

THE EFFECTS OF CATIONS ON ACTIVATED
SLUDGE CHARACTERISTICS

by

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(ABSTRACT)

This research was prompted by a field study performed at the Celanese Corporation Wastewater Treatment Plant, Narrows, VA., in which calcium chloride addition had improved sludge characteristics that were believed to have deteriorated because of sodium hydroxide additions for pH control.

Research objectives were to determine whether the observed improvements during the full-scale plant study were caused by the addition of divalent cations and whether the deterioration of the sludge was due to sodium ion additions.

Bench-scale, activated sludge reactors were fed wastewater from the Celanese plant to model plant conditions. Sodium was added in an attempt to cause deterioration of the sludge characteristics. Magnesium and calcium were used as divalent cations to try to improve the sludge characteristics.

Results of the study indicated that the magnitude of the effects seen in the full-scale plant study could not be reproduced in the laboratory. Magnesium produced little or no effect on the system and calcium improved the sludge characteristics slightly. Sodium caused

deterioration of the sludge but not as dramatically as the full-scale study. This suggested that sodium alone did not adversely affect the sludge but rather, sodium hydroxide might have been combined with organics in the waste which then affected the system.

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I. INTRODUCTION

Flocculation and settling are two of the most important phenomena in activated sludge systems. These phenomena influence effluent suspended solids and BOD whose concentrations are regulated by discharge limits. Activated sludge systems remain a popular choice for the treatment of industrial wastes but these wastes often produce a sludge with poor flocculation and settling characteristics, resulting in inefficient treatment and sludge disposal problems.

Studies in the past have suggested that divalent cations are necessary for a sludge to flocculate well and that sodium may promote deflocculation. However, specific limits are not available, as not much research has been performed in connection with activated sludge systems and these cation effects. This study was prompted by research performed at the Celanese Corporation Wastewater Treatment Plant. Sodium hydroxide appeared to have deteriorated sludge characteristics at the plant and calcium chloride, added as a divalent ion, improved the characteristics markedly.

Specific objectives of this study which may clarify the role of cations in activated sludge are as follows:

- a) determine whether the results observed at the Celanese Wastewater Treatment Plant were effects caused by the addition of divalent cations,

- b) investigate whether the deterioration associated with the addition of sodium hydroxide was a direct result of the sodium ion or instead, by compounds formed from the reaction of sodium hydroxide with constituents in the wastewater,
- c) determine whether there was a specific concentration where sodium caused detrimental effects to the system,
- d) determine whether there was an optimum concentration of the divalent cations, calcium and magnesium, where the best operational parameters could be maintained.

II. LITERATURE REVIEW

The impact of monovalent and polyvalent cations on both anaerobic and activated sludge systems is of interest to environmental scientists and engineers. Most commonly, the role of cations as coagulants to produce hydrometal complexes has been of interest. Additionally, problems in connection with the uptake of heavy metals into biological sludges is of concern.

The scope of this section will be to provide a review of the literature which deals with three different cations: magnesium, calcium, and sodium, and the research which has been conducted on their role in the characteristics of activated sludge. The literature suggests that there are two major opposing views on the role of these cations in activated sludge. One view, which will be expanded upon in this paper, states that these cations are necessary for a sludge to flocculate well. The other view holds that they have no influence on sludge characteristics.

MICROBIOLOGICAL STUDIES

Much of the research on the role of cations in microbial populations was conducted in the early part of the century by microbiologists. Their main interest lay in discovering what effects, of any, these cations had on the respiration of microorganisms. They were interested in looking at the stimulation, toxicity and antagonistic effects which different salts had on microbial populations.

Hotchkiss (1922) showed stimulating effects of $MgCl_2$, $CaCl_2$, and $NaCl$. The magnesium and calcium solutions optimized the respiration at 0.05 M and the sodium at 0.25 M concentrations. A level of toxicity was also defined for each solution where growth was no longer stimulated but inhibited. An interesting observation that she made in her studies was that those bacteria grown in the calcium and magnesium solutions tended to grow in clumps and settled out of the solution to the bottom of the tubes. In contrast, solutions containing sodium produced a homogeneously suspended growth as did her controls. Similar results were also described by Winslow and Haywood (1931), who defined a specific potency for each cation according to their stimulating and inhibiting effects. In contrast to Hotchkiss, they defined stimulation around 0.008 M and toxicity beyond 0.02 M for both calcium and magnesium.

Ingram (1939, 1940) found that in low concentrations of salts, the rate of oxygen uptake by Bacillus cereus was increased and in high concentrations was decreased. He also found that when the range of concentrations over which stimulation occurred was smaller, it was caused by the cations with greater valence. He noted that the anions associated with the cation had little or no effect on the stimulation assumed to be caused by the cation. Holmes and Sherman (1921) showed the same characteristic effects of cations and also showed how the anions connected with these cations had a more noticeable effect on the growth of the organisms.

