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## The Chemical Buildup in a Closed Water System Using Recycled Fiber Furnish

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THE CHEMICAL BUILDUP  
IN A CLOSED WATER SYSTEM  
USING RECYCLED FIBER FURNISH

BY

STEPHEN R. TREMONT

A THESIS SUBMITTED IN FULFILLMENT  
OF THE COURSE REQUIREMENTS FOR  
THE BACHELOR OF SCIENCE DEGREE

WESTERN MICHIGAN UNIVERSITY

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In recirculating whitewater in a closed water system, the solids will increase leading to operational problems such as corrosion, scale, reduced drainage rates, reduced wire life, increased temperatures, felt plugging, foam, and dirt. In dealing with these problems, whitewater samples from a conventional seven vat cylinder board machine were tested for chemical composition. The machine operates on a closed water loop and produces approximately 250 tons per day recycled boxboard. Tested anions included chloride, silica, phosphates, nitrates, sulfate, sulfide and tannin-lignin. Cations analyzed included calcium, barium, iron, aluminum and copper. Tests were conducted over an eighteen day machine running period to determine trends in concentration levels. It was found that the anionic character of the whitewater was increasing while the cationic character tended to decrease. Indirectly board caliper could have played a role in controlling ion concentration by a filtering mechanism. The large increase in tannin-lignin concentrations are believed to increase the anionic colloidal properties and thus increase the cationic demand of the water. This behavior may in fact activate corrosion of cationic metal pipes used for water transport.

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When stock goes onto the wire of a fourdrinier or cylinder machine at from half to one percent consistency, the paper web forms on the wire while most of the carrying vehicle, the water, goes through the wire. This is the white water, carrying with it solids consisting of fiber, filler, chemicals and color. The richness, or high solids content of white water varies greatly with the furnish being used to make a specific paper product. Where long-fibered pulps are used, with little or no filler, the white water will contain only a small amount of fine fibers. If the shorter pulps are used, such as hardwood soda, and groundwood, with or without filler, the white water will be quite rich in fiber(1).

On a cylinder machine, new stock coming from the regulating box has a consistency of about 3% and that of the sheet leaving the cylinder couch mold is 12 to 14%. It is evident that more water is fed to the vat system than is taken away with the sheet. The cylinder mold shower adds additional water; therefore provision is made at the end of the vat to overflow the water containing the least amount of stock. This water overflows spill dams at the ends of each cylinder and is usually collected in a divided white water pit so as to segregate water from the liner molds from that of the filler molds(2).

When recycled paper and paper products are used as the furnish, there is a wide variety of fibers, fillers, chemicals and colors which will eventually end up in the white water of a cylinder machine. This array of solids will be both suspended and dissolved solids and the types and amounts of these solids will depend on the types of papers making up the recycled furnish. The amounts of dissolved and suspended solids will gradually increase thus causing operational problems. "In the reuse of process water in a pulp and paper mill situation several types of problems can arise including those associated with

slime, foam, pitch, dirt, increased temperature, corrosion, scale formation, dissolved solids buildup (alum, starch, rosin, drainage aid, retention aid), total solids buildup (fines, clay, titanium dioxide), sizing difficulties, felt plugging, reduced wire life, reduced drainage rate, shower plugging and pH control."(3) Also, "the dispersion action of starch derivatives used as paper additives results in significant white water turbidity, retention, and increased consumption of fillers."(4)

Internal systems closure represents one alternative measure for pollution abatement in paper and board mills. Such measures have several advantages over external treatment measures provided care is taken to avoid impairing operating conditions and/or product quality. [ Experience gained in many mills with the closure or partial closure of the white water circuit showed that a substantial part of conventional discharged pollutants can be excluded from effluents and reused in paper products without negative effects. ] By closing the white water circuits on paper and board machines, environmental protection of waterways from mill discharges can be achieved(5). A closure, however, has both its advantages and disadvantages.

[ In closing a system, for whatever the reason may be, problems do accompany the closure. "It has been frequently observed at the mill that when color of process water intensifies, certain troubles are experienced such as lowering of brightness and the degrees of sizing of paper. ] One of the causes may be increase in humic substances in the water. Humic acids increase electronegativity of fiber surface and surface conductivity."(8) Also, "simple calculations show that complete closure of the water cycle will lead to salt accumulation in the water. Moreover, [ anaerobic breakdown of sulfates can lead to formation of corrosive hydrogen sulfide. These problems can be avoided by not completely closing the system. Instead of fresh water, biologically purified outside effluents may added to such a system."(9) ]

The concept of a closed white water system has been a subject of discussion since 1929. "Many of the problems of white water systems; slime, foam, scale circulation, paper quality, fiber recovery, etc., are still a challenge to the papermaker. The effects of performance and maintenance of papermaking equipment in a closed system on the corrosion resistance of existing or proposed materials of construction are a matter of concern. Changes in corrosion conditions are related to increased concentration of solids and dissolved salts, pH changes, higher temperatures and more elaborate water treating chemicals.

The major factors determining the corrosivity of white water are concentrations of dissolved solids and gases, pH, temperature and velocity. These factors vary widely with the type of recycled water clarification system used and the particular grades being produced."

Presently water reuse is extensively practiced in the manufacture of paperboard, fine papers and tissues. The concentration range of dissolved solids in recycled water is 6000 to 70,000 ppm for board and 1600 to 5000 ppm for fine and publication paper.

The relative amount of each component of the dissolved solids in the water varies with the type of furnish, the papermaking additives, and feedwater hardness. From a corrosion standpoint, the aggressive anions are chlorides, sulfur compounds and carbonates while influential cations are the ferric and manganous ions as well as the calcium, magnesium and barium scale formers.

The pH range reported for most recycled white water systems is 4.0 to 7.0. The pH is known and controlled in the paper forming stage, but little is known of its fluctuation in other locations in the systems.

The temperature in systems nearing full closure is reported to be in the 130 to 160°F (54 to 71°C) range. Corrosion kinetics are temperature dependent and higher temperatures will increase corrosion rates."(14)



Stark, Weather and Frost(15) qualitatively discussed the water recycling experiences in board manufacture where corrosion was given as the most perplexing problem. Methods of monitoring and controlling pH, temperature, suspended solids, and gases were considered essential in white water systems using conventional clarifiers.

Fluchner(16) reports corrosion problems in German mills on tissue machines. Galvanized pipelines transmitting clarified white water failed by corrosion after one year in recycling condition. The water was high in dissolved solids, and the pH at times was as low as 3.6. Even with pH maintained above 7.0, pitting corrosion due to chloride attack was reported for stainless-steel-clad headboxes.

Brecht(17) reported corrosion as the most difficult problem in German mills manufacturing paperboard and packaging grades. Their attempts to relate corrosion to specific electrical conductivity did not correlate well with concentrations of chlorides and sulfates. There was some indication of less corrosion under conditions of low conductivity and above neutral pH. In slightly acidic white water of high electrical conductivity, only stainless steel or plastics were suitable. The reported range of chlorides concentration was 600 to 3000 ppm while for sulfate from 1000 to 3200 ppm.

In a 1971 survey of 85 North American mills only 18% of all machines operating with some degree of white water closure indicated more severe corrosion. This low value was attributed to extensive use of stainless steel<sup>and</sup> plastic.(18)

### Corrosion

Corrosion is the deterioration of metal by either electrochemical or bacterial means. Corrosion rate is affected by the complex interaction of factors including

- a) dissolved solids, chlorides, sulfates, sulfides, etc.
- b) hardness
- c) alkalinity
- d) temperature
- e) pH
- f) contact of dissimilar metals

- g) dissolved oxygen levels
- h) level of carbon dioxide concentration

The intensity of dissimilar metals problem is related to their relative position in the galvanic series. Corrosion is a difficult problem to control due to the number of factors affecting the rate of corrosion. Corrosion appears as a problem in increased downtime and maintenance costs.

Techniques available to control corrosion include

- a) pH adjustment
- b) cathodic protection
- c) protective coatings
- d) addition of chemical inhibitors

Some of the chemical inhibitors available are calcium bicarbonate, chromates and dichromates, nitrates, polyphosphates, silicates, sodium benzoate and organic inhibitors. However there is no universal corrosion inhibitor for white water systems, an inhibitor which may be satisfactory in one system may be ineffective in another.

Under aerobic conditions electrolytic corrosion tends to dominate but under anaerobic conditions bacterial corrosion becomes very important. In the presence of sulfate, sulfate reducing bacteria contribute to increased corrosion rates. These bacteria are able to use cathodic hydrogen which would otherwise impede or stop the corrosion process. An effective control of bacteria induced corrosion is through the use of an effective biocide.(3)

### Scale

Scale is the deposit that results from the crystallization, precipitation or coagulation of non-resonous substances. As different from pitch and slime, scale is usually associated with one of four anions namely carbonate, silicate, sulfate or oxylate. These anions in combination with the cations calcium, magnesium, manganese, iron, aluminum and barium are the source of most scale difficulties. The most prevalent scale is that resulting from calcium and magnesium carbonate. The usual way to control scale is through control of hardness level of

the water, the cation level. Water containing soluble ferrous and manganous compounds will favor the growth of iron and manganese using bacteria which may contribute to scale problems. Excessive concentrations of alum can lead to precipitation of aluminum hydroxide which may form chemical slime. The traditional methods for scale control are use of sequestering or dispersing agents. The common ones are polyphosphates, ethylene diamine tetracetic acid (EDTA) and synthetic organic polyelectrolytes.(3)

#### Slime-Odor

When the water system is closed the concentration of dissolved solids builds in the system. The associated higher carbohydrate and nutrient levels constitute a more favorable environment for bacterial growth. A potential counteractant to biological growth resulting from this enriched environment is the increased concentration of any biocide which is being added to the system. Also the water system temperature may shift from the mesophylic range of 20°C to 35°C to the thermophylic range of 75°C, thus causing a shift in the bacterial population. Thermophylic bacteria tend to form spores and these are more difficult to kill.(3)

#### Product Mottle

In more extensive white water reuse the concentration of dissolved solids may build to a point where it can affect the appearance of the board. Board manufactured in high recycled whitewater systems has been observed to have a slightly mottled pattern on its surface. The pattern is dissolved if water is applied to the surface and allowed to dry. This observation suggests that the mottled appearance is associated with the dissolved solids which have accumulated in the water system. Since the material browns on drying, the implication is that it is possible to associate it with dissolved organics.(8)

### Metals

The presence of metals in domestic sewage, industrial effluents and receiving streams is a matter of serious concern because the possible toxic properties of these materials may adversely affect sewage treatment systems or the biological systems of the receiving streams. Metals may be determined by absorption spectrophotometry, polarography or colorimetric methods.(12)

### Foam

Foam is produced when air or some other gas is introduced beneath the surface of a liquid that expands to enclose the gas with a film of liquid. Absolutely pure liquids do not foam. However in the whitewater system, the effects of constantly circulation or aerating the the water combined with the buildup of solids causes extensive foam problems. Although defoamers do cut down on the problem, the particular defoamer needed depends on the type of operation involved.

### Felt Plugging

Felt plugging is usually associated with long fibers although the presence of large colloidal particles may also add to this problem.

### Pitch

Pitch problems are both paper and pulp related. Pitch is considered to be a resin based deposit of widely varying composition originating in the extractive fraction of wood. Pitch is a major problem because it

- 1) agglomerates and also occludes other matter to form visible "dirt" in the final product
- 2) plates out and collects on process equipment such as screens, fillers, refining equipment and the paper machine
- 3) reduces pulp brightness and brightness stability.

Hardwoods generally present more of a problem than softwoods since hardwood species generally contain more unsaponifiable matter than softwoods.(19)

### Wire Life Reduction

The effects of increased temperatures and buildup of corrosive anions tend to reduce the wire life of metal screens used on paper machines. The use of synthetic screens or metal plating can help control this problem.

#### Total Solids Buildup

Total solids buildup results partially from the buildup of fines, clay and titanium dioxide whereas dissolved solids buildup is related to alum, starch, and retention/drainage aid buildup.

#### Increased Temperatures

Increased temperatures results from constant circulation of the whitewater. Since little or no fresh water is added to fully closed systems, the thermal energy of the water is transferred to wires, felts and the machine housings causing operational problems.

#### Reduced Drainage Rates

Reduced drainage rates occur when solids begin to build. The solids clog the pores in the sheet thus inhibiting the free passage of water.

Because of the various problems that must be overcome when a mill switches from an open to closed water system, such a transition should be done gradually by reducing the amount of fresh process water. In this connection a laboratory study was carried out to determine the effects of white water reuse up to 30 times on its content of suspended and dissolved solids. The contents of both mineral and organic residues increased in direct proportion to the number of times of recycle. The average fiber length of the pulp gradually dropped from the initial 1.9mm to 1.1mm after 22 recycles. The addition of up to 20% white water pollutants had no significant effect on the mechanical strength of the paper.(10)

St. Regis Paper Company carried out extensive laboratory, pilot plant, and mill trials to determine the changes in composition and quality of water flowing to the headbox as the percentage of machine white water recirculated in the mill is increased and how these changes affect the quality of the paper and

the wet-end chemistry on the paper machine.(11) The pilot trials were carried out on the paper machine at Western Michigan University and the mill trials were carried out with the same furnish as with the mill trials on a commercial machine at the company's Sartell, Minnesota integrated pulp and paper mill producing uncoated grades, principally supercalendered catalog paper. The pilot machine trials showed that increasing the white water recirculation from 80% to 97% increased the electrolyte level from 800-1000 to 4000 ppm. It was found that as increased amounts of white water are recirculated in the mill, the concentration of electrolytes in the headbox increases dramatically. Many of the normal wet end processes, especially those depending upon ionic forces of attraction and repulsion (formation, retention, drainage, etc.) were altered in the high salt environment. The physical and optical properties of paper were not affected by salt levels up to 4000 ppm. There was, however, a loss of tear and slight loss in tensile strength at higher salt levels. It was concluded that increasing the white water recirculation at the Sartell mill should not have any adverse effects on the quality of the catalog paper.

In 1968, the Halltown Paperboard Company of Halltown, West Virginia decided to close the water cycle(6). The decision to close the water cycle was taken for two reasons: first, the stream into which the mill's effluent was discharged flowed into the Shenandoah River and hence into the Potomac which was being promoted as a national river: and secondly, because it was unlikely that the mill would be able to satisfy federal or local standards. The new system would utilize three pumps to deliver all waste water to a ninety foot diameter Dorr-Oliver clarifier. Retention time in the clarifier would be 12 hours minimum. Effluent from the clarifier would pass through a metering flume to two parallel sedimentation basins and then into a surge tank. Efforts to aid settling by floccing aids would take place in a mixing chamber before the sedimentation basins. Sludge, containing fiber, would be continuously returned from the clarifier to one of the two filler

pulpers as the chief source of water for that pulper. The skimmings from the clarifier would then be flushed to a pair of parallel connected lagoons through a pipeline. The settled water would then be used whereas in the past, the occasional presence of fiber had prevented the reuse of any water in these areas. Also any settled water would pass through a second metering flume to the inlet of a treatment plant for further clarification and reuse wherever water of maximum clarification was needed.

