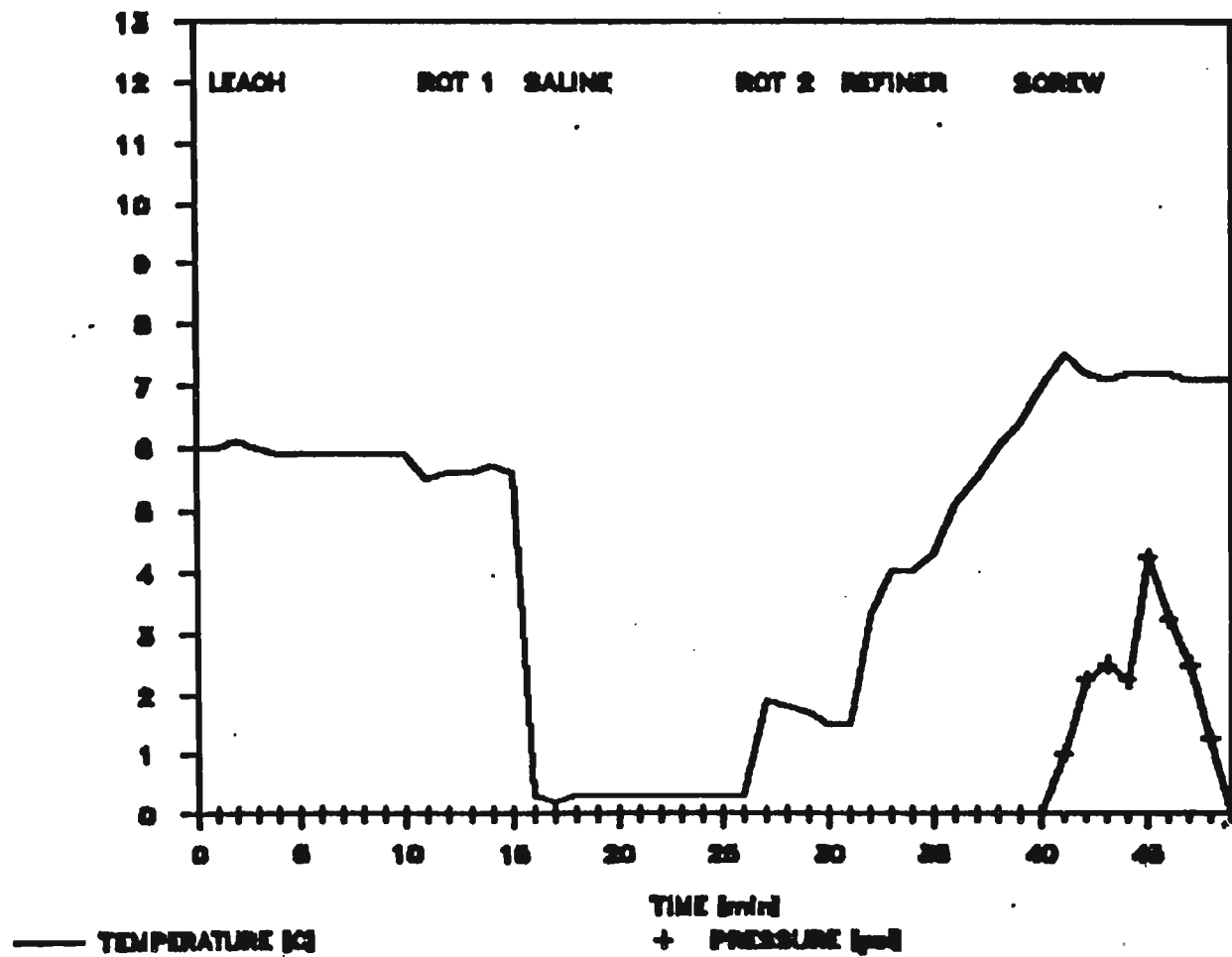


FIGURE 3.9  
SURIMI PROCESS DATA  
DECEMBER 16, 1986 4 DAY FROZEN COD

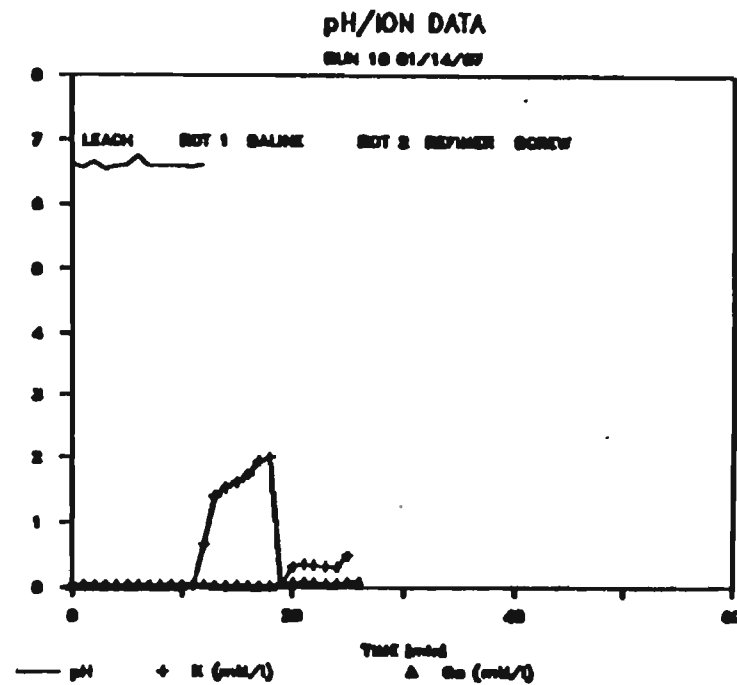
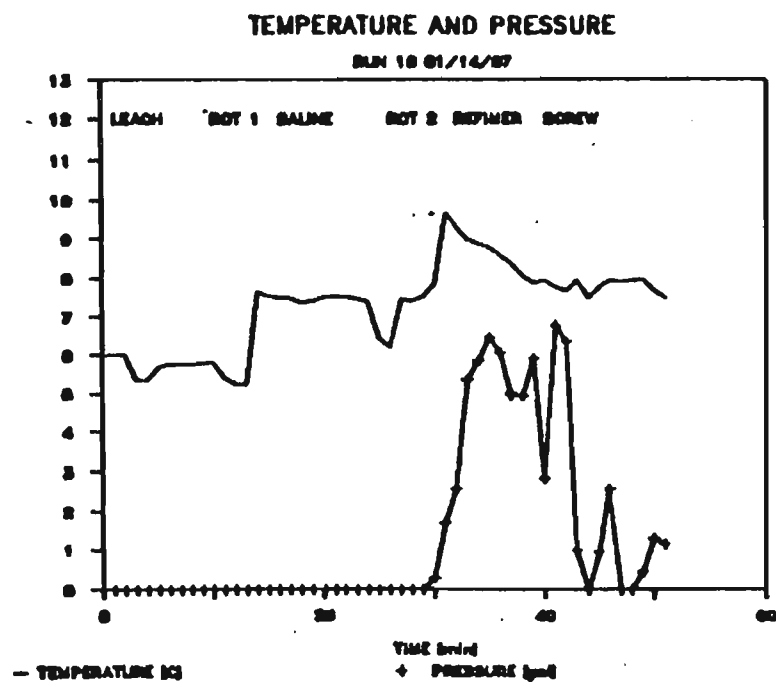
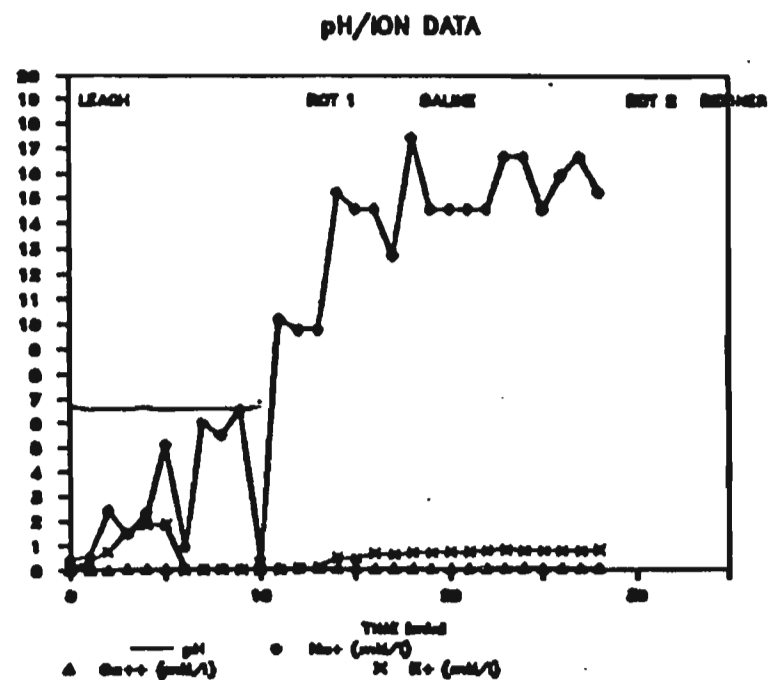
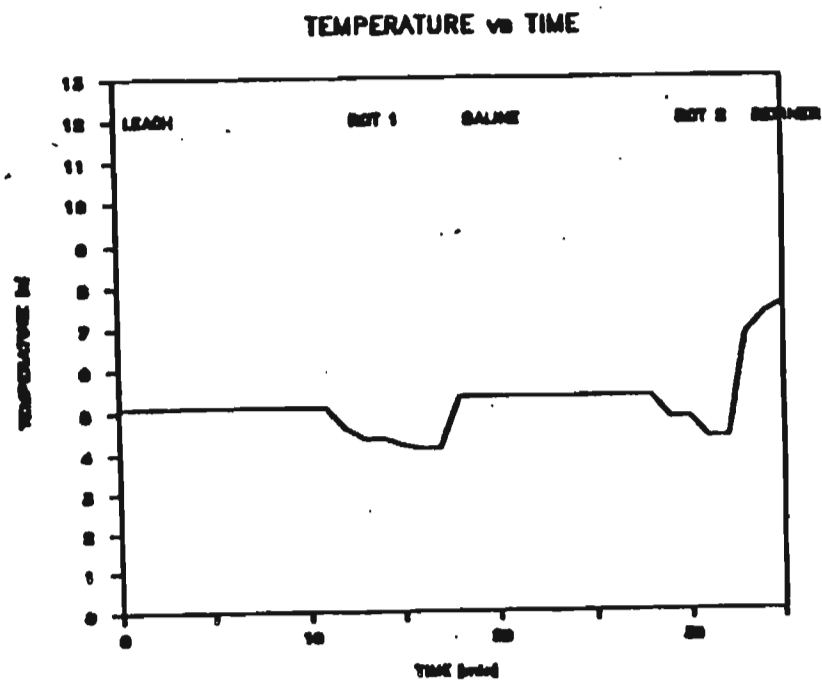