ROLE OF CATIONS IN THE SETTLING OF SLUDGES

It has been well documented that the microorganisms in an activated sludge are composed of bacteria with negative surface charges. The intensity of this charge is dependent upon the concentration and nature of the inorganic materials present at the surface of the microorganism. These materials can result from adsorption/absorption processes bringing polymers of polyvalent metal ions to the surface, or from the metabolic formation of capsular polymers (Forster et al., 1980). Pavoni et al. (1972) have shown these polymers to be composed of DNA, RNA, proteins and carbohydrates. Tago and Aida (1977) found the mucopolysaccharide to be the floc-dependent polysaccharide.

Metal ions are one of the most common trace nutrients found in wastewater and have proven to be of great use in coagulation of colloidal particles in other forms of treatment. Therefore, it is not unlikely that they should play an important role in the floc formation seen in activated sludge systems. Tezuka (1968) has proposed a theory in which the negatively charged cell surfaces are surrounded by cations which are bridged to the cells by ionic bonds. He proposed that this occurs in the presence of both magnesium and calcium and with non-viable cells, concluding that flocculation was a physiochemical process rather than a physiological one. In contrast to other studies, he did not get good flocculation when magnesium or calcium salts were added but rather, found both ions were required.

Mill (1963) proposed a similar theory of flocculation using a strain of yeast which forms aggregates similar to those in activated sludge. He found calcium to be an essential requirement for flocculation. He found other ions could also aggregate the cells, but stated that there was no evidence that they were working in the same manner as calcium, nor that they combined with the same cell groups. He postulated that these calcium ions were forming bonds between a combining site on each of the two cells. This combining site, he concluded, might be a carboxyl group which would form ionic bonds, but that hydrogen bonds were also present. These hydrogen bonds may be formed as cells get pulled closer together and will form between complimentary carbohydrate structures in the cell walls. The evolved complex assumes a chelating nature with calcium-complexing groups in specific spatial relationships. His study included sodium ions which antagonized the function of the calcium. He concluded that the sodium ion, being of similar radius, could displace calcium in its specified sites, but the study showed that the sodium deflocculated the sludge.

Another theory proposed by Busch and Stumm (1968) is that divalent cations form complexes or ion pair formations between functional groups of polyelectrolytes and a counter ion near the surface of the bacteria which in turn enhances the adsorption of polymers at the bacteria-solution interface. The negatively charged surface creates a greater cation concentration in its vicinity, enabling this complex formation. They also state that a minimum level of 3×10^{-4} M magnesium or calcium was needed for good flocculation in the presence of polymers. In the

absence of polymers, concentrations of more than 10^{-1} M calcium or magnesium were needed to produce aggregation.

The concept of cation adsorption has been studied further. Forster and Lewin (1972) performed a study of the adsorption of magnesium and calcium by extracellular polymers. They proposed two mechanisms of uptake by bacterial surfaces: 1) chemisorption by the biopolymers at the immediate surface and 2) extensive uptake of metals by diffuse extracellular biopolymers. They also showed that water molecules, bound to the surface of the polymers, could be exchanged for calcium ions. Novak and Haugan (1979), in a study of chemical sludge conditioning, added $MgCl_2$ to an eluted sludge and found that it resulted in a considerable decline of synthetic cationic polymer requirements. They believed that this result indicated that the salts played a role in sludge behavior by enhancing the adsorption of the natural anionic polymers to the sludge floc.

Although most of the previous studies conclude that the cation effect is a physiochemical phenomena, other studies focused on the biological nature of cations. In a study by Endo et al. (1976), they found that calcium was needed in the growth phase of the bacteria in order to produce flocculating organisms. They found that cells grown in low levels of calcium would not flocculate even when additional calcium was added to the cultures. They concluded that the presence of calcium in the growth medium is required for the synthesis of a component or components which are essential for bacterial flocculation. They also observed the onset of deflocculation in the late stationary phase of

growth which was dependent on the concentration of the calcium in the medium.

Kakii et al. (1985) studied the ions present in an activated sludge. They found relatively large amounts of calcium (11-28 mg/gSS) in the sludge along with aluminum and iron. They found even larger amounts of calcium in the mixed liquor contained within the aeration tank with low levels of magnesium, but did not detect aluminum and iron. They studied the effect of calcium on the 30 minute settling volume and found it decreased from 26 to 23% on addition of 1mM of calcium, but no further decrease was observed at higher concentrations. They extracted the calcium from the solution and found that SVI and turbidity decreased with increasing amounts of calcium added back in.

The binding of calcium was also studied. When 40 mg/L of calcium was added, the amount bound to the sludge, 11.7 mg/gSS, corresponded to 81% of the calcium which had been extracted by acid treatment. Upon examination of the sludge, they found the metals to be in three groups: 1) precipitated metals trapped in the sludge matrix, 2) metals bound to extracellular polymers and 3) metals in intracellular form. Since they could only remove 50% of the magnesium, they concluded that it was in an intracellular form and that calcium, which was easily removed, was in the extracellular fraction. They also concluded that the amount of calcium in the aeration tank was near saturation and that calcium bonded strongly to activated sludge.