This system was designed as described above for a number of reasons;

1. It would satisfy state requirements concerning stream quality during start-up etc.
2. It was simple
3. It was not expected that the retention of color in the recycled water would add to present problems within the system, but at least color would be eliminated as a concern of the public.
4. A high biological oxygen demand(BOD) in the system was expected but it should stabilize and not cause unreasonable product limitations.
5. Slime problems were not expected to be worse. In fact, the proper combinations of biocides, which do not deteriorate very readily, could actually reduce the costs in this area.
6. The mill would be more independent in terms of water supply, especially in periods of ice, drought etc.
7. It is desirable to minimize wet sludge handling and maximize fiber retention.
8. Low operation costs once capital expenditures were made.

The expected benefits at Halltown included a guaranteed water supply and maximum reuse of water. Although the system was developed, further literature concerning the effectiveness of the system was not available.

In 1974, a Russian mill, the Lvov Board Mill was experiencing a shortage of process water, as its sources are artesian wells. The mill was faced with the necessity of introducing a closed water cycle. The first step in this direction was an improvement in the waste water treatment system to increase its degree of purification, which up to then was only 40-50%. The fibers recovered from two Waco filters were to be reused in stock preparation. The partially clarified

white water goes to two vertical sedimentation tanks where it is treated with aluminum sulfate and polyacrylic amides. The amount of aluminum sulfate added was 240 g/l, while the amount of PAA was 10 g/l. The purified white water contained 58 mg of suspended solids per liter, having a pH of 6.5, a chemical oxygen demand (COD) of 192 g/l and permanganate oxidizability of 150 mg/l. The white water was used for washing felts and cylinder mold wires for its two cylinder mold machines whose trimmed width was 2,100mm.(7) Further information on this systems effectiveness or problems encountered was not available.

The Brown Company Boardmill of Kalamazoo, Michigan produces approximately 400 tons of recycled boxboard per day. The mill operates on two cylinder board machines which produce quality board consisting of seven layers; one topliner, one backliner, one underliner and four filler layers. The largest of the two machines, number five, has a web width of 140 inches. This machine operates on a closed waterloop consisting of three sub-loops: a primary loop, a stock preparation loop, and a save-all loop.(fig. 1) The primary loop is the major consumer of water.(fig. 2) Here water which passes through the cylinder screen along with cylinder shower water falls to silo below the machine. A fanpump draws water from the silo and mixes it with stock from a headbox located directly above the machine. The diluted stock is then passes through a 75 h.p. Black Clawson pressure screen. Accepts from the screen will go directly to the formers to be used in the board. The primary loops for the topliner and backliner are similar to the filler primary loop just described except the stock passes through a battery of Bird triclean centrifugal cleaners after the pressure screen to insure a good clean stock in these layers.

Excess water from the silos along with machine screen rejects will be sent to the stock preparation and saveall loops.(fig. 3) Here the water enters a Polydisk saveall which separates the water into a clear water reserve and a cloudy water reserve. The difference between the two is that the cloudy water



is richer in fines and solids than the clear water. The cloudy water is sent through a Jonnson screen and back to the saveall. Clear water is sent to a white water supply tank. The saveall operates in a fashion similar to a Buchner funnel. Here water is filtered through a mat of fibers in order to filter out the solids to obtain cleaned process water. The polydisk operates by rotating a series of disks, circular in design, in a vat of stock. The disk is covered with a fine mesh screen on the outside and is under pressure on the inside in order to pull water through the screen. As the disks rotate, a mat of fibers is formed on the outside and water is sucked through this mat. On the upturn of the disks, the filter mat is washed off by the use of disk showers which use water from the clear water reserve. Stock that is washed off the disk is sent to the polydisk stock dump chest where it is sent to a headbox. From the headbox it is mixed with water from the white water supply tank and sent to the thickener. Just as the name implies, the thickener increases the consistency of the stock. This stock is sent to a filler stock dump chest, after the thickener. It is then passed through the refiners and sent back to the filler primary loop. White water from the thickeners is sent to another white water supply tank which is also fed by the filler reserve white water tank. This is then used to feed the filler and broke hydropulpers. In forming the sheet layers, water leaves with the plies and is evaporated in the dryer section. This water loss is made up for by introducing fresh water to the system. The fresh water used for the system is ground water from a well. This well water is both "hard" and high in ferrous iron content.

#### Water Classification

#### Acidity

Acidity is a method of expressing the capacity of water to donate hydrogen ions and gives an indication of the water's corrosiveness. The acidity of natural

waters is normally very low unless strongly acidic industrial waters have been introduced. Acidity can be caused by weak organic acids such as carbonic, acetic or tannin acids, or by strong mineral acids such as sulfuric or hydrochloric acids from industrial wastes. Hydrolyzable inorganic salts such as ferrous and aluminum sulfate also contribute to the acidity of a water.

Acidity is classified by the pH value of the titration end point. In non-polluted waters the acidity is due primarily to dissolved carbon dioxide which can be neutralized by titration to its neutralization end point at pH 8.3. This value corresponds to the color change of phenolphthalein indicator and is commonly called the Phenolphthalein Acidity. For systems which are more complex (such as industrial wastes or buffered solutions) a pH of 3.7 has been arbitrarily chosen which gives an estimate of the strong mineral acids present. Methyl orange end point is difficult to see, bromophenol blue indicator is a good replacement. Bromophenol blue indicator gives a sharp yellow to pure green end point. Acidity can also be determined by using a pH meter to follow the solution pH to the correct end point value as the standard base is added(12,13).

#### Alkalinity

Alkalinity refers to the capability of water to neutralize acids. The presence of carbonates, bicarbonates, and hydroxides are the most common causes of alkalinity in natural waters. The levels and types of alkalinity are directly dependent on the source of the water. Natural surface and well waters usually contain less alkalinity than sewage or wastewater samples. High levels of alkalinity indicate the presence of strongly alkaline industrial waste. Alkalinity is expressed as "P" (phenolphthalein) or as "T" (total) alkalinity. Both types are determined by titration with sulfuric acid standard solution, 0.020 N, to an end-point evidenced by the color change of a standard indicator solution or determined with a pH meter. Low alkalinity concentrations are determined by measuring the amount of standard acid necessary to affect a pH change of 0.30 units, starting between

pH 4.3 and 4.7. The "P" alkalinity is determined by titration to a pH of 8.3 (the phenolphthalein end point) and registers the total hydroxide and one half the carbonate present. The total alkalinity includes all carbonate, bicarbonate and hydroxide alkalinity. The "T" alkalinity is determined by titration to a pH of 5.1 (alkalinity approx. 30 mg/l), pH 4.8 (alkalinity approx. 50 mg/l), pH 4.5 (silicates or phosphates present), pH 3.7 (industrial waste or complex system). (12,13)

#### Aluminum

Aluminum is the earth's most abundant metal and is present in natural waters from contact with rocks, soil, and clay. Alum coagulation in water clarification systems may also contribute to aluminum content of treated water, though only 20 to 50 ug/l aluminum remain in the finished product from a well controlled operation. The aluminon method is one of the oldest and most thoroughly documented methods available for determining aluminum in water. Aluminon indicator combines with aluminum in the sample to form a red-orange color, the intensity of which is proportional to the aluminum concentration. Ascorbate reagent is added to remove iron interference(12,13).

#### Barium

Barium is relatively abundant in nature, 16th in order of rank, though only trace amounts are usually found in water. Barium concentrations average about 0.05 mg/l in potable waters but may range as high as 0.9 mg/l in some natural waters. More than 1.0 mg/l barium implies the water is not suitable for drinking and being polluted by industrial wastes. Barium present as the sulfate which is held in suspension by a protective colloid. The amount of turbidity caused by the fine white dispersion of particles is directly proportional to the amount of barium present. Barium stimulates the heart muscle. A barium dose of 550 to 600 mg is considered fatal to humans. Afflictions arising from its consumption, inhalation, and absorption involve the heart, blood vessels, and nerves(12,13).

### Cadmium

Cadmium is highly toxic when taken by mouth or inhaled and has been implicated in some cases of food poisoning. A concentration of 200 ug/l has been found lethal to certain fish. Recent work has shown, however, that traces of cadmium may be essential to proper diet. Cadmium may enter a water supply as the result of plating bath or other industrial discharges, or through the deterioration of galvanized plumbing. The cadmium concentration of drinking water in the United States is estimated to vary between 0.4 to 60 ug/l with an average of 8 ug/l. Public Health Service drinking water standards limit the concentration of cadmium in acceptable potable water to 10 ug/l. Minute quantities of cadmium are suspected of being responsible for adverse renal arterial changes in human kidneys(12,13)

### Calcium

Calcium is the fifth most common element and is found in most natural waters at levels ranging from zero to several hundred milligrams per liter.

Calcium contributes to the hardness properties of water and test results are usually reported as calcium hardness, mg/l equivalent calcium carbonate. The EDTA titration for calcium is similar to the method for measuring total hardness, calcium plus magnesium, differing in the choice of indicators and a higher reaction pH to remove magnesium interference. The presence of calcium in water supplies results from passage through or over deposits of limestone, dolomite gypsum, and gypsiferous shale. The calcium content may range from zero to several hundred mg/l, depending on the source and treatment of the water. Small concentrations of calcium carbonate combat corrosion of metallic pipes by laying down a protective coating. Appreciable calcium salts, on the other hand, break down on heating to form harmful scale in boilers and pipes. Chemical softening is employed to reduce the calcium and the associated hardness to tolerable levels(12,13).

#### Carbon Dioxide

Carbon dioxide is present in all surface waters in amounts generally less than 10 mg/l. Though higher concentrations in ground waters are not uncommon. The dissolved carbon dioxide has no harmful physiological effects on humans and is used to recarbonate water during the final stages of water-softening processes and to carbonate soft drinks. High concentrations of dissolved carbon dioxide are corrosive and have been known to kill fish.

#### Boron

Trace amounts of boron are found in many drinking waters and in some natural waters. The amount present is usually less than 0.1 mg/l, higher amounts not uncommon in some areas. Small amounts of boron are essential for plant growth, but waters containing one to two milligrams per liter of boron or more have an adverse effect on vegetation. Large doses of boron in humans can affect the central nervous system. Drinking water concentrations

less than 1.0 mg/l are generally considered harmless. High boron concentrations are usually caused by residue from cleansing agents and by industrial wastes(12,13).

### Chlorides

Chlorides are present in all potable water supplies and in sewage, usually as a metallic salt. When sodium is present in drinking water, chloride concentrations in excess of 250 mg/l give a salty taste. If the chloride is present as a calcium or magnesium salt, the taste detection level may be as high as 1000 mg/l chloride. Chloride is essential in the diet and passes through the digestive system unchanged to become one of the major components of raw sewage. The wide use of zeolite in water softeners also contributes a large amount of chloride to sewage and wastewaters. High chloride concentrations in water are not known to have toxic effects on man, though large amounts may act corrosively on metal pipes and be harmful to plant life. The maximum allowable chloride concentration of 250 mg/l in drinking water has been established for reasons of taste rather than as a safeguard against physical hazard. The Mohr Argentometric Method is the most widely known test for chloride and uses a chromate indicator. The sample is titrated with a silver nitrate standard solution to selectively precipitate first the chloride present, then the chromate. The end point of the titration is indicated by the appearance of a red silver chromate precipitate(12,13).

### Chlorine

Chlorine is added to public drinking supplies, sewage treatment plant effluents, and swimming pools to destroy harmful bacteria. A constant level of 1.0 mg/l free chlorine is generally adequate to control bacteria without causing a noxious odor or taste. Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms exist in the same water and can be determined together as the total

available chlorine. Free chlorine is present as hypochlorous acid and or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride, and other chloro derivatives(12,13).

#### Sodium Chromate

Sodium chromate is often added to water in industrial cooling towers to inhibit corrosion of metal pipes and fittings. Alkaline solutions of sodium chromate give a strong yellow color. In acid media, however, the solution is orange and the sample must be treated to raise the pH to give the yellow color necessary for the determination since the intensity of the yellow color is directly proportional to the amount of sodium chromate present(13).

#### Chromium

Chromium may be present in water as the hexavalent chromate or the trivalent chromium form, though trivalent chromium rarely occurs in potable water. Hexavalent chromium enters a water supply through industrial wastes from metal plating baths and from industrial cooling towers where chromate is used to inhibit metal corrosion. Chromium is an objectionable contaminant due to its suspected carcinogenic effects. Chromium present in potable waters above a 3.0 ug/l level indicates the presence of industrial wastes. Concentrations greater than 50 ug/l are sufficient grounds for rejection of the water supply(12,13).

#### Copper

Copper may occur in natural waters, wastewaters and industrial effluents as soluble copper salts or as precipitated copper compounds on suspended solids. Trace amounts of copper are necessary for normal body metabolism and its absence is known to cause nutritional anemia in children. Large oral doses of copper can cause emesis, and may eventually result in liver damage. Though copper salts are often added to ponds to control aquatic plant life,

large amounts have been shown to be toxic to fish. Copper is not generally considered a health hazard, but more than 1.0 mg/l can impart a bitter taste to the water. The average concentration of copper in potable waters is 0.03 mg/l, occasionally ranging up to 0.06 mg/l in natural waters from some areas. A maximum of 1.0 mg/l copper is recommended for all public drinking supplies, and concentrations above 3.0 mg/l are regarded as sufficient grounds for rejection of the supply. A good method for measuring copper is the Bicinchoninate Method due to its ease of analysis, high sensitivity and freedom of interference from those materials normally found in water and wastewater. The indicator gives an intense purple color when copper is present so a spectrophotometric test can be run(12,13).

#### Cyanide

Cyanide is extremely toxic and occurs primarily in industrial effluents. Metal cleaning and electroplating baths, gas scrubbers, gas works and coke ovens, and other various chemical treatments are the main sources of the cyanide found in industrial wastes. Natural waters do not contain cyanide and its presence normally indicates contamination from an industrial source. Proper neutral or alkaline chlorination of wastewaters containing cyanide will reduce the level well below maximum limits(12,13).

#### Hardness

Originally the hardness of a water was understood to be a measure of the capacity of the water for precipitating soap. Soap is precipitated chiefly by the calcium and magnesium ions commonly present in water, but may also be precipitated by ions of other polyvalent metals such as aluminum, iron, manganese, strontium, and zinc, and also by hydrogen ions. Hardness is defined as a characteristic of water which represents the total concentration



of calcium and magnesium expressed as their calcium carbonate equivalent. Hardness concentrations were originally expressed as grains per gallon but are now commonly reported as milligrams per liter,  $1.0 \text{ g/gal} = 17.16 \text{ mg/l}$ . The hardness test is the most frequently performed analysis in the water industry. Large amounts of hardness are undesirable for aesthetic and economic reasons in many industries and must be removed before the water is suitable for use; e.g. the beverage, food, laundry, metal finishing, textiles, and pulp and paper industries. Levels about 500 mg/l hardness are undesirable for domestic use(12,13).