FIGURE 3.10  
**SURIMI PROCESS DATA**  
JANUARY 14, 1987 4 DAY TRAWLER COD



**FIGURE 3.11**  
**SURIMI PROCESS DATA**  
**JANUARY 21, 1987 FROZEN CAPLIN**

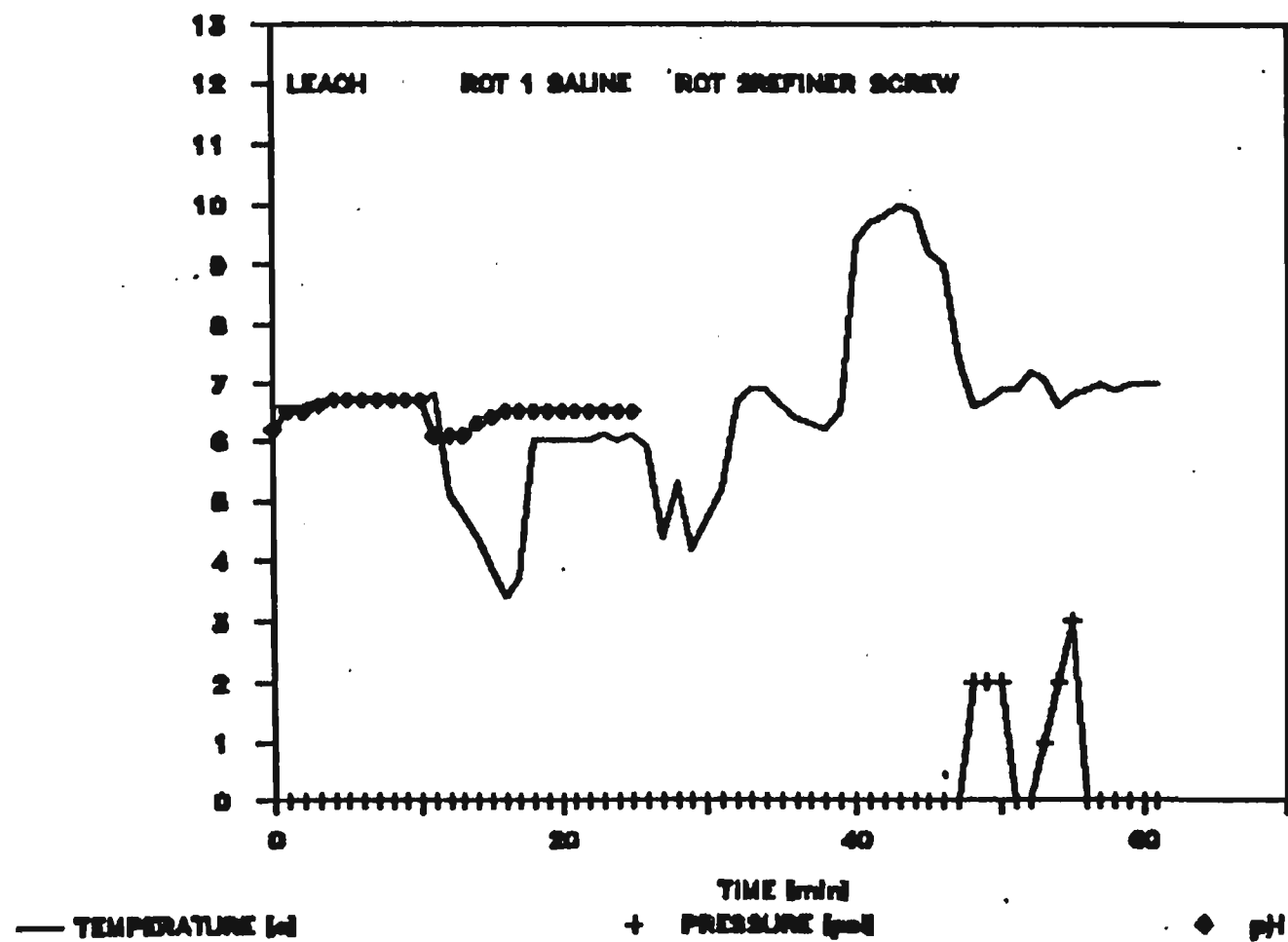


FIGURE 3.12

**SURIMI PROCESS DATA**  
**FEBRUARY 13, 1987 4 DAY FROZEN COD**

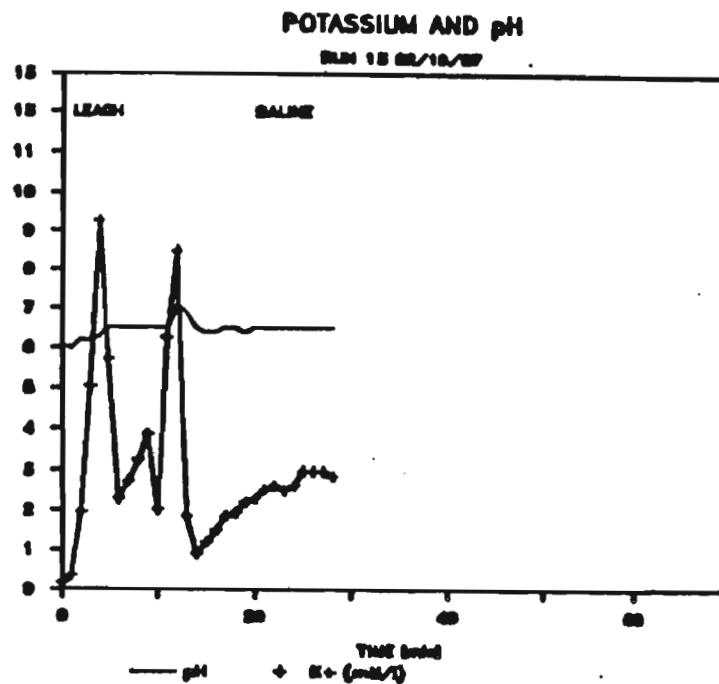
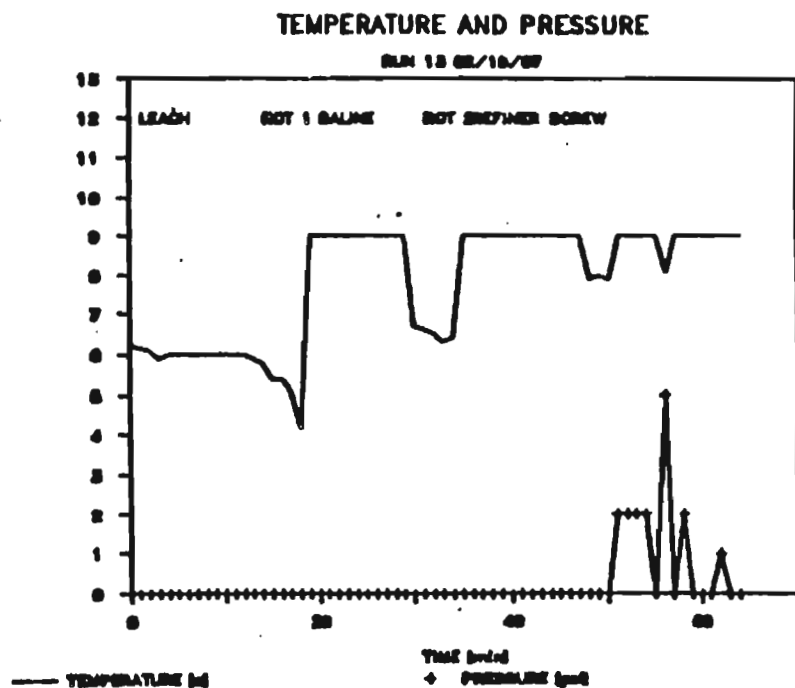


FIGURE 3.13

**SURIMI PROCESS DATA**  
FEBRUARY 19, 1987 8 DAY-TRAWLER COD

PH CONTROL EXPERIMENT  
pH CONTROL (not adjusted)