Contrasting the different effects of calcium and magnesium on activated sludge, Forster et al. (1980) performed a study measuring the

settling volume index, the bound water content and the sludge surface charge. They found that magnesium created a decrease in negativity of the surface charge, decreasing the SVI as the concentration increased. The magnesium was not adsorbed onto the sludge, nor did it change the bound water concentration on the surface. Calcium did not affect the negativity, nor did it decrease the SVI. However, it did adsorb to the surface, displacing bound water molecules. So again it appears that magnesium and calcium have different actions on an activated sludge. In the case of magnesium, Forster suggested that some other constituent causes the magnesium to be attached to the sludge. It is interesting to note that he did not observe better settling with the calcium as all the other studies have thus far.

Kincannon and Gaudy (1966) presented a study of the effects of high concentrations of NaCl on an aerobic system. They found sludges developed in low salt concentrations to be more tolerant of shock loadings, but sludges developed in high salt concentrations could not withstand sudden decreases in salt. Low-salt sludges showed a slight decrease in substrate removal efficiency when shocked; high salt sludges showed a reduction of 75% in efficiency of substrate removal when dosed with fresh water. Those sludges developed in mediums of 30,000 mg/L to 45,000 mg/L of salt sometimes showed complete deflocculation and sometimes did not. High-salt sludges removed COD at a lower rate and tended to release cellular intermediates and end products during glucose metabolism. High-salt sludges could also be characterized by low protein and carbohydrate content and a high RNA and lipid content.

High-salt sludges showed a much higher ratio of respiration to synthesis.

In contrast to most studies which show metal ions to influence sludge properties, Sato and Ose (1982) performed a study which showed little effect of salts on activated sludge. They concluded that these ions were of no consequence in the floc formation between extracted biopolymer and kaolin. Because the surface of the kaolin is inorganic and therefore not similar to the surface of a microorganism, these studies may have little validity in biological systems. The study shows that floc formation may be both a function of a surface reaction as well as biopolymer action.

STUDIES IN ANAEROBIC SYSTEMS

Although this paper deals with aerobic systems, much pertinent work has been conducted in anaerobic systems. Mahoney et al. (1987) studied the granulation of the sludge in an up-flow anaerobic sludge blanket by the addition of 100 mg/L calcium. The granules formed were larger than in other reactors and settled 304 times faster. Microscopic studies showed that the microbial cell surface charge became very negative and that the intercellular spaces contained fibrillar extracellular polymeric substances which would bind cells better with the assistance of calcium as a binding factor.

McCarty and McKinney (1964) studied salt toxicity and antagonism in anaerobic digesters. They found that cations were more toxic on a slug basis in contrast to a constant feed basis. They found an increasing order of toxicity based on equivalent concentrations to be: 1) calcium,

2) magnesium, and 3) sodium. They also found that sodium toxicity up to 3500 mg/L could be eliminated by 500 to 1,000 mg/L of calcium or magnesium, acting as an antagonist.

Kugelman and McCarty (1965) conducted a similar study. They provided optimum ionic concentrations for anaerobic systems at 0.01 M for monovalent ions and 0.005 M for divalent ions, concluding that lower or higher concentrations resulted in less than maximum efficiency in the system. They also defined relationships of ions to minimize inhibitions caused by excessive concentrations of one ion. They found that by adding the optimum concentrations of several other ions, they could better maximize antagonism.

Kugelman and Chin (1971) took the information gained in the microbiology studies on stimulation and toxicity of cations and applied them to anaerobic waste treatment. They defined toxicity and stimulation on a metabolic rate and a concentration basis. Research was conducted with both potassium and sodium. Their methods of reporting were quite interesting: they reported the effect of synergy, antagonism and stimulation through kinetic parameters using the monod model of kinetics. In this way, they could come up with design parameters for their systems. These methods could very well be used for aerobic systems as well.

SUMMARY

To summarize the most important points gained in this literature review:

1. Calcium and magnesium seem to have a positive effect in improving sludge characteristics.
2. High concentrations of sodium may deflocculate sludges.
3. There are certain concentrations which are past the point of stimulation and are considered toxic to an aerobic system.
4. Mechanisms by which these salts work are probably both physical and chemical in nature.

Throughout this review, one can see that the studies on activated sludge have been limited. The research to date has been disjunctive. More large-scale studies will be needed in the future to resolve the inconsistencies in the literature.

III. METHODS AND MATERIALS

This chapter will outline the overall experimental approach including experimental objectives, methods of sampling, analysis and operation as well as a description of the equipment which was used.

EXPERIMENTAL OBJECTIVES AND APPROACH

The objectives of this research were achieved by evaluating the effects caused by the addition of calcium, magnesium and sodium on an activated sludge system. The parameters monitored were chosen so that they might show the effects of each cation or cation concentration on settleability, dewaterability, general health of the system or operating efficiency.