### Iron

Natural waters contain variable but minor amounts of iron despite its universal distribution and abundance. Iron in ground waters is normally present in the ferrous,  $\text{Fe}^{2+}$ , or soluble state which is easily oxidized to ferric,  $\text{Fe}^{3+}$ , or insoluble iron on exposure to air. Iron can enter a water system by leaching natural deposits, from iron-bearing industrial wastes, effluents from pickling operations or acidic mine drainage. Iron in domestic water supply systems stains laundry and porcelain. Taste thresholds of iron in water are 0.1 mg/l ferrous ion and 0.2 mg/l ferric ion. Water in industrial processes must usually contain less than 0.02 mg/l total iron. A good method for iron analysis is the 1,10-Phenanthroline Method. The 1,10-Phenanthroline reagent gives an orange color with ferrous iron and is free from common interferences so a good spectrophotometrical analysis can be made.

### Lead

Lead is seldom found in ground waters in more than trace quantities and averages about 10 ug/l. Natural waters also contain very low levels of

lead due to its tendency to be precipitated by a large number of substances. The level of lead in public water supplies is usually very low, less than 10 ug/l, unless storage tanks have been painted with a lead-base paint or lead piping or fixtures are used in the delivery system. Lead is a serious poison which tends to accumulate in the bone structure when ingested in levels exceeding the natural elimination rate of about 300 ug Pb/day. Lead in water normally indicates the intrusion of industrial mine, or smelter wastes, or the decomposition of lead plumbing fixtures and pipes(12,13).

### Manganese

Manganese is present in ground waters as the divalent ion,  $Mn^{2+}$ , due to the lack of subsurface oxygen. Surface waters may contain combinations of manganese in various oxidation states as soluble complexes or as suspended particles. The occurrence of manganese in public water supplies presents more of an economic problem than a potential health hazard. Manganese causes dark stains in laundry and on plumbing fixtures, tends to deposit in water lines, and imparts an objectionable taste to beverages such as coffee and tea. Manganese in natural waters rarely exceeds 1.0 mg/l, but levels of 0.1 mg/l are sufficient to cause taste and staining problems. The Periodate Oxidation Method gives a simple, rapid test for high concentrations of manganese. The determination is made by oxidizing the manganese to the deep purple permanganate ion,  $MnO_4$ , and measuring the amount of color development(12,13).

### Mercury

Mercury is not commonly found in natural waters and its presence indicates pollution by industrial wastes from metal processing, pharmaceutical, or chemical manufacturing plants. Mercury can also enter the water system through agricultural pesticide, herbicide, and fungicide residues, or through residual medicinal compounds. Organic phenyl and alkyl mercury residues,

typically as phenyl mercuric acetate or methyl mercury, are the most commonly found mercury complexes in water, and have nearly identical toxicity properties as elemental mercury. Prolonged mercury ingestion can cause loss of muscle control, kidney damage, personality changes, and permanent brain damage. Both inorganic and organically bound forms of mercury can be absorbed through the skin, causing burns and damage to internal membranes. Acute dosages in humans usually cause death within ten days(13).

#### Nickel

Nickel is seldom found in natural waters but is often present in industrial wastewaters as a corrosion product of stainless steel and nickel alloys, and from metal plating baths.

#### Nitrate

Nitrate represents the most completely oxidized state of nitrogen commonly found in water. Nitrate-forming bacteria convert nitrites into nitrates under aerobic conditions and lightning converts large amounts of atmospheric nitrogen,  $N_2$ , directly to nitrates. High levels of nitrate in water indicates biological wastes in the final stages of stabilization or run-off from heavily fertilized fields. Nitrate-rich effluents discharged into receiving waters can degrade water quality by encouraging excessive growth of algae. Drinking waters containing excessive amounts of nitrates can cause infant methemoglobinemia, blue babies(12,13).

#### Phosphorus

Phosphorus occurs in natural waters and wastewaters almost solely as phosphates. Phosphates are widely used in municipal and private water treatment systems and are commonly grouped into three types: orthophosphate, condensed (pyro, meta, or other poly) phosphate, and organically bound phosphate. The orthophosphate is the only form determined directly. The other types require

pretreatment for conversion to the orthophosphate form for analysis. Phosphates enter the water supply from agricultural fertilizer run-off, water treatment, and biological wastes and residues. Industrial effluents related to corrosion and scale control chemical processing, and the use of detergents and surfactants contribute significantly. Condensed phosphates are the forms commonly used in treating water systems and boilers, and in detergent formulations. After being dissolved in water, these are converted to orthophosphates at different rates depending upon their types, the temperature of the water and the pH. A certain amount of phosphate is essential to organisms in natural waters and is often the limiting nutrient for growth. Too much phosphate can produce eutrophication or over-fertilization of receiving waters especially if large amounts of nitrates are present. The result is the rapid growth of aquatic vegetation in nuisance quantities, and an eventual lowering of the dissolved oxygen content of the lake or stream due to the death and decay of aquatic vegetation(12,13).

### Silica

Silica normally exists as an oxide,  $\text{SiO}_2$ , as in sand or as a silicate,  $\text{SiO}_4^{4-}$  or  $\text{SiO}_3^{2-}$ . Silicon is the world's second most abundant element and is present in most waters. It has no known toxic effects and is used to form protective inner coatings on pipes to inhibit corrosion. A silica cycle occurs in many bodies of water containing organisms, such as diatoms, that utilize silica in their skeletal structures. The silica removed from the water may be slowly returned by resorption to the dead organisms. Among the methods for silica removal are ion exchange, distillation, the hot and cold lime soda-magnesium processes, the ferric hydroxide process, and the fluosilicate process. The Silicomolybdate Method involves the reaction of ammonium molybdate with silica and phosphate to form a yellow color. Citric

acid is added to destroy the phosphomolybdic acid complex (the yellow color formed due to the phosphate) but not the silicomolybdic acid complex. For large amounts of silica the remaining yellow color is intense enough to be read directly. For low concentrations, an amino acid reducing agent is used to convert the faint to yellow color to a dark blue for spectrophotometric analysis (12,13).

### Sodium

Sodium is the sixth most common element and is present in nearly all natural waters. Brines, hard water, and water softened with sodium-form resin exchange units have sodium concentrations. Sodium is usually analyzed by flame photometric or gravimetric techniques, both of which are time consuming and involve sophisticated equipment (12,13).

### Sulfate

Sulfate appears in natural waters in a wide range of concentrations. Mine waters and industrial effluents frequently contain large amounts of sulfate from pyrite oxidation and the use of sulfuric acid. Also due to the use of sulfate in the Kraft process of papermaking, it may enter a water system. Public Health Service drinking water standards call for not more than 250 mg/l of sulfate because of its cathartic action. The taste threshold of magnesium sulfate is 400 to 600 mg/l and for calcium sulfate is 250 to 800 mg/l. Sulfate may be either beneficial or detrimental in water used for manufacturing and domestic supply. The presence of sulfate is advantageous in producing desired flavors in the brewing industry. In domestic water systems, sulfates do not appear to cause any increased corrosion on brass fittings but concentrations above 250 mg/l do increase the amount of lead dissolved from lead pipes (12,13).

### Sulfide

Sulfide is a poisonous by-product of the anaerobic decomposition of organic matter and is commonly found in sewage and industrial wastewaters. Sulfide can be present as the free sulfide ion,  $S^{2-}$ , or as dissolved hydrogen sulfide,  $H_2S$  and  $HS^-$ . The toxicity of hydrogen sulfide is equivalent to that of hydrogen cyanide but its offensive odor is detectable long before toxic levels are reached. A test for sulfide is based on the ability of hydrogen sulfide and acid-soluble metallic sulfides to convert N,N-dimethyl-p-phenylene-diamine oxalate directly to methylene blue. The intensity of the methylene blue color developed is directly proportional to the amount of sulfide present in the original sample. Strong reducing agents such as sulfite, thiosulfite, and hydrosulfite interfere by reducing the blue color or preventing its development (12,13).

### Sulfite

Sulfite is most commonly found in boiler and boiler feedwater where it is used to inhibit corrosion by reducing dissolved oxygen. It may also be found in industrial wastes such as paper mill effluents. Sulfite is not commonly present in natural waters since it readily oxidizes to sulfate (12,13).

### Tannin and Lignin

Tannin occurs in natural waters in varying concentrations as a product of vegetative decomposition. Industrial wastes from tanning industries nearly always contain some tannin, as do boiler water residuals where tannin has been added to help prevent scale production. Lignin is a natural plant product discharged as a paper pulp manufacturing waste. Tannin and lignin both contain hydroxyl groups and exhibit similar properties in water. Results are normally reported as total tannin and lignin present expressed as mg/l tannic acid.

## Zinc

Zinc concentrations in most water supplies average about 1.0 mg/l but may range as high as 50 mg/l in some areas. Though zinc is commonly found in many natural waters, the deterioration of galvanized iron and leaching of brass can add substantial amounts. Industrial effluents may contribute large amounts of zinc, and high concentrations suggest the presence of lead and cadmium, common impurities from the galvanizing process. Zinc is essential to human metabolism and has been found necessary for proper body growth. High concentrations of zinc in water act as stomach irritants but the effects are temporary. Concentrations above 5 mg/l show no harmful physiological effects but can cause a bitter taste and/or an opalescence in alkaline drinking water. For this reason, the maximum recommended zinc concentration in public drinking water supplies has been set at 5 mg/l. Zinc can be determined by complexing it with cyanide, then freezing it with cyclohexanone to be complexed with zincon, 2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene (12,13).

## Turbidity

Turbidity occurs in most surface waters as the result of suspended clay, silt, finely divided organic and inorganic matter, plankton and other micro-organisms. Turbidity measurement of water is important to those industries where the product is destined for human consumption, such as the food and beverage industries, and municipal water treatment plants (12,13).

## pH

pH is defined as the logarithm of the reciprocal of the hydrogen ion activity expressed in moles per liter. More simply, the pH value of a water sample expresses its tendency to accept or donate hydrogen ions on a scale of 0, very acidic, to 14, very basic. Pure water at 25°C is neutral and has a defined pH value of 7.0. The pH value represents the instantaneous hydrogen

ion activity rather than the buffering capacity or the total reserve as in acidity and alkalinity tests. Most natural waters range from pH 4 to pH 9 and are often slightly basic due to the presence of carbonates and bicarbonates. A major deviation from the normal pH for a given water indicates the intrusion of strongly acidic or strongly basic industrial wastes. pH adjustment is a common practice in water treatment processes and is used to control corrosion within the distribution system.

### Specific Conductance

Specific conductance as it applies to water analysis is a measurement of water's capacity for conveying electrical current and is directly related to the concentrations of ionized substances in the water. Once correlations have been made between conductance values and the characteristic norms of the system being monitored, it becomes a useful measurement in managing water processing. Depending on the particular application, a change in conductivity can signal such things as the need for adding chemicals or regenerating the system. Specific conductance measurements are commonly used to determine the purity of demineralized water and total dissolved solids in boiler and cooling tower water (12,13).

### Oil and Grease

Oil may be present in natural waters from the decomposition of plankton and/or higher forms of aquatic life. Most oils and greases are insoluble in water but can be emulsified or saponified by alkalis, detergents, or other chemicals. Some lighter petroleum fractions evidence a light water solubility and may form a slick on the water surface. Oil or grease in water generally indicates pollution from industrial wastes (12,13).



### Experimental Procedure

White water samples were collected from the filler primary loop. Since there are five primary loops for the filler cylinders, cylinder loop number three was chosen for sampling. Samples collected for analysis were collected in such a way as to provide the most representative a sample as possible. In general, they were taken near the center of the vessel or duct and below the surface. Only clean bottles, beakers, or self-sealing plastic bags were used.

Samples were taken as closely as possible to the source of the supply to minimize the effects of a distribution system. The white water was allowed to run for sufficient time to flush the system, and the sample container was filled slowly with a gentle stream to avoid turbulence and bubbles. Fresh water samples from wells should be collected after the pump has run long enough to be delivering water that is representative of the ground water feeding the well. Fresh water samples were collected at the calendar stacks where it is used as cooling water.

Generally as little time as possible elapsed between collecting the sample and making the analysis. Depending on the nature of the test, special precautions in handling the sample may also be necessary to prevent natural interferences such as organic growth or loss or gain of dissolved gases. If samples could not be tested immediately, storing in a refrigerator is necessary. However, biological growth may appear in samples stored over long periods of time.

All of the colorimetric and titrimetric tests used for whitewater analysis should be performed with sample temperatures between 20°C (68°F) and 25°C (77°F). Water samples were analyzed using a DR/2 spectrophotometer by Hach Chemical Co. and also by titration methods.

For an experimental run, fresh well water samples were analyzed and recorded as day zero. After the cylinder machine had been running for approximately one week, samples were collected and tested for certain cations and anions which may cause operational problems with water reuse. The white water was monitored for

18 days to detect any changes in the concentrations with machine running time.

The methods used for the water analysis are listed in the appendix.

### Results

Data obtained for the test period of January 24 through February 10 is shown in table 1. This data is also plotted (Fig. 4-14) on graphs drawn by the computer terminal at Western Michigan University. Since fresh water is used for makeup water when the system is flushed for cleanup, the values of fresh water concentrations were plotted at day zero. Since tests were started 9 days after the machine had a startup, the curve drawn over the first eight days is insignificant and only represents the computer's attempt to connect the points with a spline curve.

Averages for the first ten days of running were tabulated and compared with values after eighteen days running time. This data is shown in table 2 along with the trends in these average values. Values for the last five days of testing were averaged and reported also.

Since tests were run for consecutive days, the relative changes in concentrations from day to day could be tabulated and these values are reported in table 3. Notice values for the changes in caliper and basis weight for the days tested. These values show the per cent increase or decrease from the results for the previous day.

### Results Discussion

The concentration silica in the whitewater as running time is increased is shown graphically in figure 4. As seen from this graph, the concentration in the fresh water is approximately 11 mg/l and does change significantly after 9 days running time. It does however show an increase after eighteen days running time. In comparing this graph to figure 14, it appears that the concentration may be related to changes in board caliper at the time of sampling. When the same caliper of board was produced, for example of the 8th and 9th of February, the concentration did show a definite increase. In table 2, the average values increased with days running

time indicating a buildup with increased recirculation.

The buildup of tannin-lignin with machine running time is shown graphically in figure 5. While the fresh makeup water contains zero mg/l of these substances there is a gradual increase after 9 days running time. The levels are reaching significant amounts after 18 days running time. This could lead to operational problems is uncontrolled. From table 2, it is obvious that the average values are increasing with days running time. In comparing this graph with figure 14, it appears that figure 5 somewhat correlates with the graph of board caliper. This again indicates that machine variables may affect the concentrations. The changes in caliper may account for the deviations or the dips and peaks, although other factors such as furnish and machine running speed may contribute. When the same caliper was produced for consecutive days however, the tannin-lignin concentrations did show an increase.