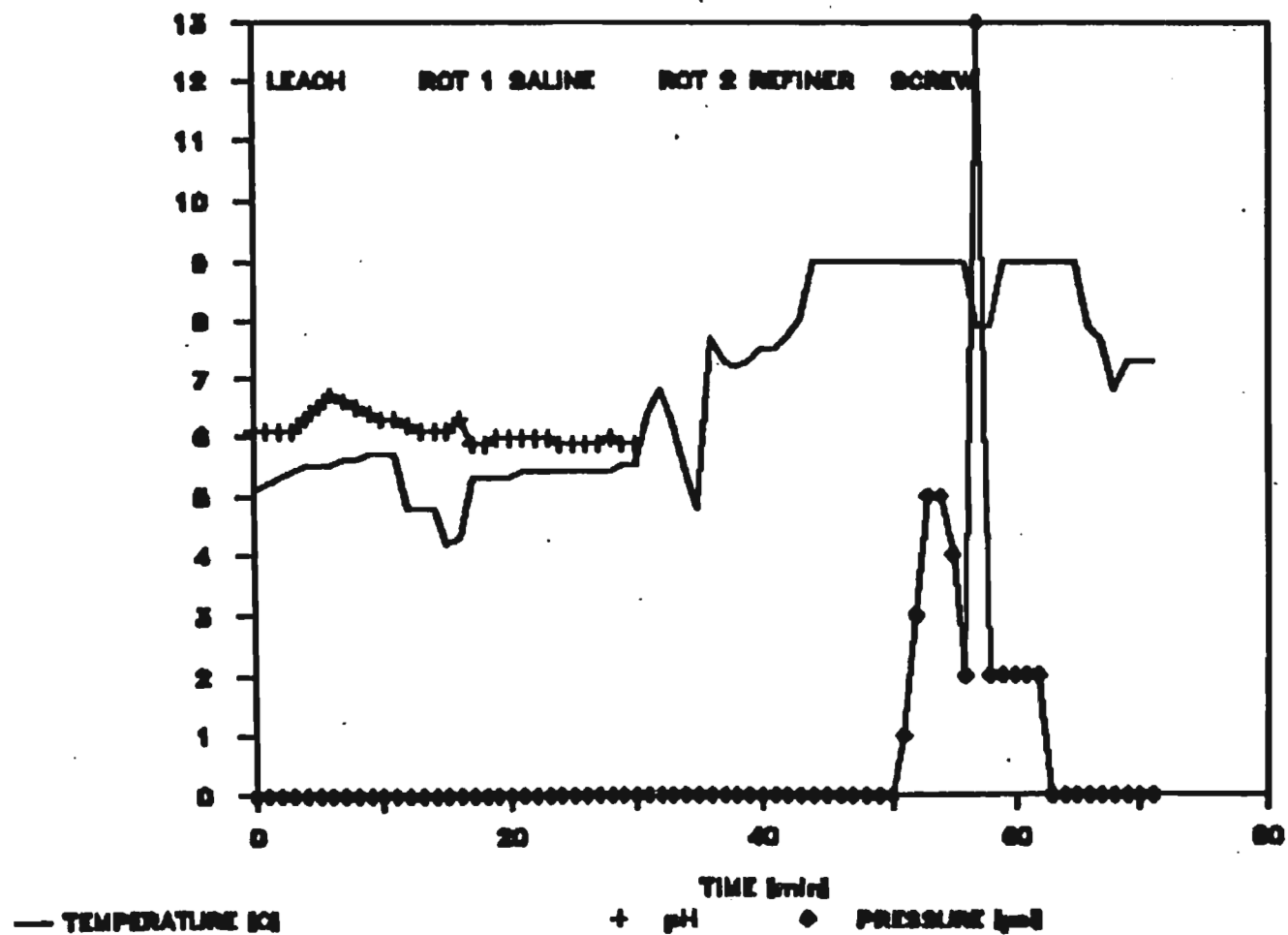


FIGURE 3.14  
**SURIMI PROCESS DATA**  
 FEBRUARY 20, 1987 9 DAY TRAWLER COD  
 PH CONTROL EXPERIMENT

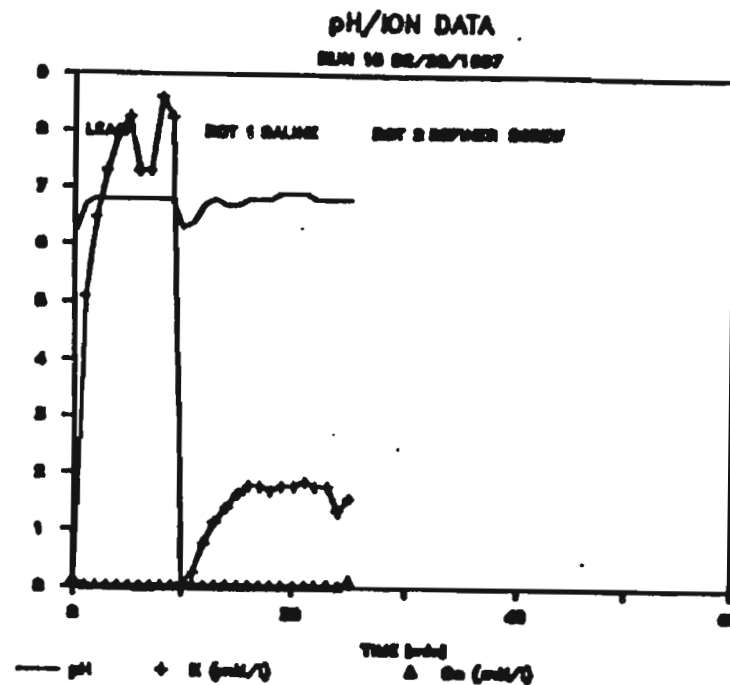
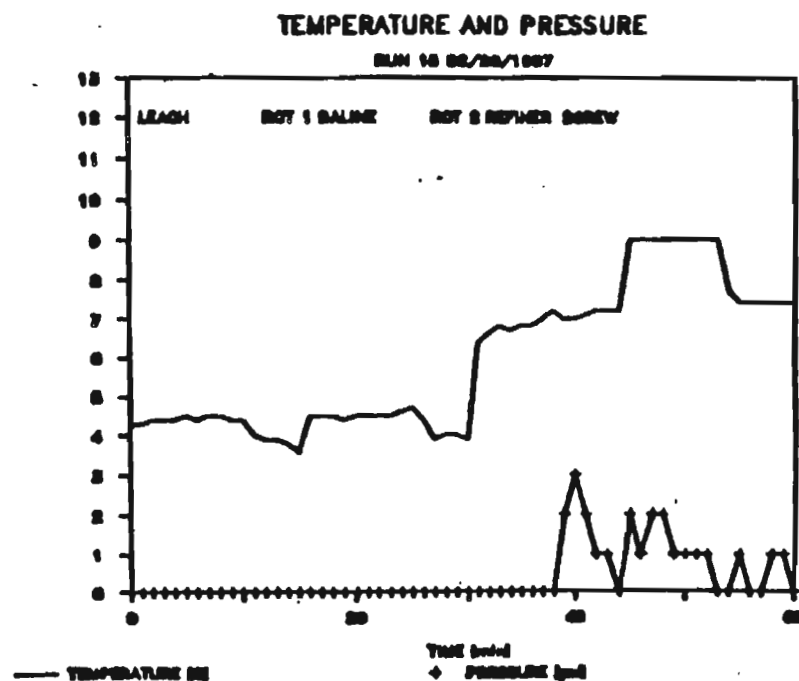


FIGURE 3.15  
SURIMI PROCESS DATA  
FEBRUARY 20, 1987 9 DAY TRAWLER COD

PH CONTROL EXPERIMENT  
pH 7.0 ADJUSTED

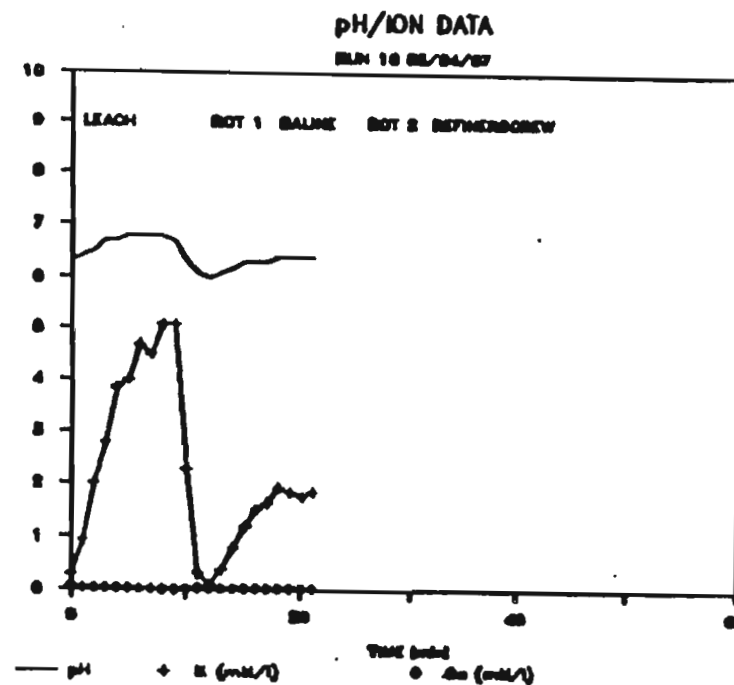
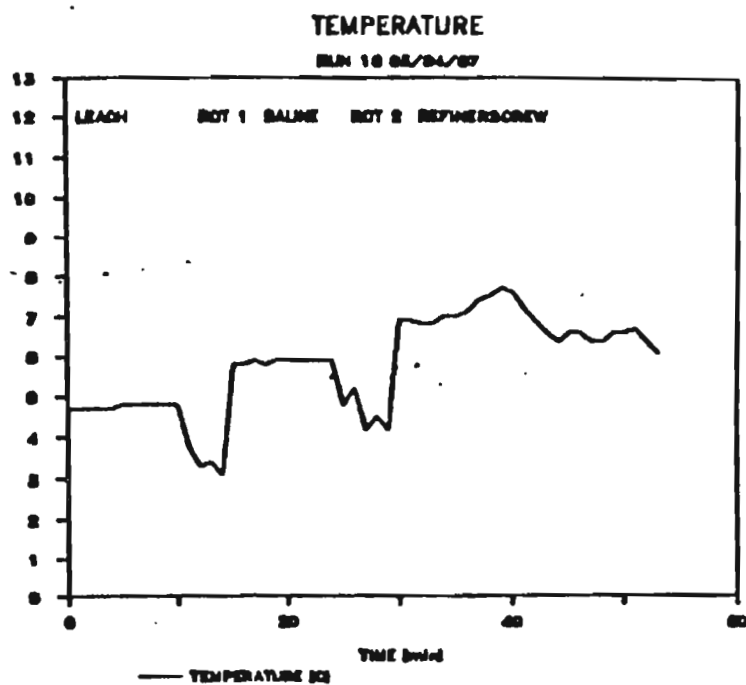
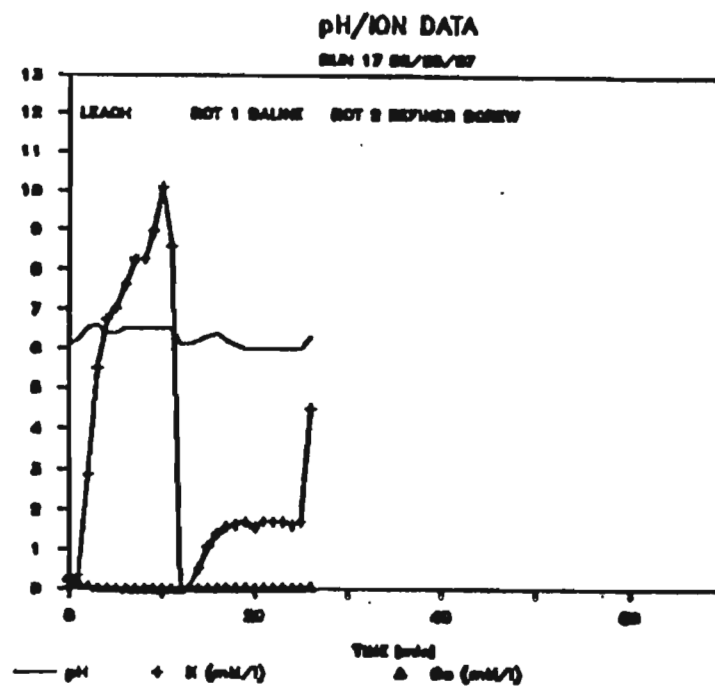
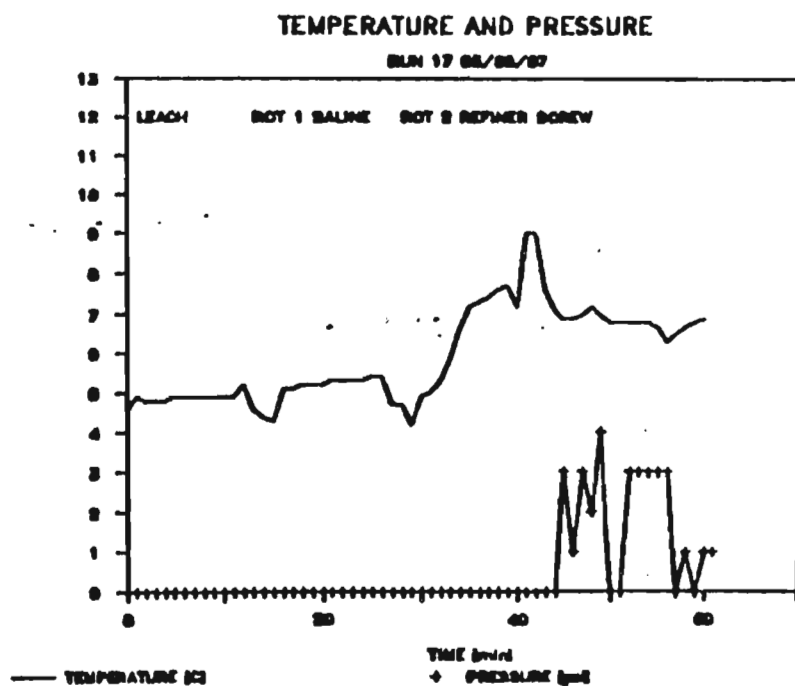


FIGURE 3.16  
SURIMI PROCESS DATA  
MARCH 4, 1987 COD FILLET

PH CONTROL EXPERIMENT  
pH CONTROL (not adjusted)