Cations were added to the reactors and the system allowed to run for an extended time. Different concentrations of three cations, Mg^{++} , Ca^{++} and Na^{+} , were the focus of these studies. Table 1 outlines the cations added and the period of time which the system was operated under these conditions. The approach to adding these cations was to use one cation and then to change the cation to another to see if there were any effects. Another tactic was to keep adding higher and higher concentrations of one cation to see what effects the higher concentrations would have, positively or negatively.

Table 1. Schedule of Cation Additions

Experimental Period	Date Cation Added	Cation	Concentration mg/L	No. of Samples Analyzed	No. of Days in System
A1	10 Feb 86	N* ⁺	50	7	21
A2	3 Mar 86	Ca ⁺⁺	50	6	16
A3	18 Mar 86	Na ⁺	50	9	21
A4	8 Apr 86	Na ⁺	500	6	14
A5	22 Apr 86	Na ⁺⁺	2500	7	16
A6	8 May 86	Ca	2500	14	33
A7	10 Jun 86	P* ⁺⁺	10	57	368
A8	17 Jun 87	Mg ⁺	500	8	26
A9	13 Jul 87	Na ⁺	3000	7	18
A10	31 Jul 87	Na ⁺	5000	3	9
A11	9 Aug 87	Na	7000	10	30
B1	10 Feb 86	N, P* ⁺⁺	50, 10	41	97
B2	18 May 86	Ca ⁺	1000	66	359
B3	17 Jun 87	Na ⁺	2000	4	8
B4	25 Jun 87	Na ⁺	3000	5	12
B5	13 Jul 87	Na, Mg ⁺⁺	3000, 500	20	59

*Nitrogen (50 mg/L) and/or Phosphorus (10 mg/L) was added at this point and all subsequent experimental periods.

SYSTEM REACTORS AND START-UP

Two completely mixed, continuous flow, activated sludge reactors were operated in parallel. These reactors were of laboratory scale with a capacity of approximately 9.25 liters each. The reactors were constructed of Plexiglas with two chambers, one for aeration and mixing, the other for settling and clarification. The chambers were separated by an adjustable baffle (see Figure 1). A porous stone diffuser was placed in the aeration chamber and air was supplied at a constant rate to provide an average dissolved oxygen level near saturation and sufficient mixing.

Influent substrate was pumped into the reactors with a Cole-Parmer Model 755330 peristaltic pump through standard plastic tubing. Effluent flowed out of the reactors through tubing connected to overflow orifices in the clarification chamber. Tubes were disinfected intermittently with a Chlorox solution and rinsed with tap water.

Sludge "seed" was obtained from the aeration basin at the wastewater treatment plant at the Celanese Corporation located in Narrows, Virginia. The sludge was put into each reactor to a volume of 9.25 liters, aeration was started and the baffles put into place so as to promote settling in the clarification chamber. Feed was started at a predetermined rate. The entire system was placed in a constant temperature room kept at $20^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

SYSTEM OPERATION

Raw wastewater from the Celanese plant was collected at the end of the equalization basin so as to get the most homogeneous wastewater