Calcium, one of the cations tested, is shown in figure 6. The fresh water appears to be quite "hard" with a concentration in excess of 160 mg/l. The curve does show that the calcium concentration is decreasing with machine running time. This trend indicates that calcium may be precipitating out as the hydroxide or forming scale on the inner walls of pipes. In comparing figure 6 to figure 14, it appears that board caliper has little influence on calcium concentration. The average values of the calcium are decreasing in table 2.

The concentration chloride is graphically pictured in figure 7. The fresh water contains over 100 mg/l and this value does not change drastically over a 9 day running period. The graph does show that the concentration is not steadily increasing or decreasing but fluctuating. In comparing the graph with figure 14, the changes in caliper may influence the chloride concentration but the data is not consistent for a direct determination of the proportionality between the two.

The concentration of iron versus days of running time is plotted in figure 8. The graph shows the iron content to be decreasing after 9 days running time and

remaining under 1 mg/l for the rest of the test period. The iron may be tied up in the water by anions already present. When a small amount of sulfuric acid was added to the sample and then the test repeated for iron, the concentration increased tremendously indicating insoluble iron complexes in the water. In comparing figure 8 to figure 14, it appears caliper had no direct influence on the iron content.

A graph of aluminum concentration versus days of running time is shown in figure 9. The aluminum concentrations are quite low in the whitewater but are fluctuating. In comparing this plot to figure 14, the board caliper may be influencing the aluminum concentrations. Since the concentration of aluminum in the fresh water is quite low, the aluminum concentrations may be due to alum in the furnish used.

Figure 10 gives a graph of phosphates versus days of running time. Here the phosphate level in the fresh water is quite low although the white water shows a definite increase with running time. This graph shows no dips and peaks as in the other graphs. Since there seems to be no dependence on caliper, the phosphates are probably entering the system from water squeezed from the felts at the couch roll nip. Detergents containing phosphates may be present in the felts from the showers used to clean them. The high level of phosphates will tend to favor bacterial growth since this is an essential nutrient. Phosphates at these high levels may be causing operational problems due to slime growth and corrosion.

The concentration nitrates in the water is given in figure 11. Here the concentrations are varying and show no steady increase with machine running time. It appears to be influenced by a machine variable or the furnish. The nitrates most likely enter the system from protein dissolved from grades previously coated and used in the furnish. In comparing this graph with figure 14, the caliper seems to affect nitrate concentration, especially at high caliper.

The calcium carbonate hardness versus days of running time is shown in figure 12. The fresh well water is quite hard but the hardness is decreasing with running

time. This gives an indication that the cationic level is decreasing or the water has a high cationic demand.

The alkalinity of the white water is given in figure 13. The alkalinity of the water is its capacity to neutralize acids. The alkalinity is not changing drastically as seen in the curve. In comparing the alkalinity curve to the caliper curve, there is evidence that an increase in caliper is related to an increase in alkalinity. However, other factors may be involved in this phenomenon.

The increase in sulfate concentration is seen in table 1. The level of sulfate after 9 days running time is quite high thus adding to the anionic character of the whitewater. The sulfide levels were quite low, yet they were larger than the fresh water concentrations. Barium was not found to be present in the white water or the freshwater.

The pH measurements on the white water showed the water to be neutral to slightly alkaline. Conductivity measurements showed the whitewater to be more conductive than the fresh water due to the higher levels of ions.

Zeta Potential measurements taken the white water samples taken in March showed a consistent value of -40 mv, indicating the colloidal particles in the water to be relatively dispersed.

### Conclusions

As evident from table 2, the anionic character of the white water is increasing from the data on silica, tannin-lignin, chloride, phosphates, and nitrates. It appears that the cationic character of the white water is decreasing from data on calcium, iron, and alkalinity. The concentrations of phosphates and tannin-lignin showed steady rises with increased running time. Fluctuations were readily observed in the concentrations of chloride, silica, calcium, aluminum, nitrates, hardness and alkalinity. The cationic demand of the water is increasing as the anions increase in concentration. This activates corrosion of cationic metallic pipes in order to meet the cationic demand.

There is evidence that changes in basis weight affect ion concentration in the water. In raising the basis weight, several machine variables are changed to compensate for a bulkier sheet. First, the machine is slowed down for handling the heavier load. Second, the consistency entering the formers is increased so a larger deposit of fibers and fillers on the wire can be achieved. Third, the higher consistency of stock running through the primary loop will tend to overload the pressure screen thus causing more screen rejects with a lowering of accepts to the formers. With more screen rejects a greater load is transferred to the saveall loop. This in turn may increase output to the clarifier or reduce saveall efficiency. So any changes in the primary loop affect the saveall loop which may combine to change operations in the stock preparation loop of the system. By this I mean that by raising the basis weight in the primary loop, the saveall loop may overload and lower its efficiency and thus lower the quality of the water returned from the saveall loop. This lower quality water then leads to operational problems if used in felt showers, cylinder showers, and hydropulpers or as process water for stock dilution and reserve water.

#### Recommendations

Due to the importance of monitoring white water systems once a closed system is put into affect, there is a need to know the effects of high ion concentrations on papermachine operations and product quality. Water reuse is not becoming an option to the papermaker but a necessity especially with stricter regulations coming into effect. By monitoring the chemical concentrations of reused water, it may be possible to predict when high levels will become an operational problem and be effectively dealt with. Further work is needed to determine the dependence of chemical concentration on machine variables which in turn affect the other loops in the system involved. By running a mass balance on all the water loops, areas where high chemical deposition is occurring can be traced to their origin. By knowing the areas where the ions and chemicals cause problems, they may then be effectively

dealt with. I hope this work presented here has raised some questions as to the affect of machine variables on chemical concentration in reused whitewater. The systems become quite complex when closure is put into affect and further research is needed to pinpoint areas in a closed loop where small changes in ion concentrations may lead to operational problems causing increased downtime and maintenance costs.

## APPENDIX

### Alkalinity

1. Take a water sample by filling a clean 50 ml graduate cylinder to the 50 ml mark. Pour the sample into a clean 250 ml Erlenmeyer flask.
2. Add 6 drops of Phenolphthalein Indicator solution and swirl to mix.
3. If the color turns pink, titrate with 0.02 N sulfuric acid to a colorless endpoint. If the color does not turn pink, proceed with step 5.
4. Multiply the number of ml of sulfuric acid used in step 3 by 20 to obtain the mg/l phenolphthalein alkalinity (as  $\text{CaCO}_3$ ).
5. Add 6 drops of Brom Cresol Green-Methyl Red Indicator Solution to the same sample and swirl to mix.
6. Continue the titration with 0.02N sulfuric acid to a light greenish blue-gray (pH 5.1), a light bluish pink-gray (pH 4.8) or a light pink (pH 4.5). Multiply the number of ml of acid used in both tests by 20 to obtain the mg/l total alkalinity.

### Aluminum      Aluminon Method using "AluVer III" Aluminum Reagent (Hach Chemical)

1. Take a water sample by filling a clean 50-ml mixing graduated cylinder to the mark.
2. Add the contents of one Ascorbate Reagent Powder Pillow, stopper the cylinder and invert several times to dissolve the powder.
3. Add the contents of one "AluVer III" powder pillow, stopper the cylinder, and invert several times to dissolve the powder. A red orange color will develop if aluminum is present.
4. Divide the solution into two 25-ml portions by filling two clean sample cells to the 25-ml mark. Add to one of the cells the contents of one "Bleaching III" powder pillow, stopper both sample cells and shake vigorously for 30 seconds. Allow at least 15 minutes from the addition of the AluVer III pillow but not more than 20 minutes before completing steps 5 and 6.
5. Place the sample cell containing the bleached portion into the cell holder. Insert the Aluminum Meter Scale into the meter and adjust the wavelength to 522 nm. Adjust the light control to read zero mg/l.



6. Place the unbleached portion of the sample in the cell holder and read the mg/l aluminum (Al).

#### Barium

1. Take a water sample by filling a clean sample cell to the 25 ml mark.
2. Add the contents of one BariVer IV Reagent Powder Pillow and swirl to mix. A white turbidity will develop if barium is present. Allow at least three minutes for the turbidity to fully develop but do not wait more than ten minutes before completing steps 3 and 4.
3. Fill another sample cell to the 25 ml mark with original water sample and place it into the cell holder. Insert the Barium Meter Scale into the meter and adjust the wavelength to 450 nm. Adjust the light control to zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l barium.

#### Calcium

1. Take a water sample by filling a clean 50 ml graduated cylinder to the 50 ml mark. Pour the sample into a clean 250 ml Erlenmeyer flask.
2. Add 1 ml of Potassium Hydroxide Standard Solution, 8 N, using a 1 ml calibrated dropper and swirl to mix.
3. Add the contents of one "CalVer II Calcium Indicator Powder Pillow" and swirl to mix.
4. Titrate the sample with "TitraVer Hardness Titrant" until the color changes from red to pure blue.
5. Multiply the number of ml of titrant used by eight to obtain the mg/l calcium (Ca) or by 20 to obtain the mg/l calcium hardness (as  $\text{CaCO}_3$ ).

#### Chloride

1. Take a water sample by filling a clean 100 ml graduated cylinder to the 100 ml mark. Pour the sample into a clean 250 ml Erlenmeyer flask.
2. Add the contents of one "Chloride II Indicator Powder Pillow" and swirl to mix.
3. Titrate the sample with Silver Nitrate Standard Solution until the color changes from yellow to red-brown.
4. Multiply the number of ml of Silver Nitrate Standard Solution by five to obtain the mg/l chloride.

### Copper

1. Take a water sample by filling a clean sample cell to the 25 ml mark.
2. Add the contents of one CuVer I Copper Reagent Powder Pillow and swirl to dissolve. A purple color develops if copper is present. Allow at least two minutes for full color development but not more than 30 minutes before completing steps 3 and 4.
3. Fill another sample to the 25 ml mark with original water sample and place it in the cell holder. Insert the Copper (Bicinchoninate Method) into the meter and adjust the wavelength to 560 nm. Adjust the light control to zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l copper.

### Hardness, Total

1. Take a water sample by filling a clean 50 ml graduated cylinder to the 50 ml mark.
2. Add the contents of one "UniVer I or II Reagent Powder Pillow" to the flask and swirl to mix.
3. Titrate the sample with TitraVer Hardness Titrant until the color changes from red to pure blue.
4. Multiply the number of ml of titrant by 20 to obtain the mg/l of total hardness as  $\text{CaCO}_3$ .

### Iron

#### 1,10-Phenanthroline Method

1. Take a water sample by filling a clean sample cell to the 25 ml mark.
2. Add the contents of one FerroVer Iron Reagent Powder Pillow to the cell and swirl to mix. An orange color will develop if iron is present. Allow at least three minutes for the color to develop but not more than 30 minutes.
3. Fill another sample cell to the 25 ml mark with the original water sample and place it into the cell holder. Insert the Iron Meter Scale and adjust the wavelength to 510 nm. Adjust the light control to zero mg/l.
4. Place the prepared sample into the sample in the cell holder and read the mg/l total iron.

### Nitrate

#### Cadmium Reduction Method

1. Take a water sample by filling a clean sample cell to the 25 ml mark.
2. Add the contents of one "NitraVer V Reagent Powder Pillow" to the sample cell, stopper, and shake vigorously for exactly one minute. An amber

color will develop if nitrate is present. Allow at least five minutes for full development but not more than 15 minutes before completing steps 3 and 4.

3. Fill another cell to the 25 ml mark with original water sample and place it in the cell holder. Insert the Nitrate Meter Scale and adjust the wavelength to 500 nm. Adjust the light control to zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l nitrate nitrogen.

#### Phosphorus, Reactive      Ascorbic Acid Method

1. Take a water sample by filling a clean cell to the 25 ml mark.
2. Add the contents of one "PhosVer III Reagent Powder Pillow" and swirl to mix. A blue color will develop if phosphate is present. Wait at least two minutes for full color development but not more than 10 minutes before completing steps 3 and 4.
3. Fill another sample cell to the 25 ml mark with original water sample and place it into the cell holder. Insert the Phosphate Meter Scale into the meter and adjust the wavelength to 700 nm. Adjust the light control to zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l of phosphate,  $\text{PO}_4$ .

#### Silica      Silicomolybdate Method

1. Take a water sample by filling a clean sample cell to the 25 ml mark.
2. Add the contents of "Molybdate Reagent Powder Pillow" for high silica range and swirl to mix. A yellow color will develop if silica and/or phosphate is present.
3. Add the contents of one Acid Reagent Powder Pillow. Let stand 10 minutes. Add the contents of one Citric Acid Reagent Powder Pillow and swirl to mix. Allow at least two minutes for the color to fully develop but not more than five before completing steps 4 and 5.
4. Fill another sample cell to the 25 ml mark and place it in the cell holder. Insert the Silica Meter Scale and adjust the wavelength to 410 nm. Adjust the light control to zero mg/l.
5. Place the prepared sample in the cell holder and read the mg/l silica as  $\text{SiO}_2$ .

#### Sulfide      Methylent Blue Method

1. Measure 25 ml of demineralized water by filling a clean 25 ml graduated cylinder to the 25 ml mark.

2. Take a water sample by filling the 25 ml graduated cylinder to the 25 ml mark.
3. Using a 1 ml calibrated dropper, add 1.0 ml of Sulfide I Reagent to each sample cell and swirl to mix.
4. Using a 1 ml calibrated dropper, add 1.0 ml of Sulfide II to each sample and immediately swirl to mix. A pink color will develop and turn blue if sulfide is present. Allow five minutes for the color to fully develop and proceed with step 5.
5. Place the sample cell containing the demineralized water into the cell holder. Insert the Sulfide Meter Scale into the meter and adjust the wavelength to 665nm. Adjust the light control to zero mg/l.
6. Place the prepared sample in the holder and read the mg/l sulfide, S.

### Sulfate

### Turbidimetric Method

1. Take a water sample by filling a clean sample cell to the 25 ml mark.
2. Add the contents of one "SulfaVer IV Reagent Powder Pillow" and swirl to mix. A white turbidity will develop if sulfate is present. Allow at least five minutes for the turbidity to fully develop but do not wait more than 10 minutes before completing steps 3 and 4.
3. Fill another sample cell to the 25 ml mark with original water sample and place it into the cell holder. Insert the Sulfate Meter Scale and adjust the wavelength to 450 nm. Adjust the light control to zero mg/l.
4. Place the prepared sample in the cell holder and read the mg/l sulfate.