**FIGURE 3.17**  
**SURIMI PROCESS DATA**  
**MARCH 5, 1987 SKINLESS COD FILLET**

**pH CONTROL EXPERIMENT**  
**pH 6.1 ADJUSTED \***

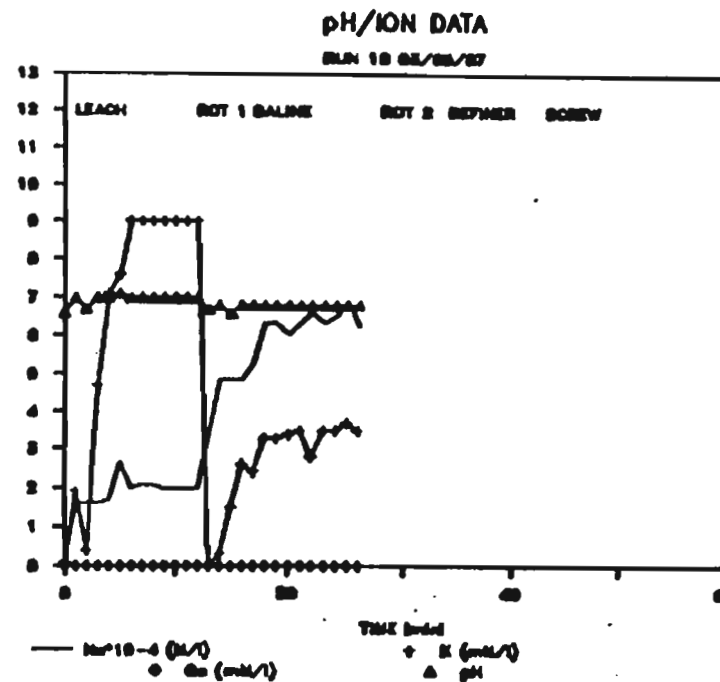
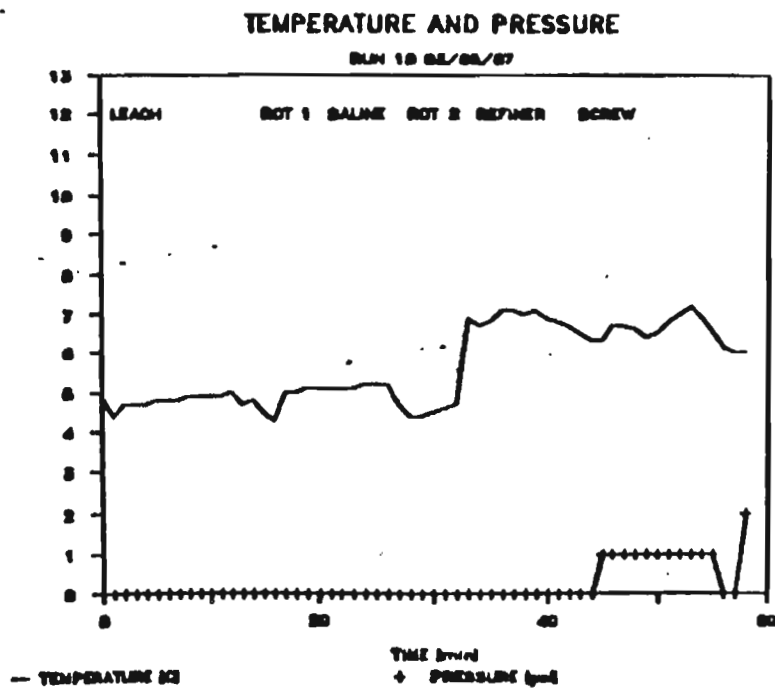


FIGURE 3.18  
SURIMI PROCESS DATA  
MARCH 5, 1987 COD FILLET  
PH CONTROL EXPERIMENT  
pH 7.0 ADJUSTED

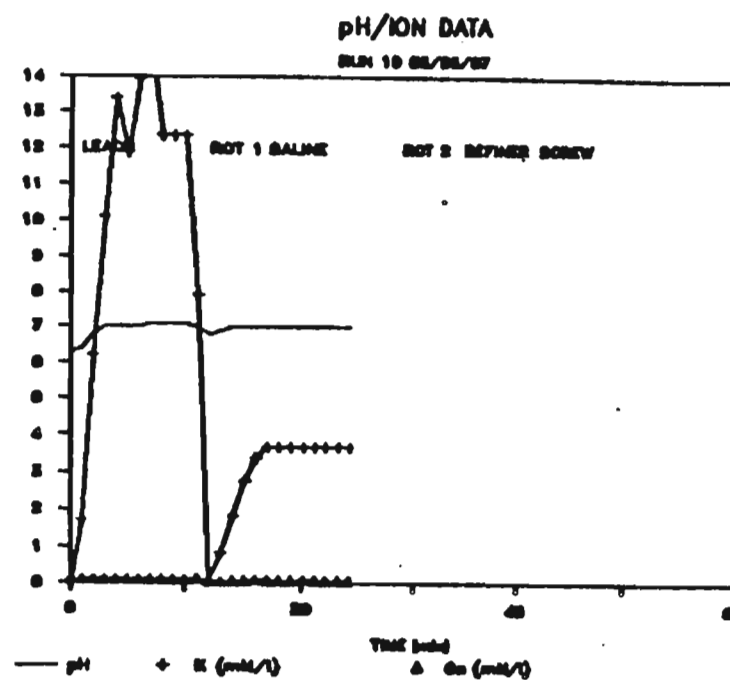
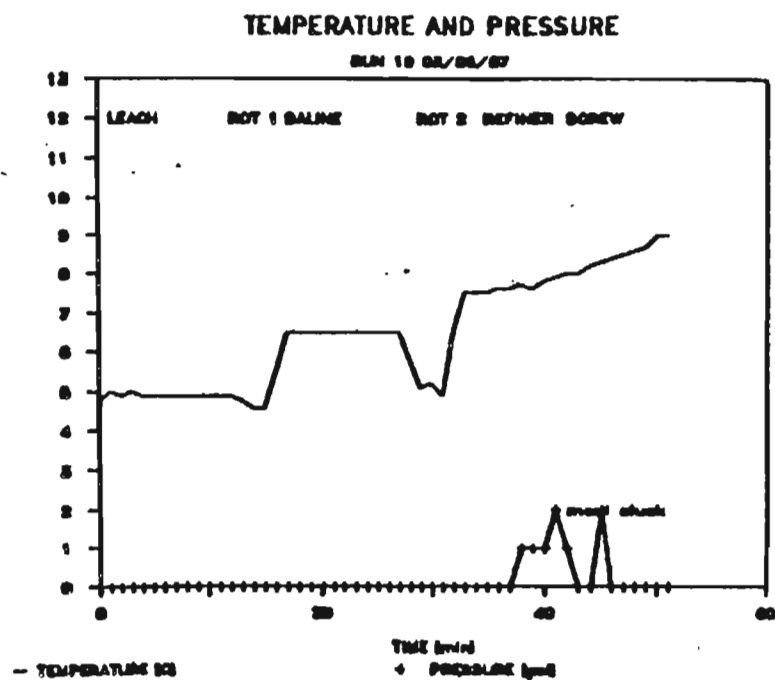
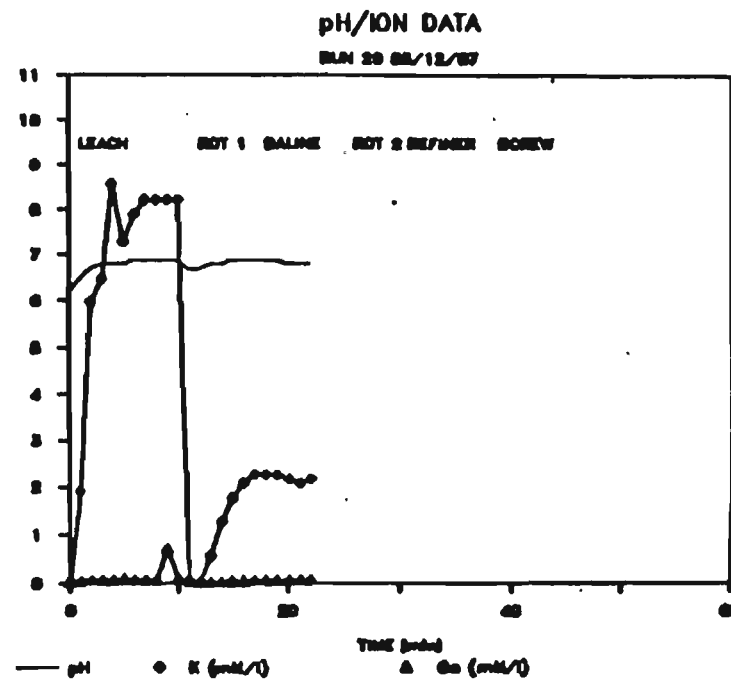
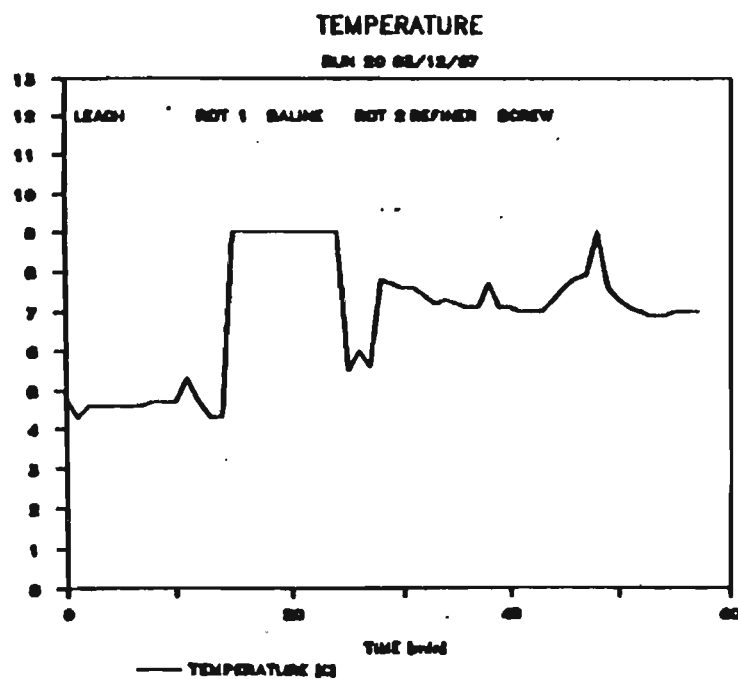