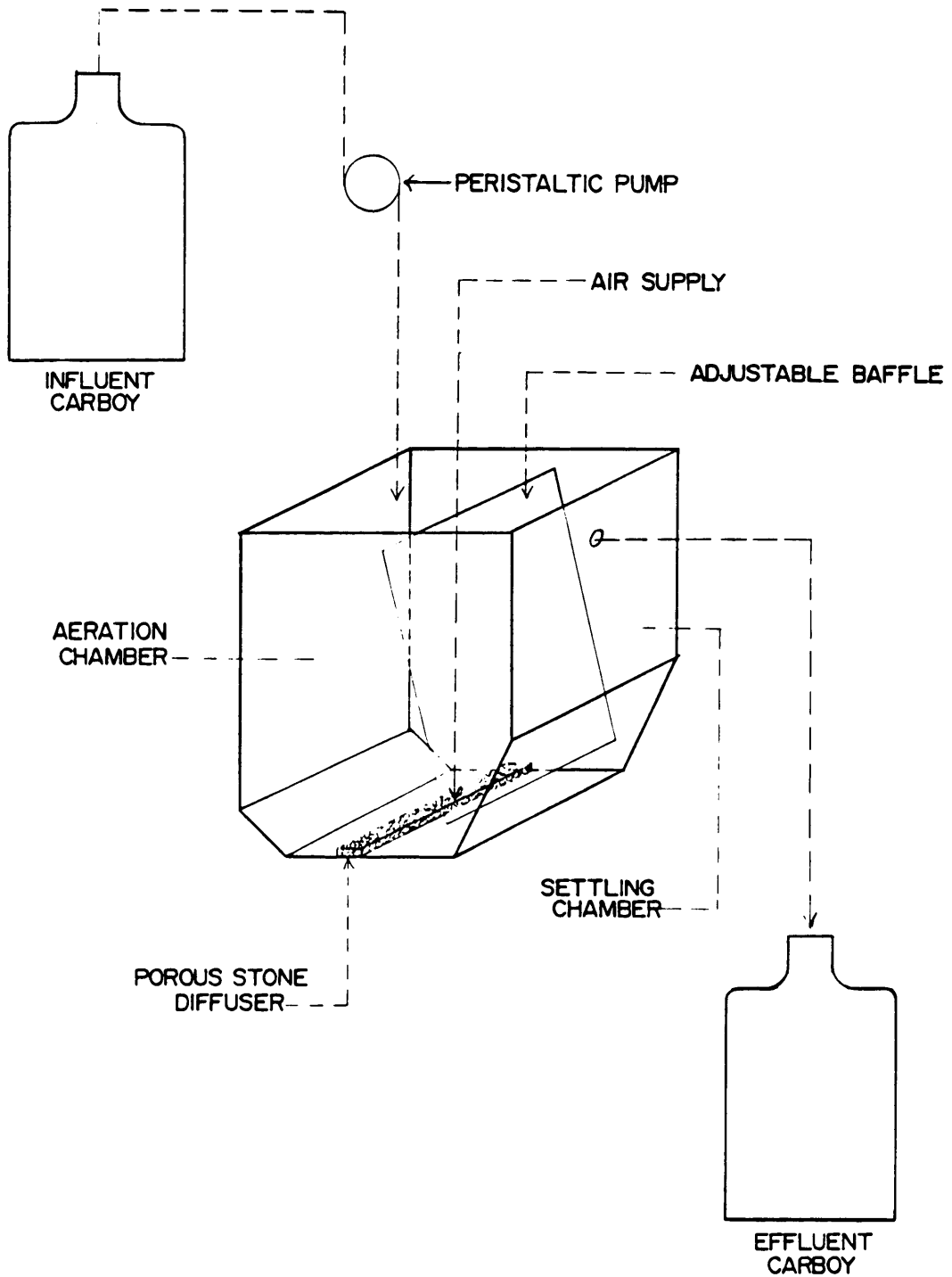


Figure 1. Completely mixed, continuous flow reactors.

possible. This wastewater was gathered in 18 liter plastic containers approximately every two weeks and kept at 4°C until ready to use. This raw wastewater was fed into the system at a rate of 3.2 millimeters per minute or 4.625 liters per day. This rate provided an hydraulic detention time of approximately two days.

Sludge was wasted at a rate of approximately 460 milliliters to provide a mean cell residence time (θ_c) of 20 days. Daily sludge wastage was performed by lifting the baffle between the aeration and clarification chambers and allowing complete mixing of the system before removing Mixed Liquor Suspended Solids (MLSS). Samples for Mixed Liquor Suspended Solids (MLSS) Capillary Suction Time (CST), and Specific Resistance were taken from this wasted sludge volume.

Since the wastewater has been characterized as nitrogen deficient at the plant, 50 mg/L of NH_4Cl as nitrogen was added to the wastewater before it was fed into both reactors.

Cations, added in the form of chloride salts, were introduced in different concentrations throughout the study period. Chloride salts were used consistently to avoid what might have been effects caused by different anions being introduced into the systems. Phosphorus was added in the form of potassium phosphate monobasic.

The reactors were monitored for operational parameters such as Mixed Liquor Suspended Solids (MLSS), Mixed Liquor Volatile Suspended Solids (MLVSS), Effluent Total Suspended Solids (TSS eff), Sludge Volume Index (SVI), Dissolved Oxygen (D.O.) and pH. Influent and Effluent

Chemical Oxygen Demand (COD), Specific Resistance, Oxygen Uptake Rate and capillary suction time analysis were performed to monitor reactor performance (See Table 2).

WASTEWATER COMPOSITION

As described earlier, the feed wastewater was obtained from the Celanese Plant. Celanese Corporation is a manufacturing operation which produces cellulose acetate resin, yarn, and tow. Although the waste streams generated are variable due to batch processes at the plant, Table 3, shows the relative composition of the wastewater. Small amounts of domestic sewage are also present in the wastewater.

ANALYTICAL METHODS AND TECHNIQUES

SOLIDS DETERMINATION (MLSS, MLVSS, TSS EFF)

Mixed Liquor Suspended Solids, Mixed Liquor Volatile Suspended Solids and Effluent Suspended Solids were determined in accordance with Standard Methods for the Examination of Water and Wastewater (1985). Sample volumes of 20 - 25 ml were used for effluent samples and 10 mL used for mixed liquor samples to facilitate ease of filtering. Samples were filtered through 5.5 cm Whatman 934 AH glass filters with a 5.5 cm porcelain Buchner Funnel. A Mettler Ac 100 Balance was used for weighing filters and aluminum pans. A number of Volatile Suspended Solids were determined analytically until an average of 70% MLSS was determined. In later calculations, $MLVSS = .70 MLSS$ was used. this Solids concentration was determined in accordance with Standard Methods for the Examination of Water and Wastewater (1985).