### Tannin-Lignin

### Tyrosine Method

1. Measure 25 ml of demineralized water by filling a clean 25 ml graduated cylinder to the 25 ml mark.
2. Take a water sample by filling the graduated cylinder to the 25 ml mark. Pour the sample into another clean cell.
3. Pipet 0.5 ml of TanniVer III Tannin-Lignin Reagent into each sample cell and swirl to mix.
4. Pipet 5.0 ml of Sodium Carbonate Solution into each sample cell and swirl to mix. A blue color will develop if tannin and/or lignin is present. Allow 25 minutes for full color to develop.
5. Place the sample cell containing the demineralized water into the cell holder. Insert the Tannin-Lignin Meter Scale and adjust the wavelength to 700 nm. Adjust the light control to zero mg/l.

6. Place the prepared sample in the cell holder and read the mg/l of tannin and lignin.

### pH

The pH of whitewater samples are taken using a standard pH meter adjusted to the correct temperature.

### Conductivity

The conductivity of the whitewater samples is taken using a conductivity bridge.

If in reading any of the measurements on the spectrometer, the readings are off scale, the sample may be diluted, and the dilution factor introduced into the results. For example, in the analysis of aluminum the spectrophotometer may read above 0.75 mg/l. Since this is beyond the last division of the meter scale, a sample dilution is necessary. The test may be repeated, but with a 25 ml graduated cylinder filled to the 12.5 ml mark with the sample and then to the 25 ml mark with demineralized water. Since the sample was diluted to twice its original volume, the meter reading should be multiplied by two to give the correct concentration of aluminum.

DATA TABLE I

	<u>FRESH WELL</u>	<u>FEB 1</u>	<u>FEB 2</u>	<u>FEB 6</u>	<u>FEB 7</u>	<u>FEB 8</u>	<u>FEB 9</u>	<u>FEB 10</u>
<u>SILICA (mg/l)</u>	11.8	12.2	11.5	15.5	-	13.75	16.0	15.0
<u>TANNIN- LIGNIN</u>	0.0	16.8	20.0	76.0	123.0	99.0	165.0	153.0
<u>CALCIUM</u>	163.0	150.4	134.4	128.0	75.0	85.0	101.6	107.2
<u>CHLORIDE</u>	110	110	115	125	81	77	161	170
<u>IRON</u>	2.2	-	.76	.52	.33	.41	.62	.99
<u>COPPER</u>	0.0	1.35	.85	-	-	-	-	-
<u>PHOSPHATE</u>	.23	.81	1.95	3.3	3.5	3.8	4.4	4.8
<u>NITROGEN NITRATE</u>	0.0	0.0	0.0	3.9	.2	1.2	2.0	.3
<u>SULFATE</u>	0.0	520	300	-	-	-	-	-
<u>SULFIDE</u>	.02	.45	.50	-	-	-	-	-
<u>ALKALINITY</u>	366	311	323	327	266	266	317	306
<u>HARDNESS CaCO<sub>3</sub></u>	408	376	336	320	187	213	254	268
<u>BARIUM</u>	0	0	0	0	0	0	0	0
<u>ALUMINUM</u>	.08	-	-	.2	.03	.23	.30	.10
<u>pH</u>	7.1	-	-	7.22	7.20	7.39	7.10	7.40
<u>CONDUCTIVITY MICROOHMS/CM</u>	7.3	-	-	1250	667	714	1111	1176
<u>CALIPER, in.</u>		.0165 .0168 .0165	.0190 .0195 .0190	.0205 .0205 .0208	.0210 .0215 .0215	.0270 .0280 .0270	.0265 .02725 .02725	.0155 .0165 .0165
<u>BASIS WT.</u>		70 70 72	78 78½ 78½	82½ 81½ 82½	85 85½ 84½	107 108 109	111 108 110	69 71 70

DATA TABLE II

	<u>AVERAGES</u>			
	<u>10 DAYS</u>	<u>18 DAYS</u>	<u>LAST 5 DAYS</u>	<u>TRENDS</u>
Silica (anion)	11.85 mg/l	13.9 mg/l	15.0 mg/l	increase
Tannin (anion)	18.4	93.3	123.2	increase
Lignin				
Calcium (cation)	142.4	111.7	99.4	decrease
Chloride (anion)	112.5	120.0	122.8	slight increase
Iron (cation)	.76	.61	.57	decrease
Copper (cation)	1.1	-	-	-
Phosphate (anion)	1.38	3.2	3.96	increase
Nitrate (anion)	0	1.1	1.52	increase
Sulfate (anion)	410	-	-	-
Sulfide (anion)	.48	-	-	-
Alkalinity	317	302	297	decrease
Hardness (cationic)	356	279	248	decrease
Barium (cation)	0	0	0	no change
Aluminum(cation)	-	.17		-
pH	-	7.26		-
Conductivity	-	984 microohms/cm		-

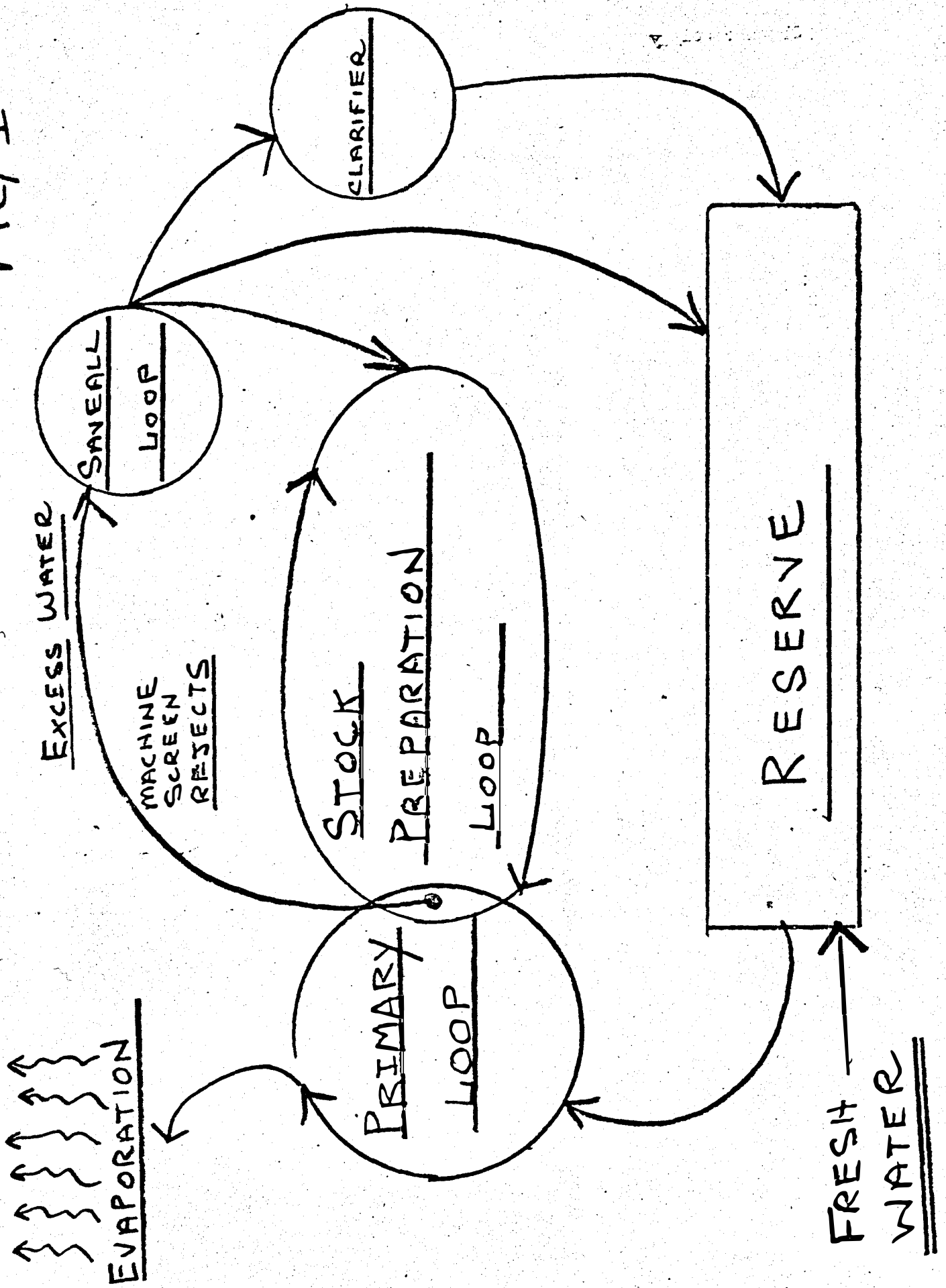
DATA TABLE III

RELATIVE CHANGES BETWEEN DAYS OF RUNNING TIME

	<u>9-10</u>	<u>14-15</u>	<u>15-16</u>	<u>16-17</u>	<u>17-18</u>
Tannin-Lignin	19.0% inc	61.8% inc	19.5% dec	67.0% inc	7.2% dec
Calcium	10.6% dec	41.4% dec	13.3% inc	19.5% inc	5.5% inc
Chloride	4.5% inc	35.2% dec	4.9% dec	109.1% inc	5.6% inc
Silica	5.7% dec	-	-	16.4% inc	6.3% dec
Iron	-	36.5% dec	24.0% inc	51.0% inc	59.7% inc
Copper	37% dec	-	-	-	-
Phosphate	140.7% inc	6.1% inc	8.5% inc	15.8% inc	9.1% inc
Nitrate	no change	94.8% dec	500% inc	66.7% inc	85.0% dec
Sulfate	42.0% dec	-	-	-	-
Sulfide	11.1% inc	-	-	-	-
Alkalinity	3.9% inc	18.6% dec	no change	19.2% inc	3.4% dec
Hardness	10.6% dec	41.5% dec	13.9% inc	19.2% inc	5.5% inc
Aluminum	-	85 % dec	667 % inc	30.4% inc	67 % dec
pH	-	.27% dec	2.6% inc	3.93% dec	4.2% inc
Conductivity	-	46.6% dec	7 % inc	55.6% inc	5.6% inc
Caliper	15.6% inc	3.4% inc	28% inc	1.0% dec	40.0% dec
Bs. Wt.	10.9% inc	3.4% inc	25.8% inc	2.8% inc	36.0% dec



FIG 1



# PRIMARY LOOP - FILLER

FIG 2

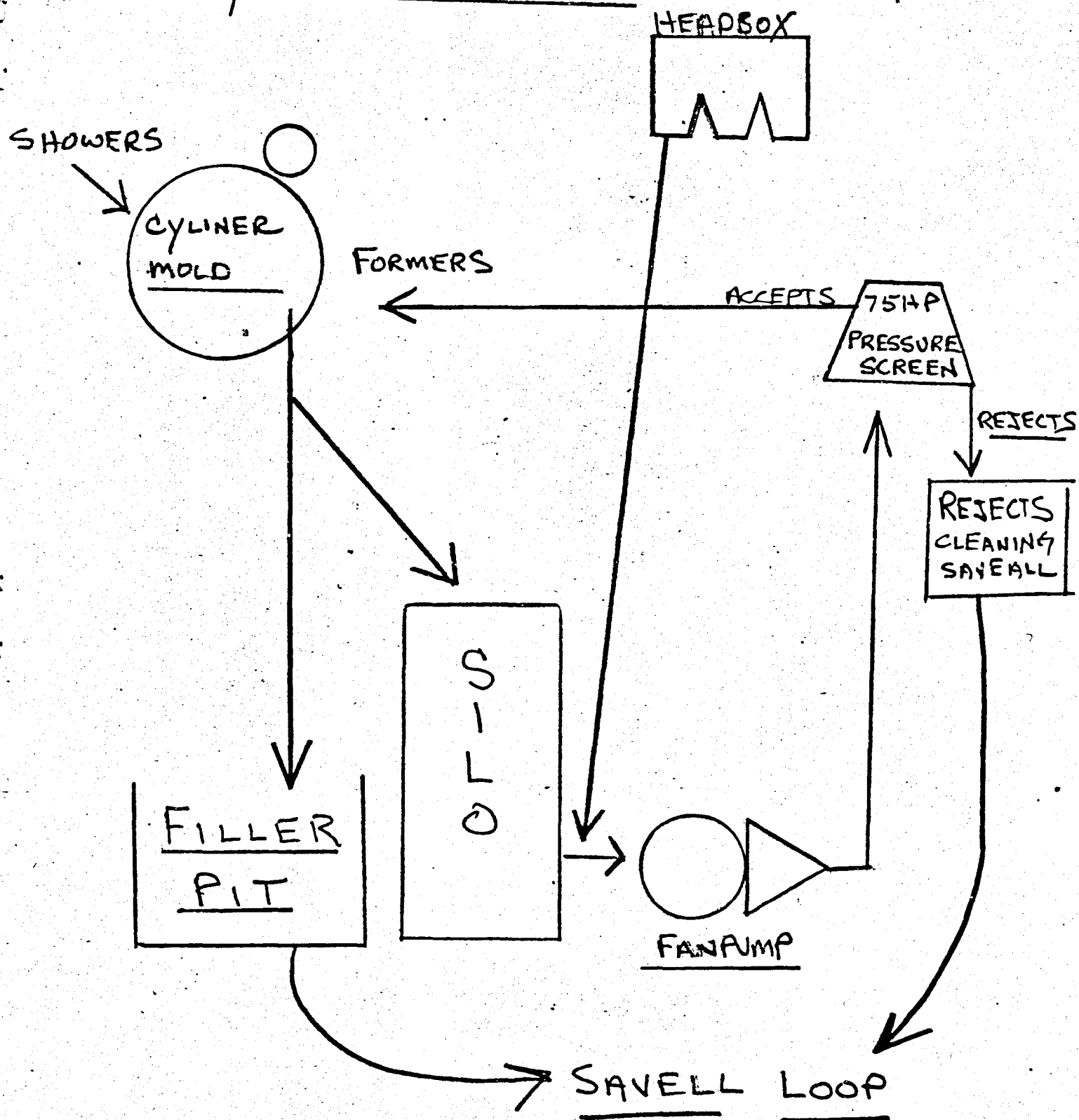
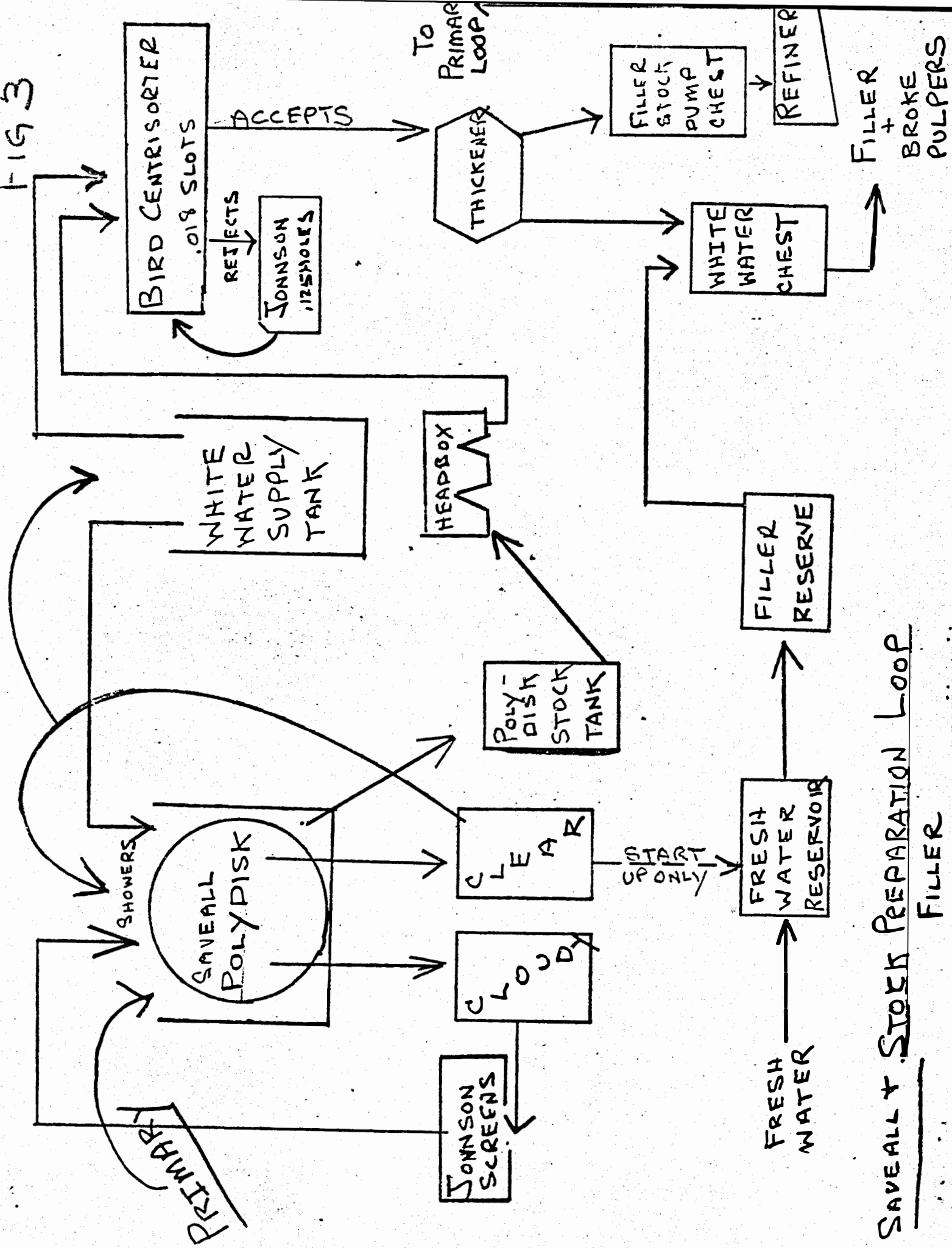