FIGURE 3.19  
SURIMI PROCESS DATA  
MARCH 6, 1987 COD FRAME WASTE



**FIGURE 3.20**  
**SURIMI PROCESS DATA**  
**MARCH 12, 1987 COD FRAMES**

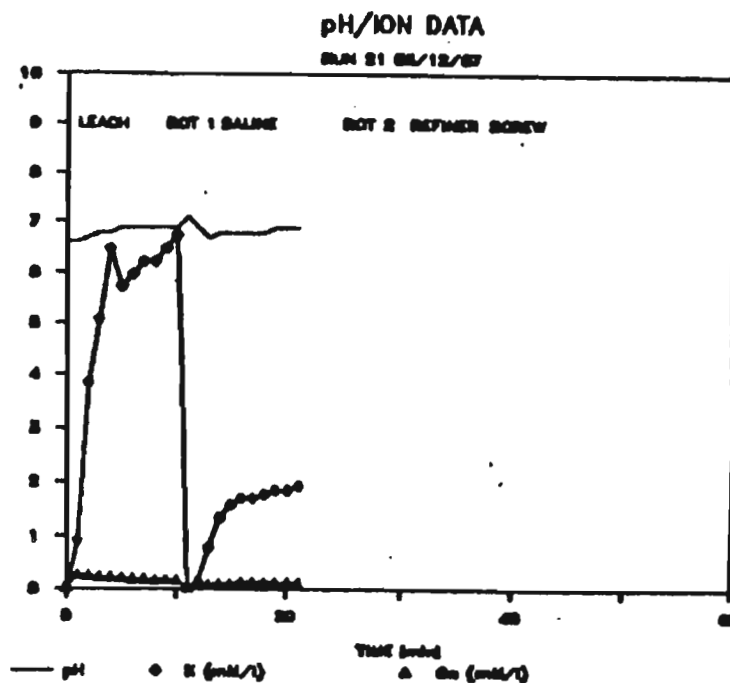
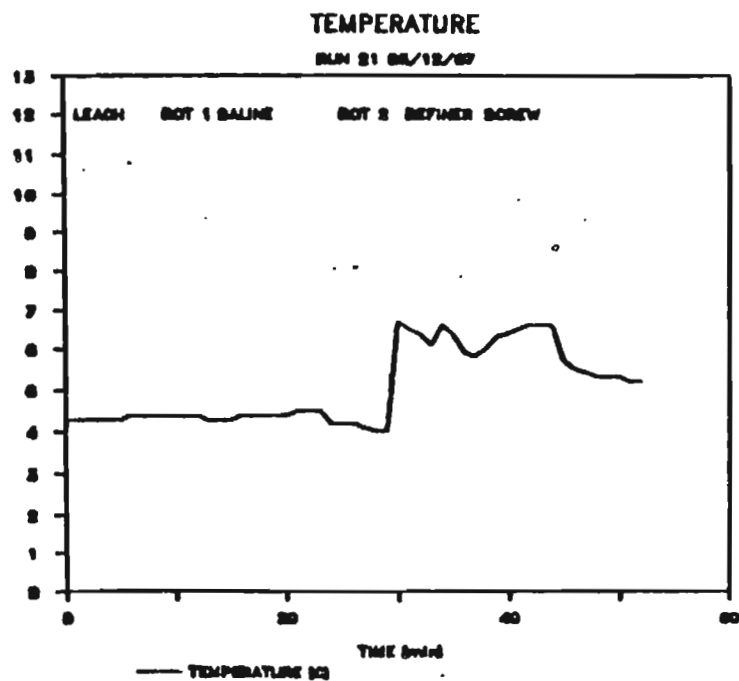


FIGURE 3.21

SURIMI PROCESS DATA

MARCH 12, 1987 COD FRAMES

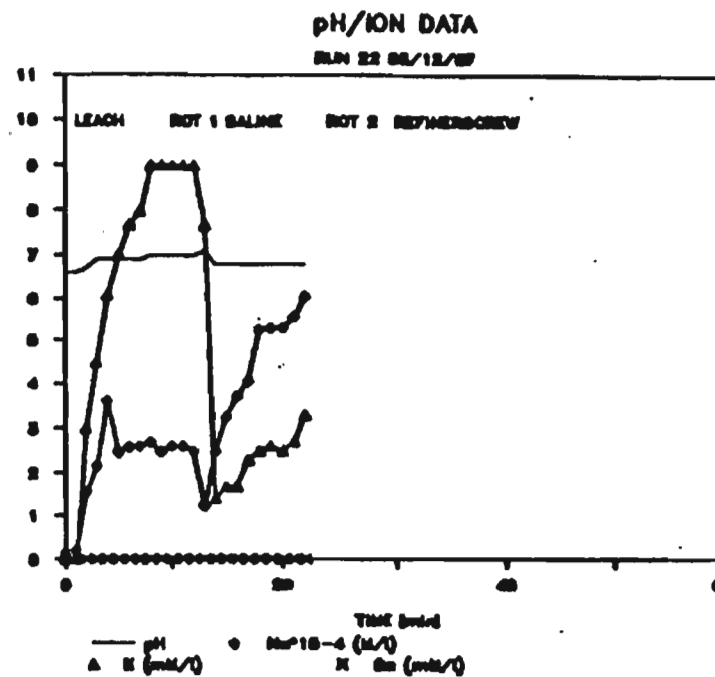
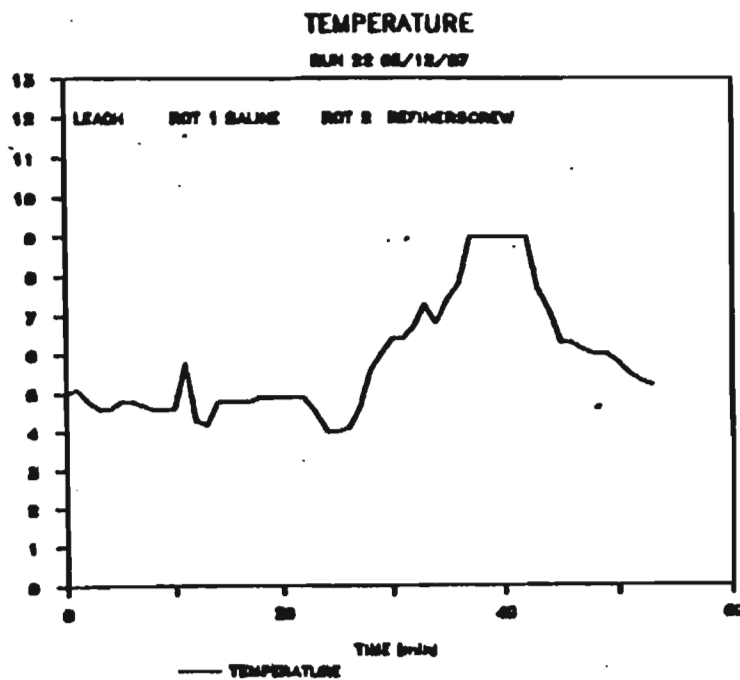


FIGURE 3.22

**SURIMI PROCESS DATA**

**MARCH 12, 1987 COD FRAMES**

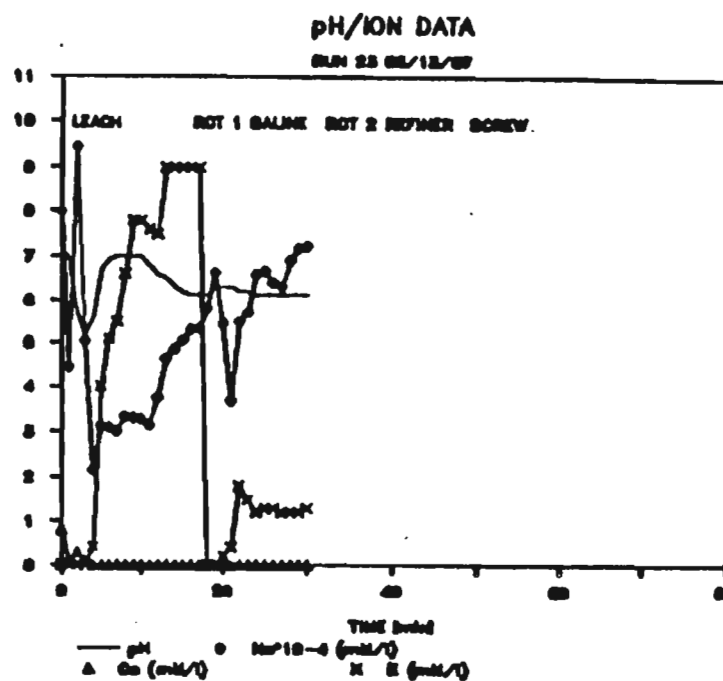
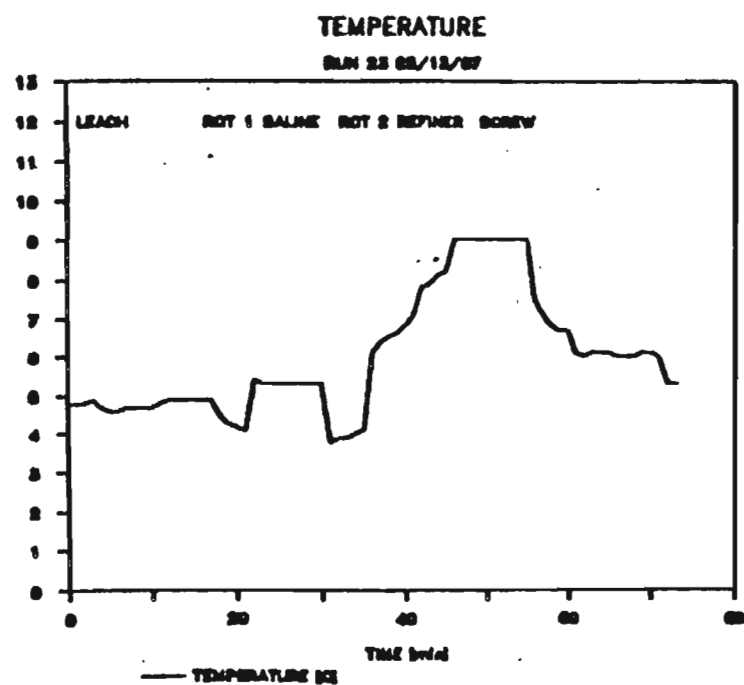