Table 2. Parameters Monitored.

INFLUENT FEED

- a. Chemical Oxygen Demand
- b. Atomic Absorption Analysis of Na+, Ca++, Mg++

MIXED LIQUOR

- a. Zone Settling Rate
- b. Dissolved Oxygen
- c. pH
- d. Oxygen Uptake Rate
- e. Specific Resistance
- f. Capillary Suction Time
- g. Sludge Volume Index
- h. Suspended Solids Concentration
- i. Volatile Suspended Solids Concentration

EFFLUENT

- a. Suspended Solids Concentration
 - b. Chemical Oxygen Demand
 - c. Atomic Absorption Analysis of Na+, Ca++, Mg++
-

Table 3. Composition of Raw Wastewater (Lee 1986)

Component	Concentration, mg/L
Acetic Acid	800 - 1,200
Ethanol	80 - 250
Acetone	60 - 150
Methyl Cyanide	20 - 50
Methyl Ethyl Ketone	1
Methanol	5 - 15
<u>Characteristic</u>	
COD	2500 - 4300
Total Nitrogen	10 - 15 (mg/L as N)
Total Phosphorus	40 - 60 (mg/L as P)
pH	3 - 5

SLUDGE VOLUME INDEX (SVI) AND ZONE SETTLING RATE.

Sludge settling characteristics were determined using the sludge volume index. The procedure used a one-liter graduated cylinder filled with 100 mL of sludge which is then allowed to settle for 30 minutes. The volume which the sludge occupies is then used in the following equation to calculate the SVI:

$$SVI = \frac{\text{Settled Sludge Volume, ml} \times 100}{\text{Mixed Liquor Suspended Solids, mg/L}} \quad [1]$$

The zone settling rate is determined by timing the sludge/supernatant interface velocity. SVI and zone settling rate were determined in accordance with Standard Methods for the Examination of Water and Wastewater (1985).

SPECIFIC RESISTANCE

A sample of 100 ml from the daily wasted sludge was filtered through a 11.0 cm porcelain Buchner Funnel, using Whatman No. 4 qualitative filter paper (see Figure 2). The volume passing through the filter (V) was measured over time (t) as well as initial solids and cake solids concentrations. The specific resistance was then calculated as follows:

$$r = \frac{2 PA^2 b}{\mu_c} \times 100 \quad [2]$$

where

- r = specific resistance, m/kg
- A = area of the filter paper, cm²
- b = slope of t/v versus v plot