Fig 3



## SAVE ALL + STOCK PREPARATION LOOP

FILLER

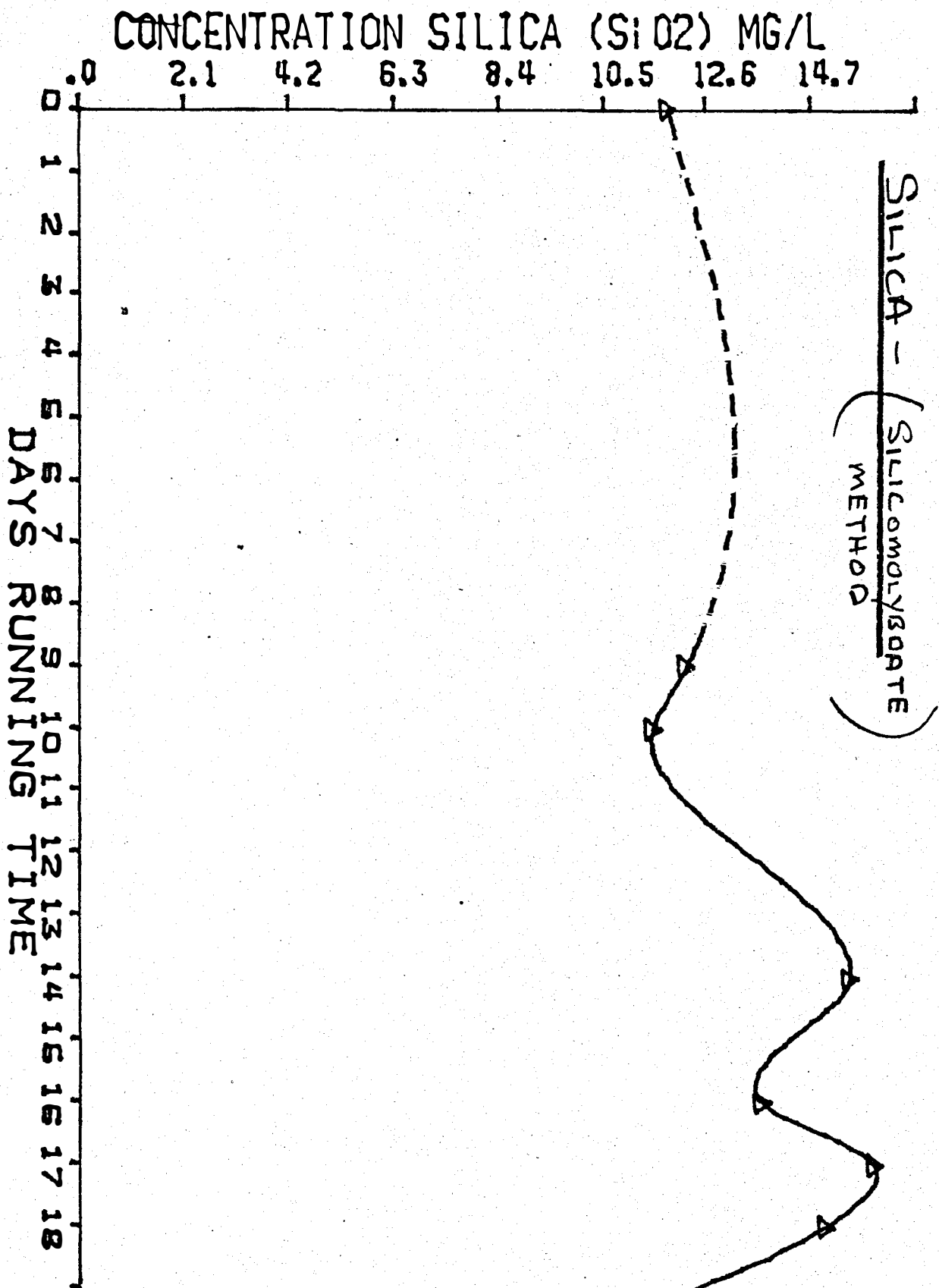
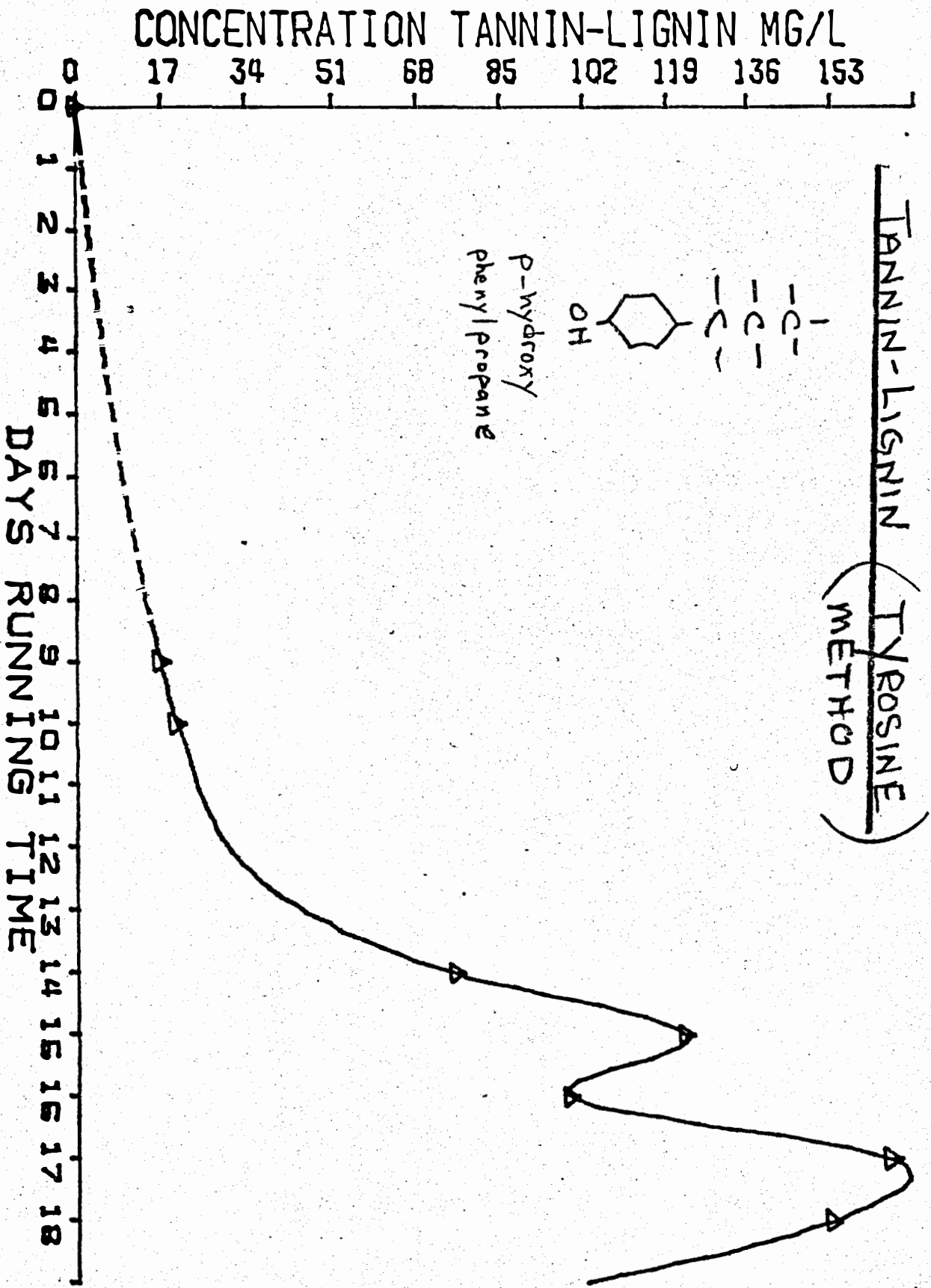
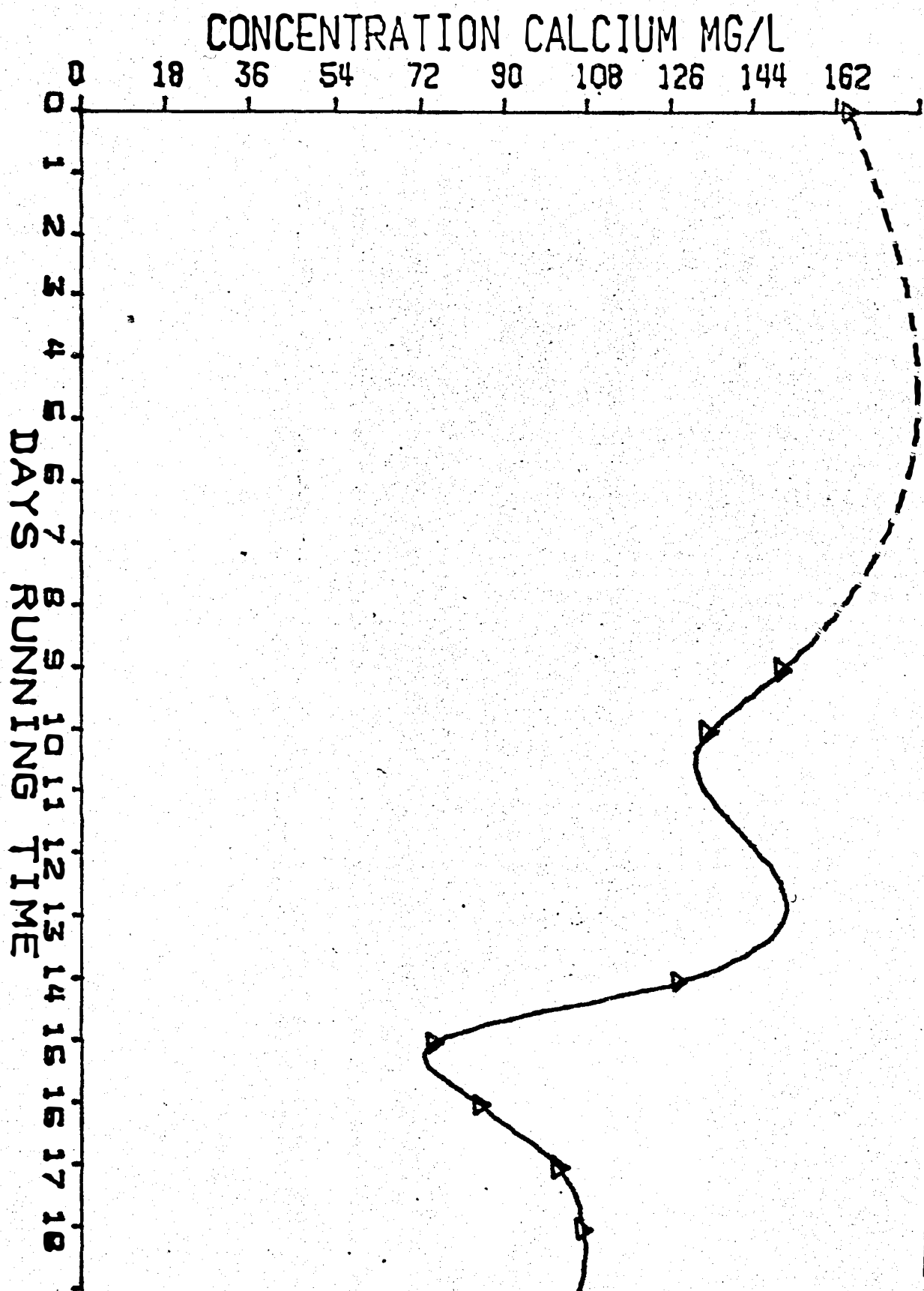