FIGURE 3.23

# SURIMI PROCESS DATA

MARCH 13, 1987 10 DAY COD FRAMES

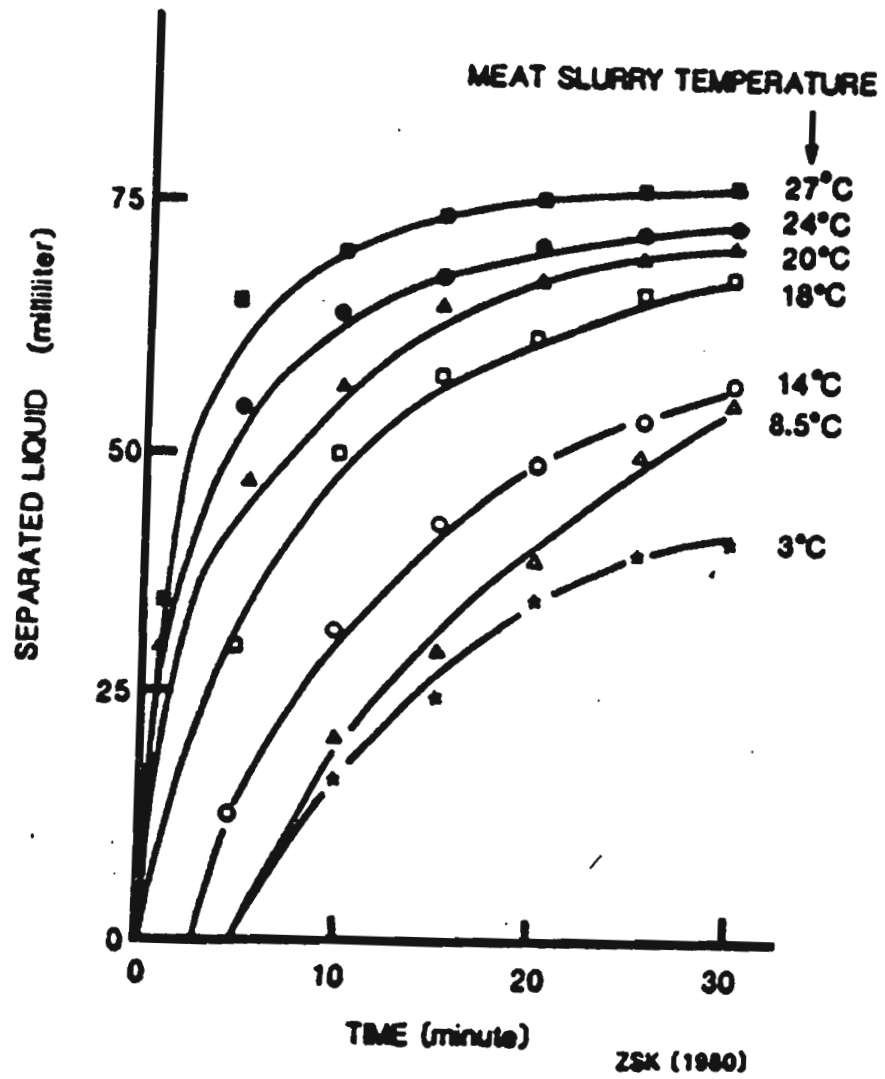
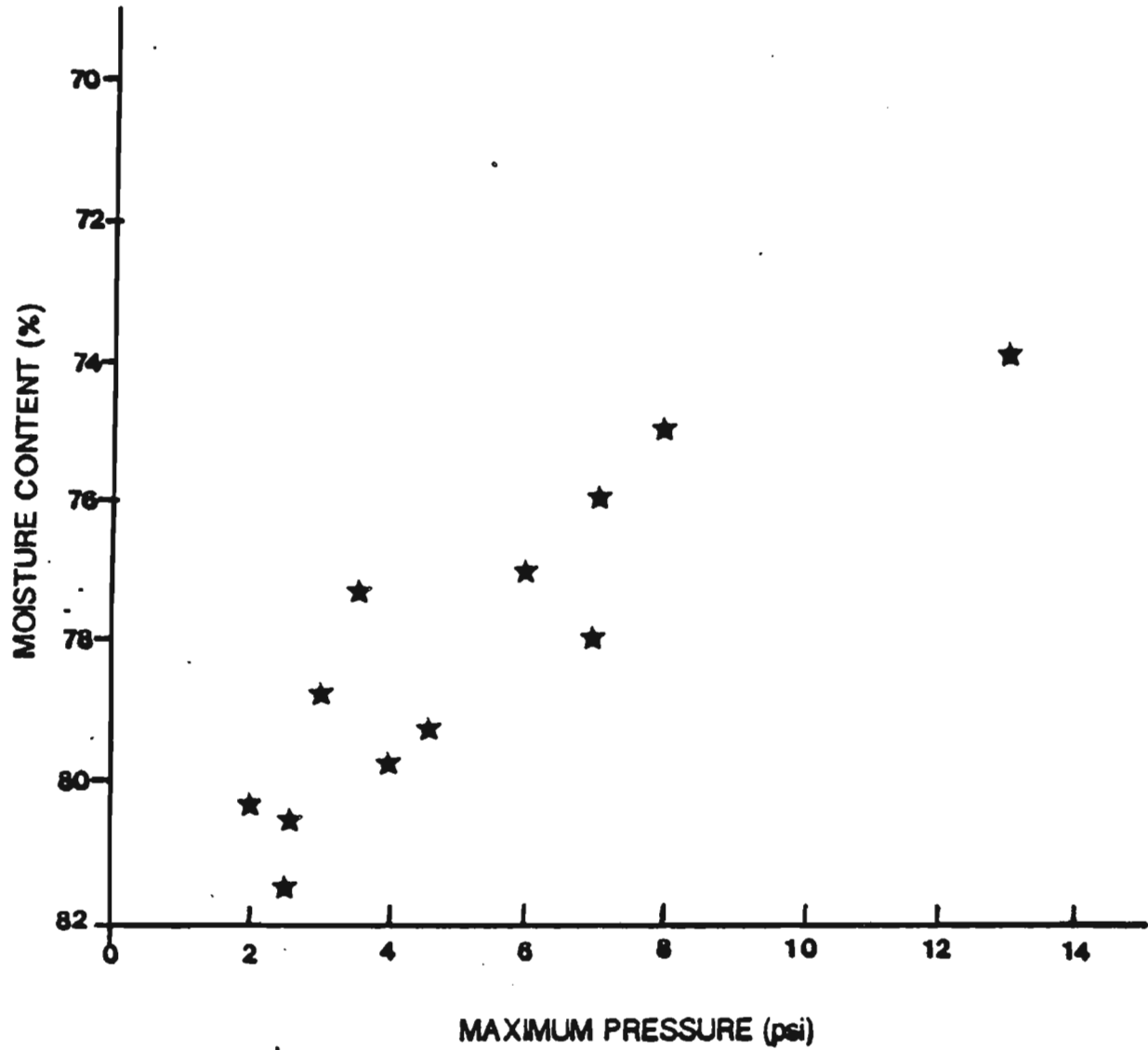


FIGURE 3.24 EFFECT OF WATER TEMPERATURE ON DEWATERING ABILITY



FIGURE 3.25 RELATIONSHIP BETWEEN SURIMI MOISTURE CONTENT AND  
MAXIMUM PRESSURE MEASURED IN THE SCREW PRESS



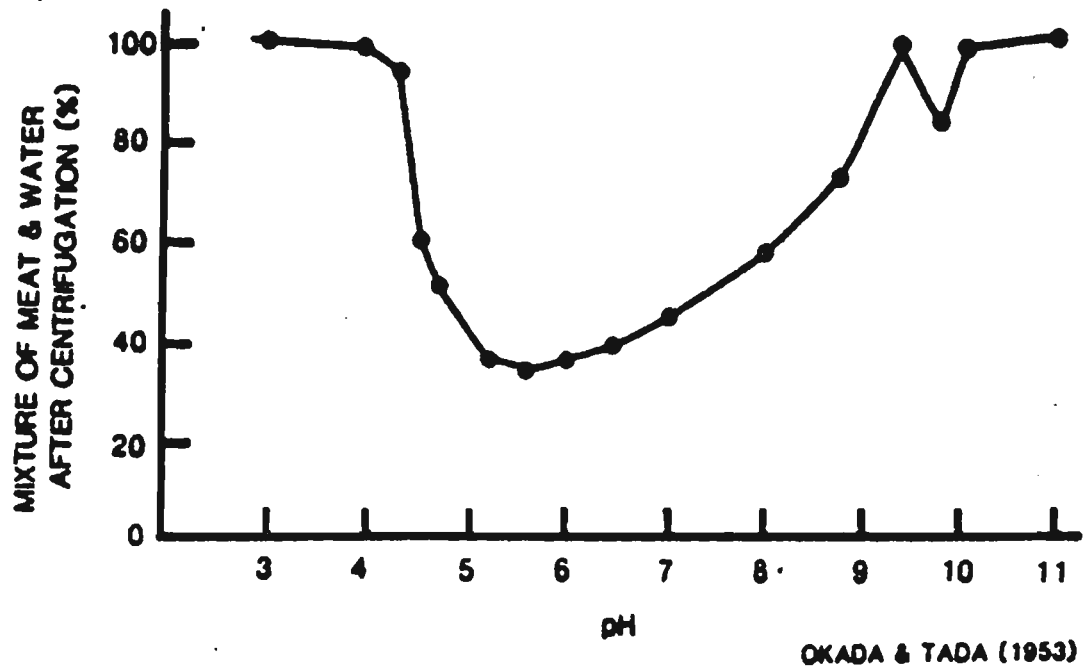


FIGURE 3.26 EFFECT OF pH ON THE WATER BINDING CAPACITY OF MYOFIBRILLAR PROTEIN

# MODULUS of ELASTICITY vs STRAIN

90 C

MODULUS of ELASTICITY (kPa)

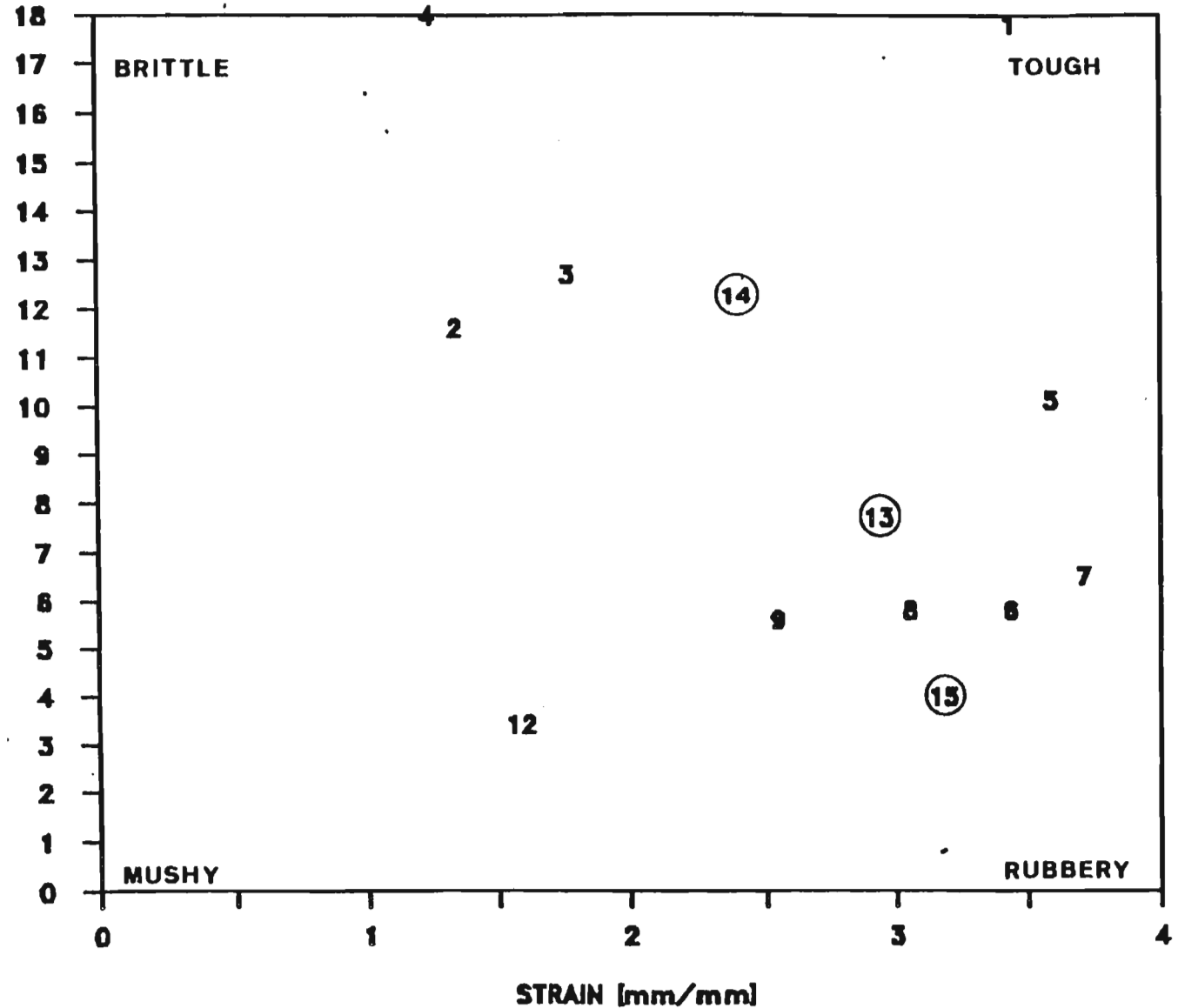


FIGURE 3.27 SUMMARY OF TEXTURAL PROPERTIES OF SURIMI GELS  
AS DETERMINED BY THE TORSION TEST (1986-87 PILOT DATA)