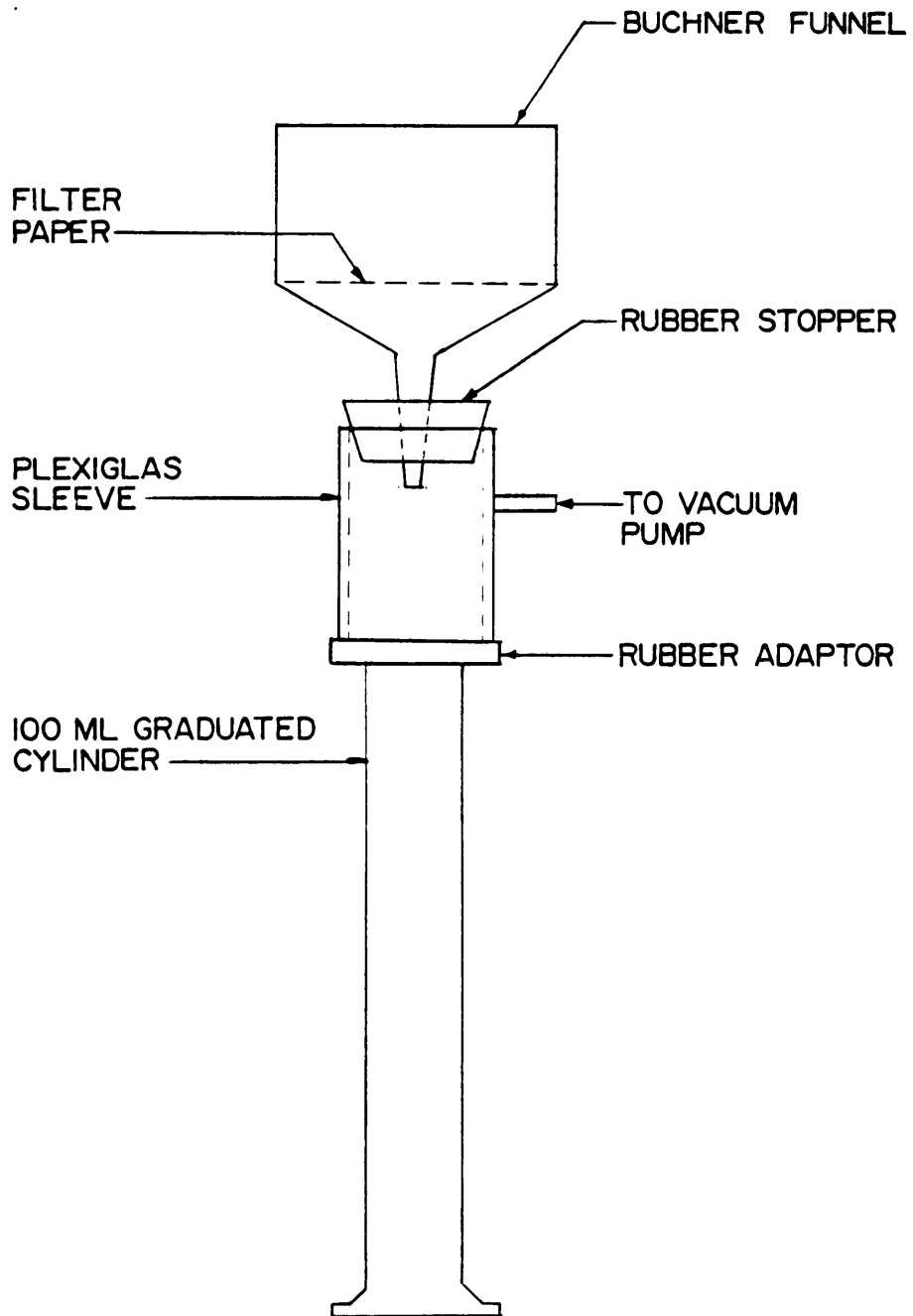


Figure 2. Apparatus for Specific Resistance Analysis.

P = pressures N/cm^2

μ = dynamic viscosity @ $20^\circ C = 1 \times 10^{-7} N \cdot sec/cm^2$

$$c = \frac{1}{\frac{100 - c_i}{c_i} - \frac{100 - c_f}{c_f}} = gm/cm^3$$

c_i = initial solids (%)

c_f = cake solids (%)

This specific resistance was determined in accordance with Standard Methods for the Examination of Water and Wastewater (1985).

CAPILLARY SUCTION TIME (CST)

Capillary suction time determinations were used to monitor the dewatering rate of the sludge. This measurement was made using a Triton HRC type 165 CST apparatus as shown in Figure 3. A small sample of mixed liquor suspended solids was placed into the sample cylinder which was placed along with the electrode plate, onto chromatography paper. The water flowing out of the sludge would then radiate out through the paper hitting one electrode to start the clock and then another which would stop the clock. Time was measured in seconds. This provided a relative measurement of the rate at which water came out of the sludge as it would be somewhat concentration dependent.

CHEMICAL OXYGEN DEMAND (COD)

The COD test was performed according to the procedure outlined in Standard Methods for the Examination of Water and Wastewater. Both the open reflux and closed reflux, titrimetric methods were used at first to establish reproducibility and when results were found to be the same,