Fig 4

FIG 5





CALCIUM - 0.02N EDTA

FIG 6

FIG 7

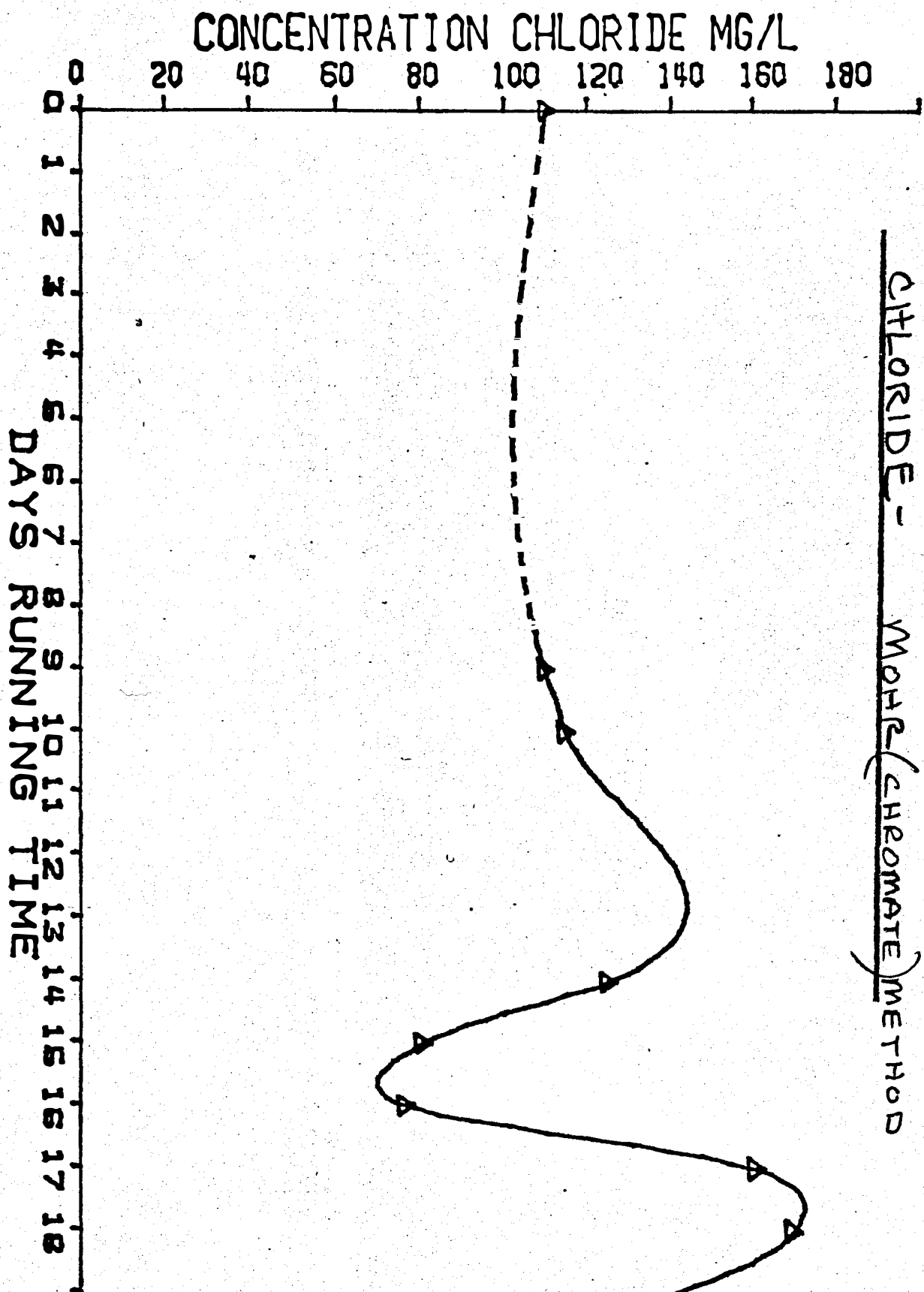
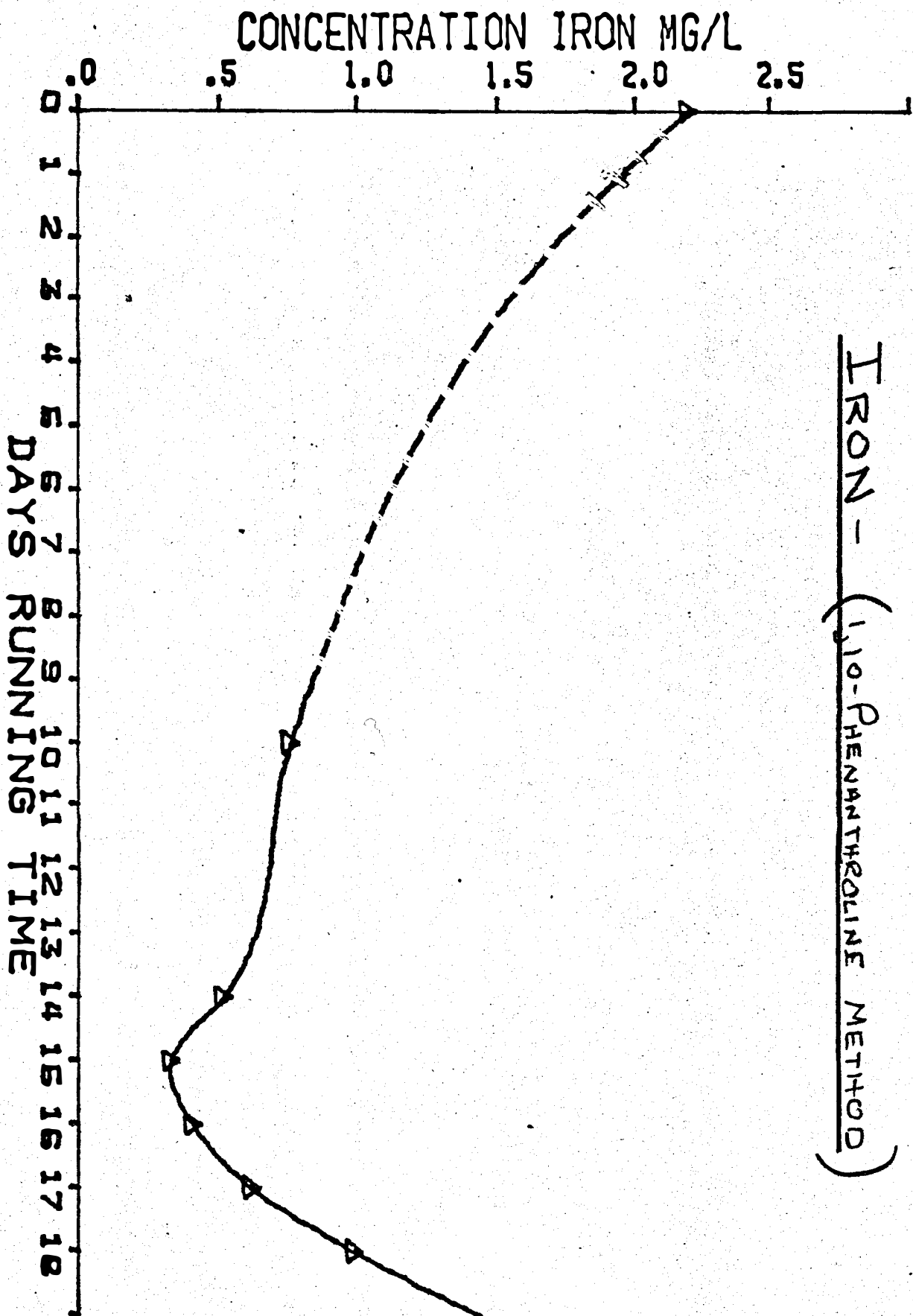


FIG 8





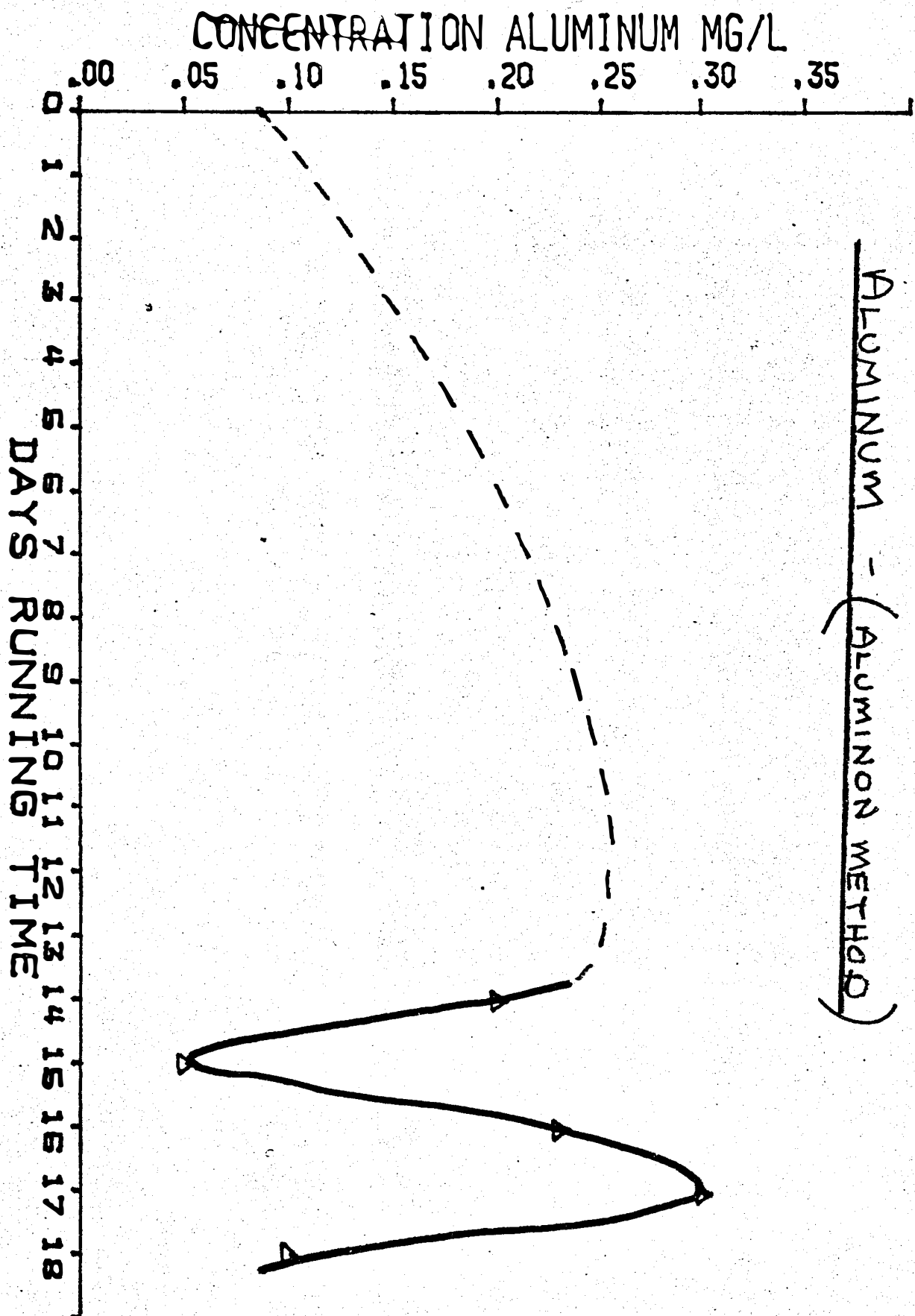
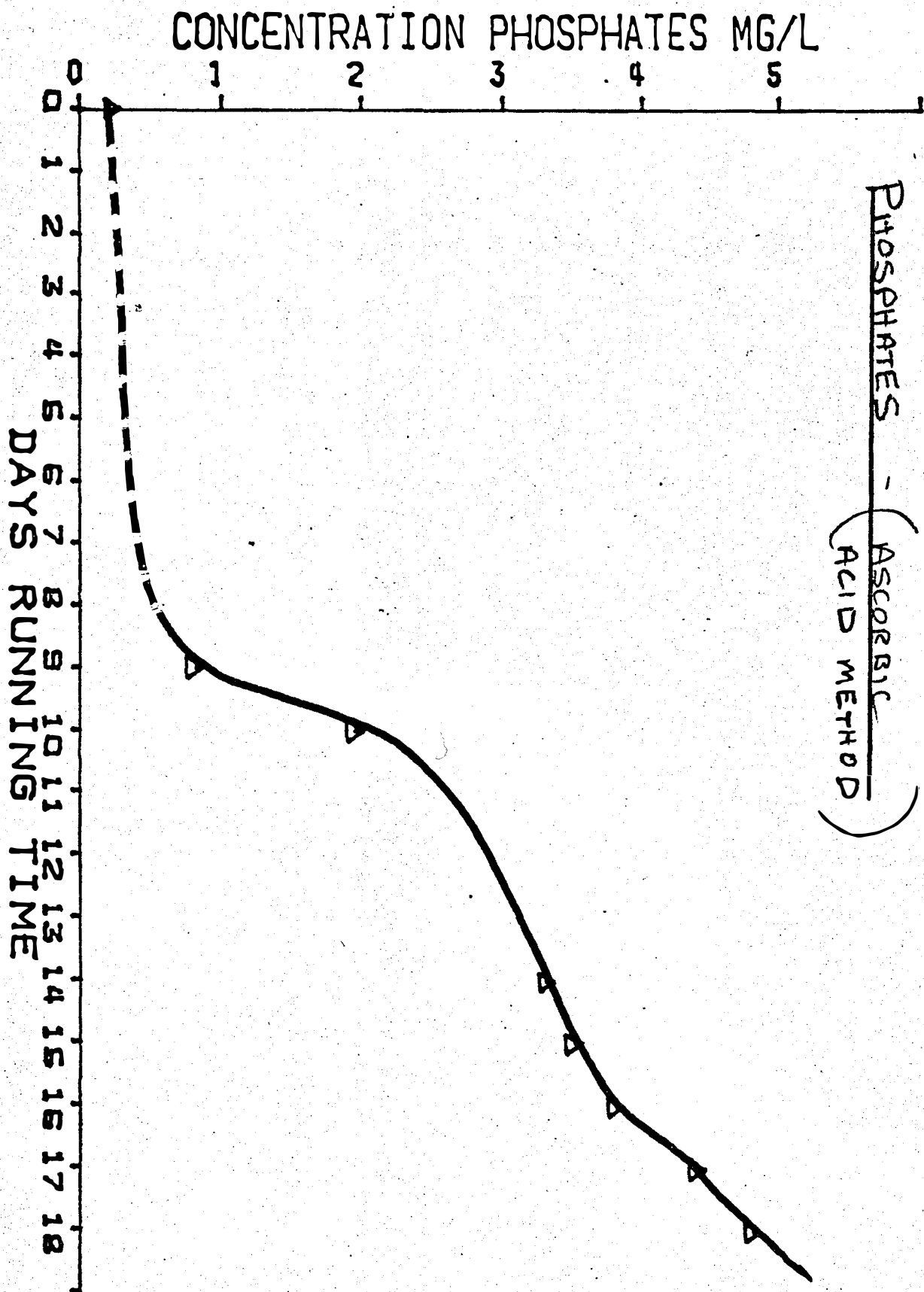