KEY			
Run	Recipe	pH	Moisture %
1	5 DAY COD FILLET	6.09	75.2
2	5 DAY COD FRAMES	7.02	76.9
3	5 DAY COD FRAMES	6.73	77.3
4	5 DAY FLOUNDER FR.	6.09	75.9
5	5 DAY TRAWLER COD	6.74	76.0
6	5 DAY TRAWLER COD	6.70	76.7
7	5 DAY TRAWLER COD	6.80	80.3
8	5 DAY TRAWLER COD	6.73	80.3
9	4 DAY FROZEN COD	N/A	79.8
10	4 DAY TRAWLER COD	N/A	N/A
11	FROZEN COD	6.8	81.5
12	4 DAY TRAWLER COD	6.7	80.5
13	9 DAY TRAWLER COD	6.9	79.3
14	9 DAY TRAWLER COD	6.1	73.9
15	9 DAY TRAWLER COD	7.0	81.5

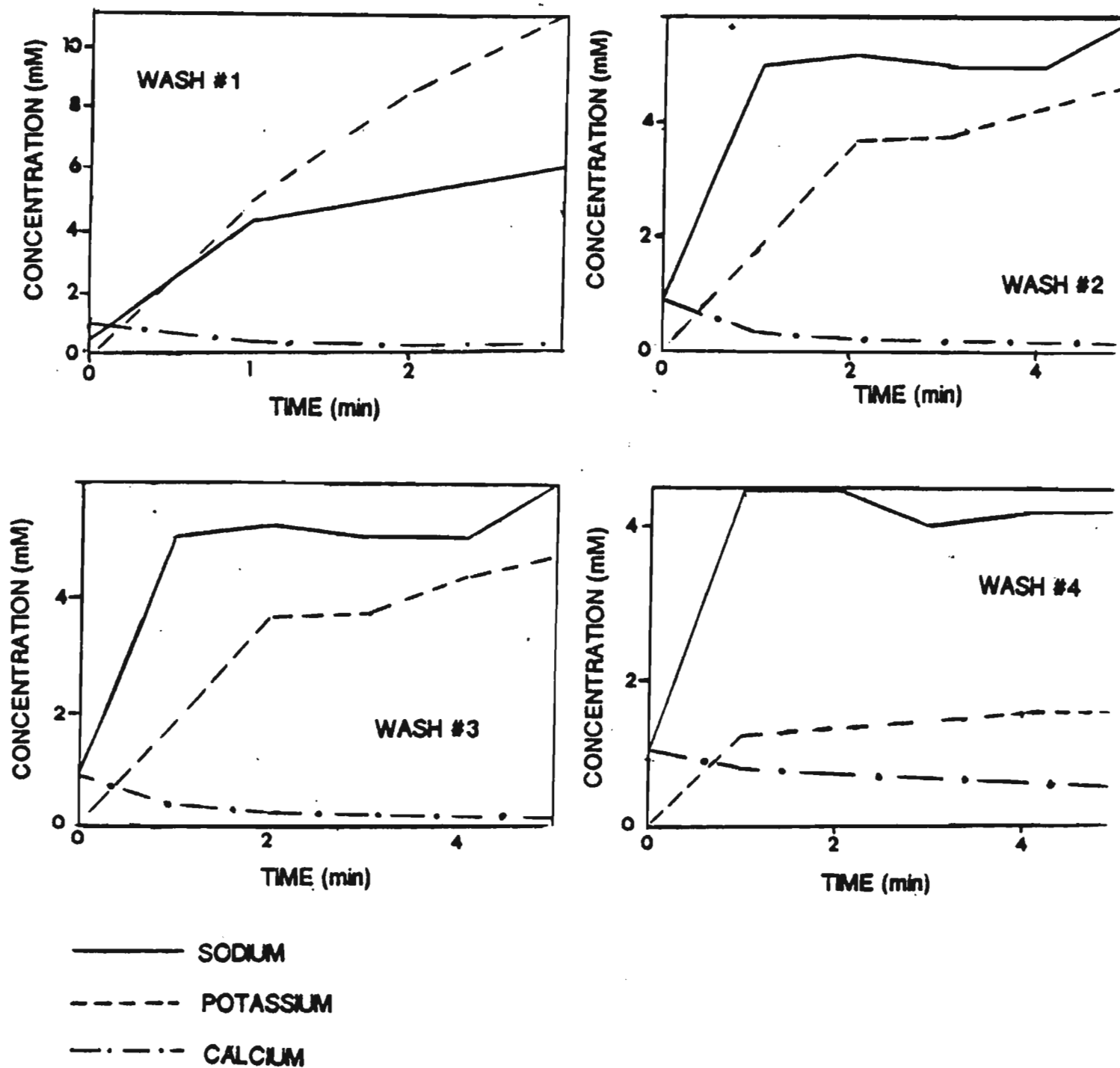


FIGURE 3.28 LEACHING PROPERTIES OF SODIUM, POTASSIUM AND CALCIUM FROM COD MINCE (5mm)

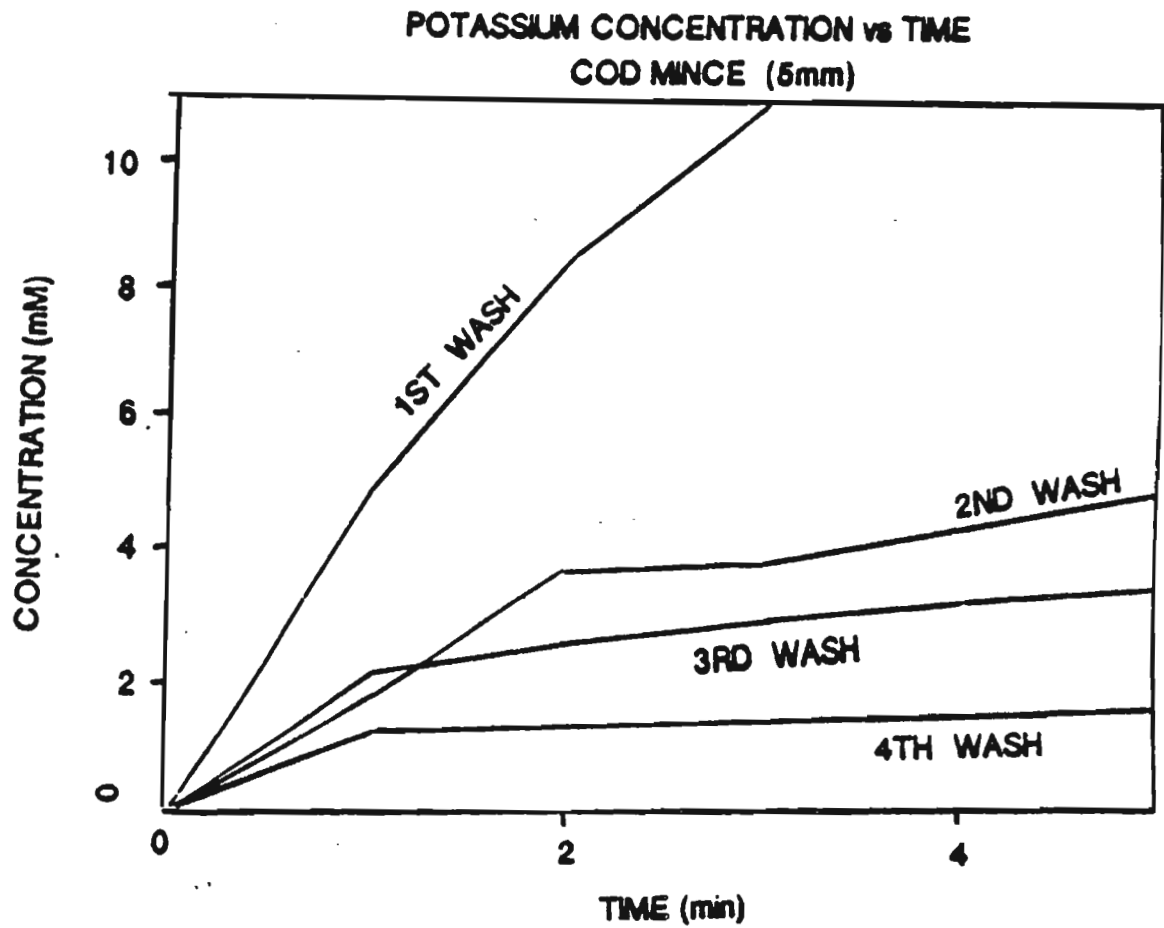


FIGURE 3.29 EFFECT OF THE NUMBER OF WASH CYCLES ON THE KINETICS OF POTASSIUM FROM COD MINCE (5mm)

# MODULUS of ELASTICITY vs STRAIN

1985/86 SURIMI PILOT COD DATA

MODULUS of ELASTICITY (kPa)

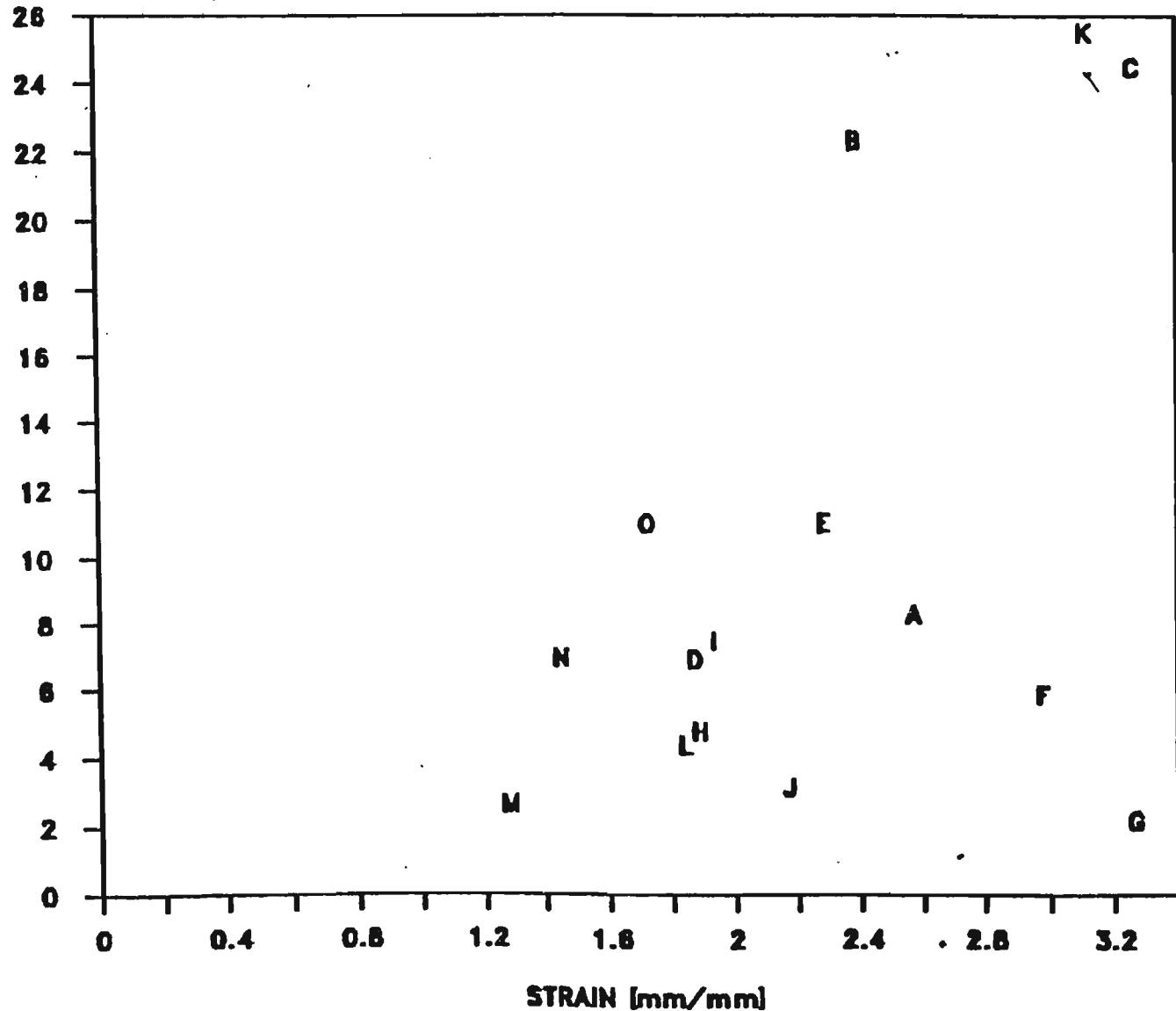


FIGURE 3.30 SUMMARY OF TEXTURAL PROPERTIES OF SURIMI GELS AS DETERMINED BY THE TORSION TEST (1985-86 PILOT DATA)

SET			
Run	Wince	pH	Moisture %
A	8 DAY SPLIT COD	7.2	80.5
B	12 DAY SPLIT COD	7.0	76.0
C	10 DAY COD FRAME	7.1	79.9
D	6 DAY COD	7.3	80.5
E	7 DAY COD	7.2	76.6
F	8 DAY COD	7.3	81.3
G	9 DAY COD	7.3	82.9
H	10 DAY COD	7.3	81.4
I	11 DAY COD	7.3	85.9
J	11 DAY COD	7.2	82.4
K	12 DAY COD	7.0	74.0
L	12 DAY COD	7.3	81.7
M	14 DAY COD	7.0	80.3
N	14 DAY COD	7.4	81.1

#### 4.0 RECOMMENDATIONS

The work completed during 1986/87 has provided: (1) a working set of process monitoring sensors; (2) physical/chemical models for the various processes; and (3) identification of critical control points in the process machinery. The future work plan should concentrate on the development of an interactive, working instrument capable of providing an operator with real time processing information. If possible, the instrument should also suggest processing modifications based on the feedstock, current operating conditions and process models. The data base for processing models should also be expanded to include the most attractive local feedstocks (e.g. ground fish frames, frozen material). To meet these objectives, two integrated approaches are necessary: (1) continue to collect data pertaining to the various process parameters to expand/confirm/refine existing models, and (2) introduce an instrument which gives the operator, in real time, the data that is collected during processing.

##### **Install Operator Feed Back "Controls"**

A real time display of process parameters should be set up to provide the machine operator with immediate information. A display mounted above the existing control panel will show pH, temperature, salinity and screw press pressure in an easily readable format. Control points will

be indicated in the display and operator prompts will be indicated. When sufficient modeling data has been formulated the controller should be expanded to provide the operator with suggestions pertaining to process modification.

#### **Data Collection**

The process monitoring system should log all process parameters as during this present year. The existing sensors will need to be refurbished. Sensors will be added to monitor phosphate, magnesium and salinity. Pressure sensors will be positioned at both ends of the screw press since this will be a critical parameter with the proposed introduction of a pre-pressurizing pump. Modifications to the existing sample collection system should be made to reduce the high maintenance problems experienced this year. Alternative methods should be investigated especially for ion-selective electrodes. Additional sensors should also be evaluated. A flow-through UV sensor to measure water soluble protein can be implemented to: (1) correlate with potassium leaching data and (2) possibly provide an improved methodology for examining leaching kinetics. Flow-through UV-monitors are based on optical measurements and are not susceptible to the same constraints as electrodes. The real time measurement of the moisture of the meat exiting the screw press is also a parameter that can influence the control of the process. Even though the press is essentially non-controllable, moisture can be modified as required using



pH and salinity adjustment.

The collection of data should also be expanded to include a systematic evaluation of the optimum processing technologies for frame wastes and frozen material. This processing data should be incorporated into the existing process model. Both frame wastes and frozen fish are likely to be the resources available for surimi processing. This is not only applicable for the local industry, but also to worldwide producers. Alaskan pollock is not a valuable species in the market place. Expertise, especially in processing frame wastes will be an important objective for future work.

## 5.0 CONCLUSIONS

- 1.0 Process monitoring equipment was installed on a Bibun surimi line in order to measure various processing parameters.
- 2.0 Surimi processing data, including pH, temperature, specific ions, processing time and dewatering pressure were measured continuously during pilot scale surimi production.
- 3.0 Process data was correlated with product information to generate a number of interesting relationships:
  - (i) The moisture content of the final product can be controlled by adjusting the pH of the leach water.
  - (ii) Potassium leaching kinetics indicated that the optimal washing time for mince is probably less than five minutes. The measurement of potassium kinetics appears feasible as a washing index.
  - (iii) The texture of the final product can be predicted by controlling the moisture of surimi and quality of the starting material.
- 4.0 A model for the leaching process based on process data and published information has been developed.

Further confirmation and extension to include frame wastes and frozen material is recommended.

5.0 A preliminary assessment of the various sensing technologies has been made. It is recommended that existing methods to measure time, temperature and pressure can be reliably adopted by processors. Ion and pH sensing technologies require further refinement for industrial application. It is also recommended that sensors for salinity, moisture and protein be investigated.

6.0 The pressure developed in the screw press is inversely proportional to the moisture content of the mince. However, the moisture content of the mince is not always a function of screw press operation. This machine is not well suited to surimi dewatering.

## **ACKNOWLEDGEMENTS**

The work described in this report was carried out with the cooperation of the Institute of Fisheries and Marine Technology. Facilities, surimi processing and product analysis were provided by the Institute.

## REFERENCES

- Arai, K., K. Kawamura and C. Hayashi (1973). The Relative Thermostabilities of the Actomyosin ATPase from the Dorsal Muscles of Various Fish Species. B.J.S.F.F.. 39(10): 1977-85.
- Barrow, G.M. (1966). Physical Chemistry. McGraw Hill, N.Y.
- Chandra, C. (1986). A Study of the Use of Cod, Cod By-Products and Crustacean By-Products for Surimi and Surimi Based Products: Part 1 - Raw Material Assessment. Can.Ind.rep.Aquat.Sci. 1492: viii + 46p.
- Childs, E.A. (1973). Interaction of Formaldehyde with Fish Muscle in vitro, J. Food Sci. 38:1009-1011.
- Geigy Pharmaceuticals - Scientific Tables. (1973). eds K. Diem and C. Lentner. 7th Edition. CIBA-Geigy Ltd. Switzerland.
- Ho, C. (1987). Personal Communication.
- Hultin, H.O. (1985). Characteristics of Muscle Tissue, in "Food Chemistry" (O. Fennema, ed.) Marcel Dekker, N.Y. pp 726-789.
- Johnston, N., N. Fearson and G. Goldspunk. (1973). The Effects of Environmental Temperature on the Properties of Myofibrillar Adenosine Triphosphatase from Various Fish Species. Biochem. J. 133: pp 735-38.
- Kim, B.Y., D.D. Hamann, T.C. Lanier and M.C. Wu. (1985). Effect of Cyclic Freezing-thawing on the Viscosity and Gel Forming Properties of Surimi. Abstr. 45th Ann.Meet. Inst.Food.Technol., Atlanta.
- Lanier, T.C. (1986). Functional Properties of Surimi. Food Technol., 40(3): 107
- Lee, C.M. (1984). Surimi Process Technology. Food Technology 38(11):69-80
- Lee, C.M. (1986). Surimi. Manufacturing and Fabrication of Surimi-Based Products. Food Technol. 40(3):115
- Lee, C.M. (1987). Personal Communication.
- Love, R. Malcolm (1980). Biological factors affecting processing and utilization. AFST, 1980 p130.

- Mohr, V. (1987). Control of Nutritional and Sensory Quality of Cultured Fish. To be published in: Proceedings of International Symposium for Seafood Quality Determination. Nov. 10-14 1986 Anchorage, AK.
- Nishimoto, J. and H. Miki. (1979). Biochemical Studies on the Keeping Quality of Fish Muscle. Mem.Fac.Fish. Kagoshima Univ. 28: 69-72.
- Okado, M. and K. Tamoto. (1986). Introduction to Surimi Manufacturing Technology. Published by the Overseas Fishery Cooperation Foundation.
- Perry, R.H. and O. Green. (1984). Perry's Chemical Engineer's Handbook (6th edition) McGraw-Hill, N.Y.
- Sonu, J.C. (1986). Surimi. NOAA Technical Memorandum NMFS. NOAA-TM-NMFS-SWR-013. For US. Dept. of Commerce.
- Suzuki, T. (1981). Fish and Krill Protein - Processing Technology. Applied Science Publishers London.
- Tanaka, T. (1981). Gels. Scientific American, January, p. 124.
- Wu, M.C., T.C. Lanier and D. D. Hamann. (1985). Thermal Transitions of Admixed Starch/Fish Protein Systems During Heating. J. Food.Sci. 50:20.
- Yamamoto, T. (1974). Frozen Surimi and Kneaded Seafoods. (Reito Surimi to Suisan Neriseihin) Nippon Srokuhin Keizai (NSK) Sha Co., Tokyo 233p. As referenced by Sonu. S.C. (1986).