FIG 9

FIG 10



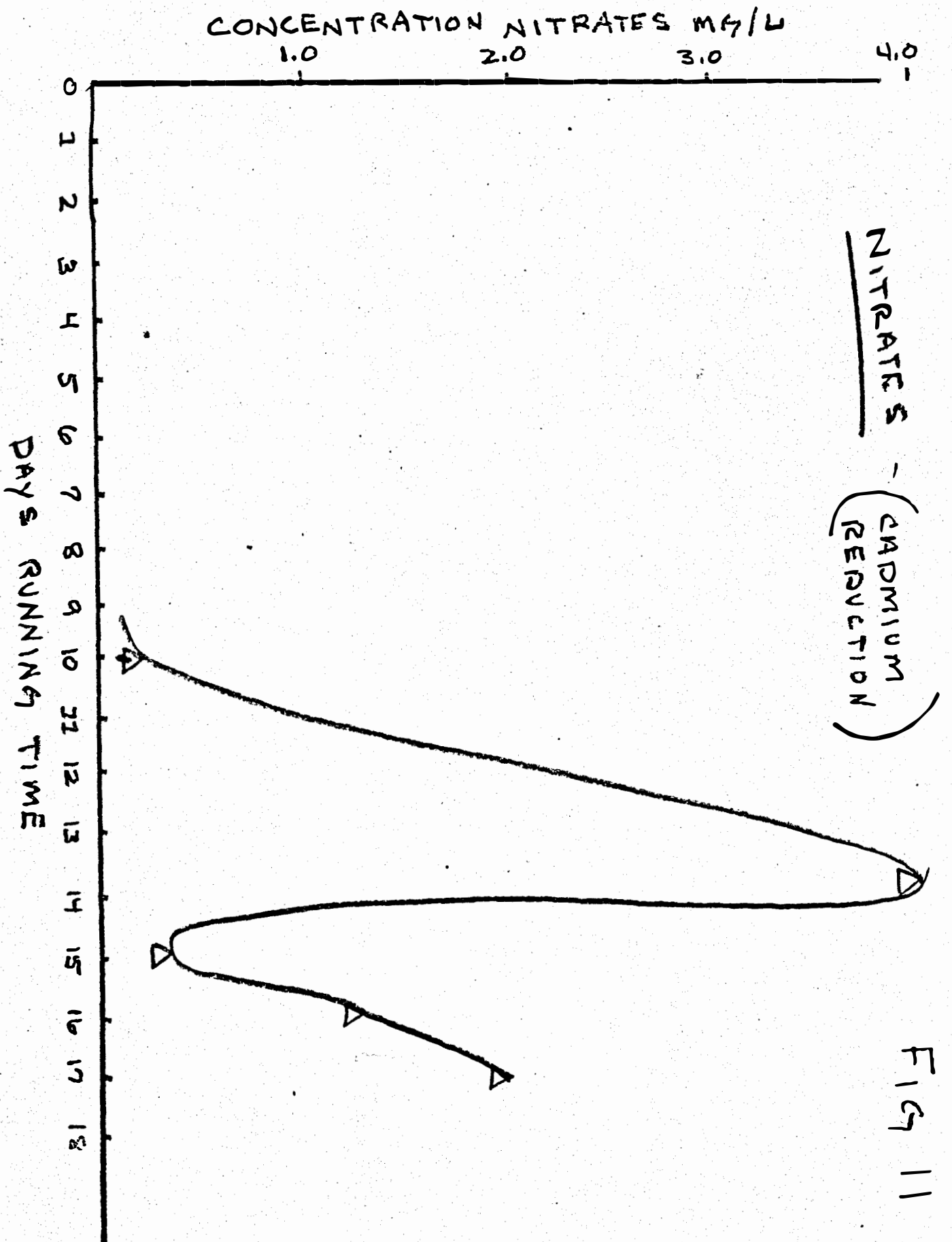


Fig 11

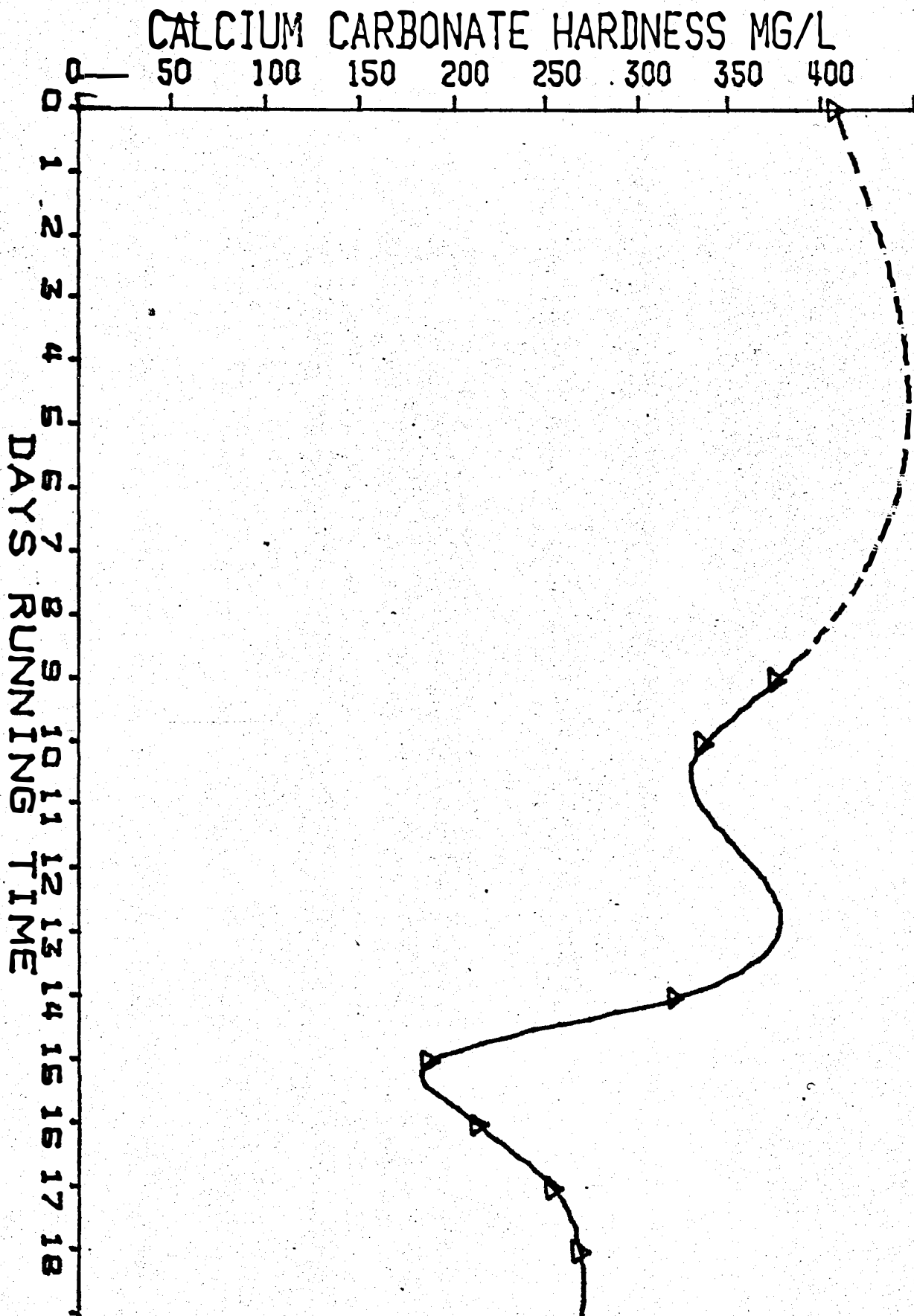
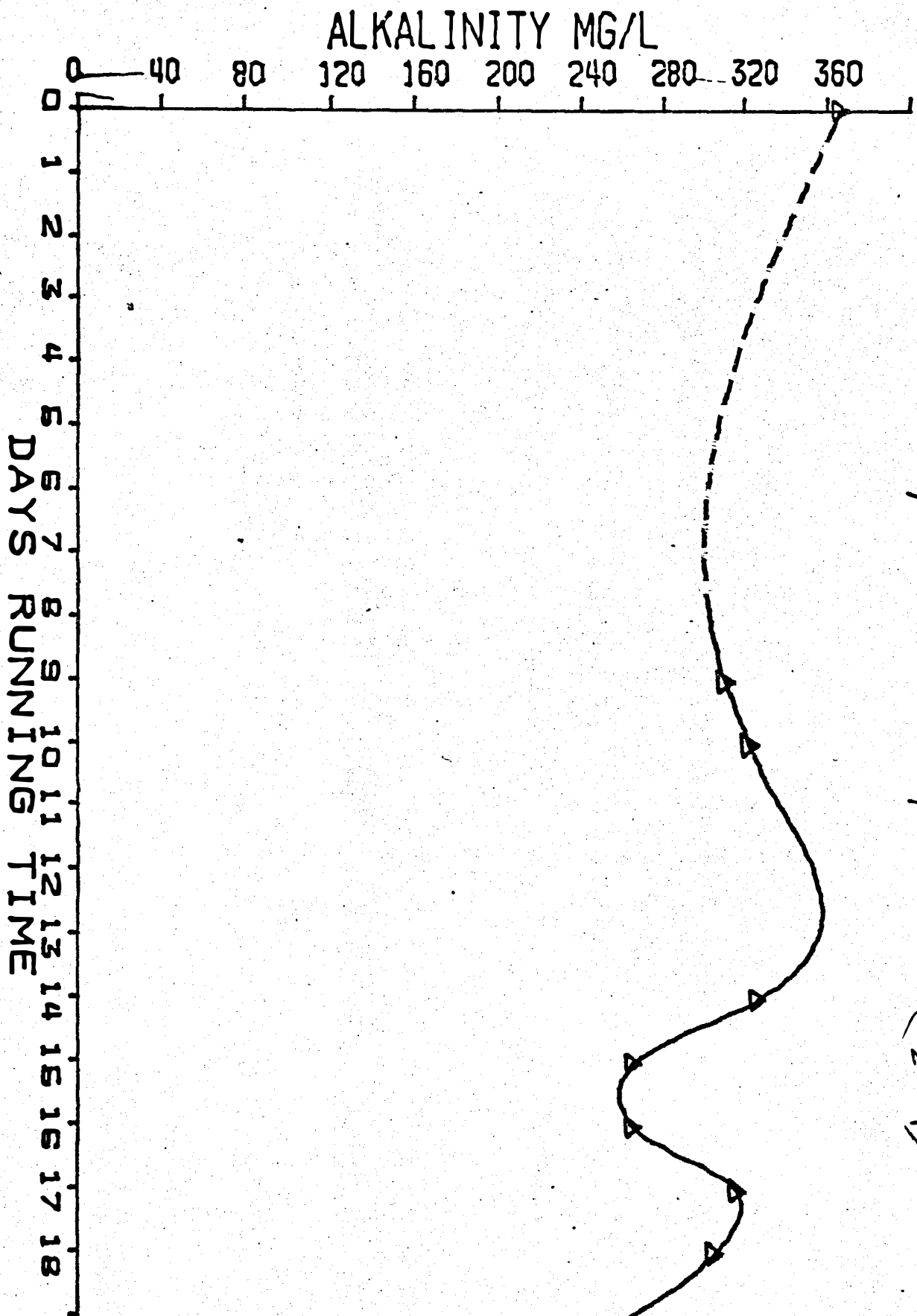


FIG 12



ALKALINITY VS. RUNNING TIME ( $H_2SO_4$ ) FIG 13

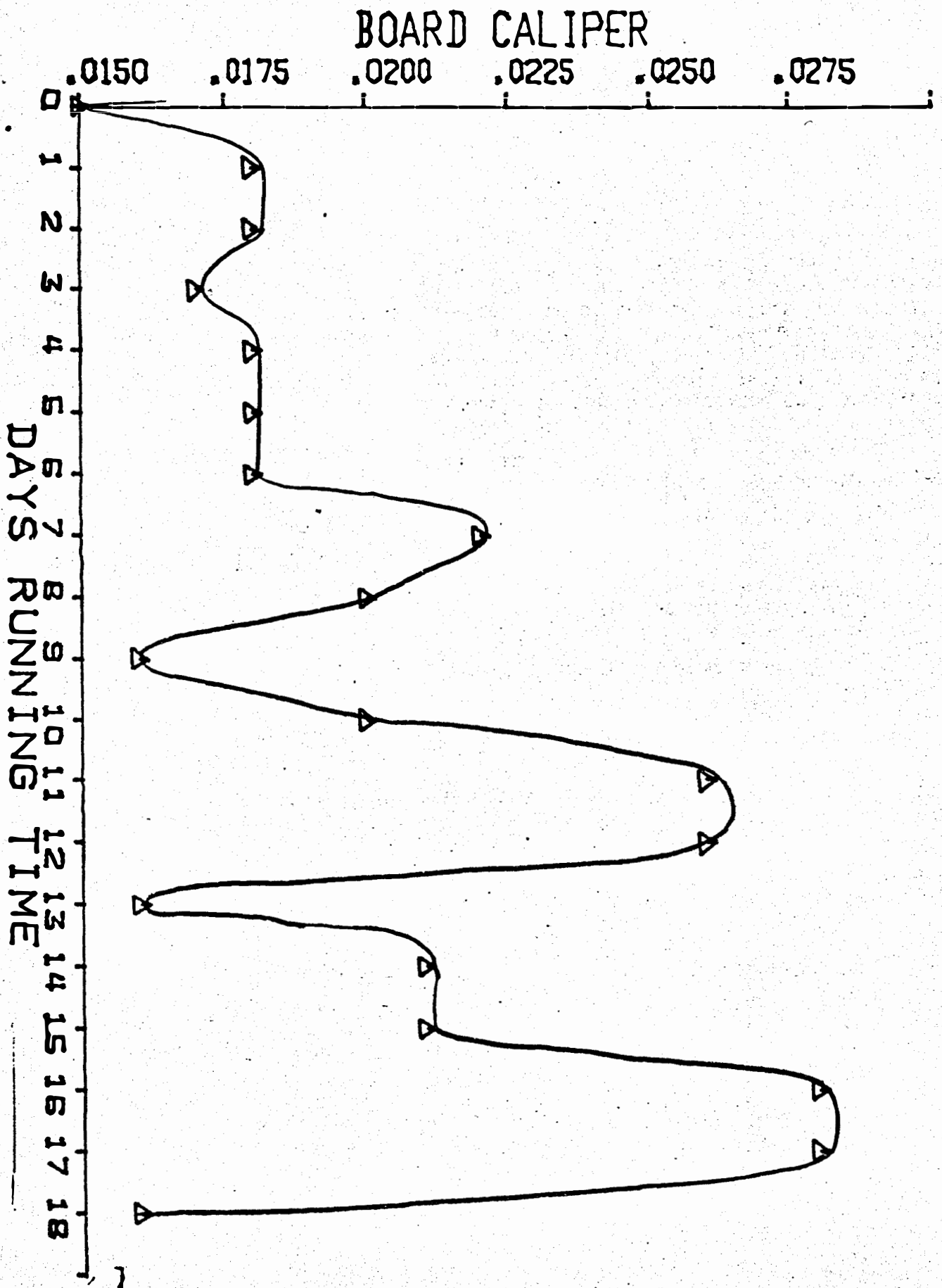


FIG 14

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