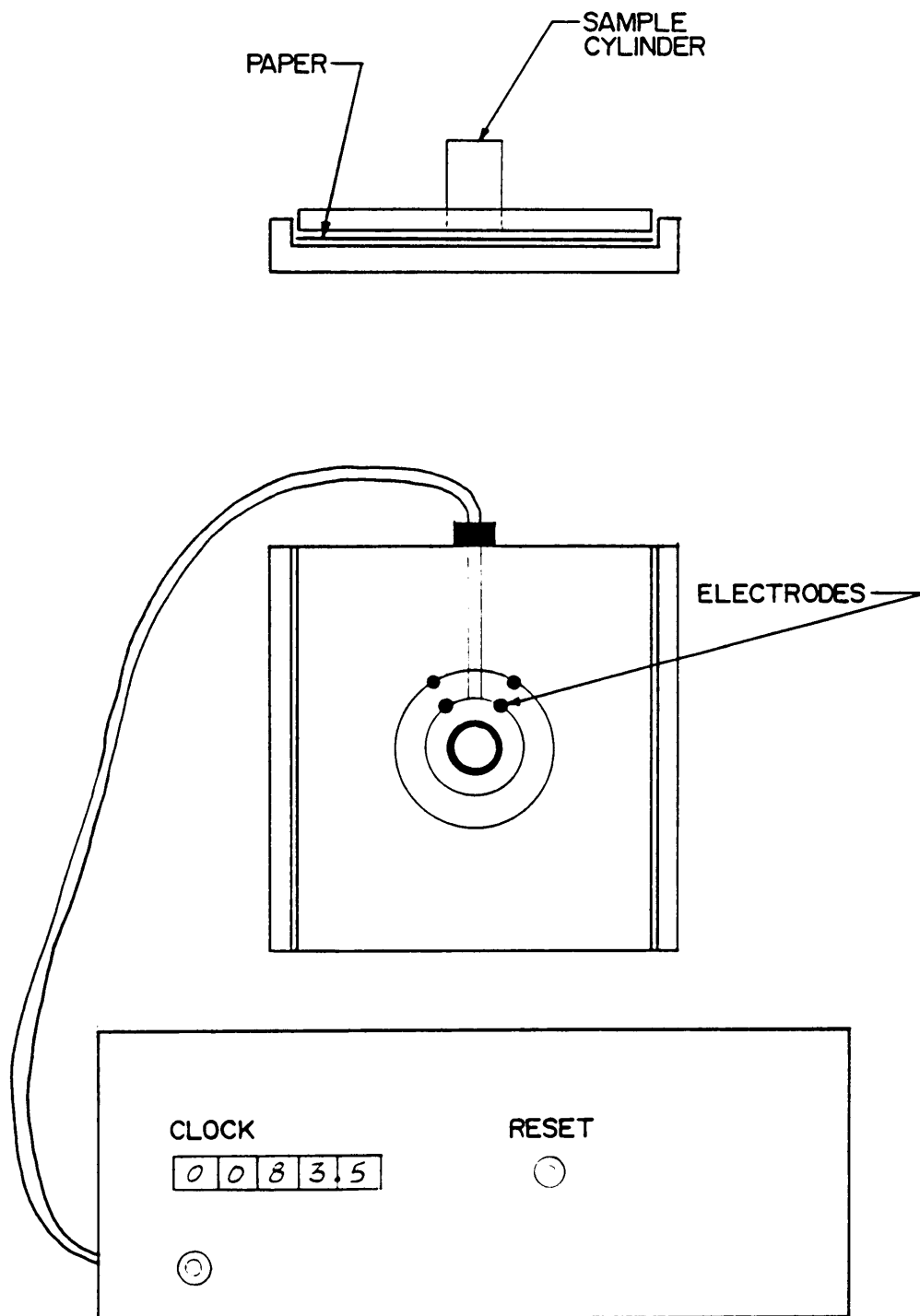


Figure 3. Apparatus for Capillary Suction Time.

the closed reflux method was used for all subsequent tests. Feed samples were taken directly from the wastewater carboys being used to feed the systems at the particular time. Effluent samples were taken from the effluent collected each day. COD measurements were made whenever other data were taken. Samples were filtered through .45 micron paper to remove any microorganisms present, acidified to pH 2 and placed at 4°C for no longer than a week before COD tests were run.

OXYGEN UPTAKE RATE (OUR)

The procedures followed for these measurements were as outlined in Standard Methods (1985). A 300 mL BOD bottle was used for holding the sample of mixed liquor suspended solids. A YSI Model 54 A Oxygen Meter (Yellow Springs Instrument Co.) with a YSI Model 5720A probe was first calibrated to the surrounding air in accordance with the manufacturer's instructions and Standard Methods (1985). The rate was determined by measuring the uptake of oxygen over time and a slope of best fit was determined by linear regression. This slope or rate was then put into this equation:

$$\text{OUR} = \frac{\text{Oxygen Consumption Rate, (mg/L)/min}}{\text{Volatile non-filterable residue g/L}} \times \frac{60 \text{ min}}{\text{hr}} \quad [3]$$

DISSOLVED OXYGEN (D.O.) AND pH

D.O. was generally measured at the same time as OUR and was used as the initial reading. Procedures followed were as outlined in Standard Methods (1985). pH was measured with a Fisher Accumet Model 610A pH meter and was performed in accordance with the glass electrode method described in Standard Methods (1985). The meter was standardized

prior to each reading with commercial buffer solutions.

CATION ANALYSIS

Influent and effluent samples were taken at sporadic intervals and analyzed for concentrations of Ca^{++} , Mg^{++} , and Na^+ ions. Procedures used are outlined in Standard Methods for the Examination of Water and Wastewater (1985). The equipment used was a Perkin-Elmer Model 703 Atomic Absorption Spectrophotometer.

IV. RESULTS AND DISCUSSION

In 1986, a full-scale study of cation effects on activated sludge settling was conducted under the guidance of Novak and Randall (1986) at the Celanese Corporation Wastewater Treatment Plant. The plant was experiencing problems with activated sludge flocculation and settling. These problems were believed to be a direct result of sodium hydroxide addition to acidic waste streams to prevent inhibition of the biological system due to low pH. Past research had suggested that both an increase in pH and the presence of sodium ions could lead to sludge deflocculation and that to counter this deflocculation, pH reduction and divalent cation addition could be used. In the plant study, divalent cations were used in the form of calcium chloride which was added directly to the waste. The results of this study can be seen in Figures 4 and 5. As is shown in these figures, the sludge characteristics (effluent suspended solids, sludge blanket height and one hour settling) over time were getting worse as long as sodium hydroxide additions continued. Once calcium chloride was introduced, a rapid recovery of the sludge flocculation and settling properties resulted.

It was the results of the full-scale study which prompted the research described herein. The main objective of this research was to simulate plant conditions in the laboratory. Four major topics of inquiry were addressed. The first topic was to determine whether the previously observed results were effects caused by the addition of divalent cations. The second topic was to investigate whether the deterioration associated with the addition of sodium hydroxide was a

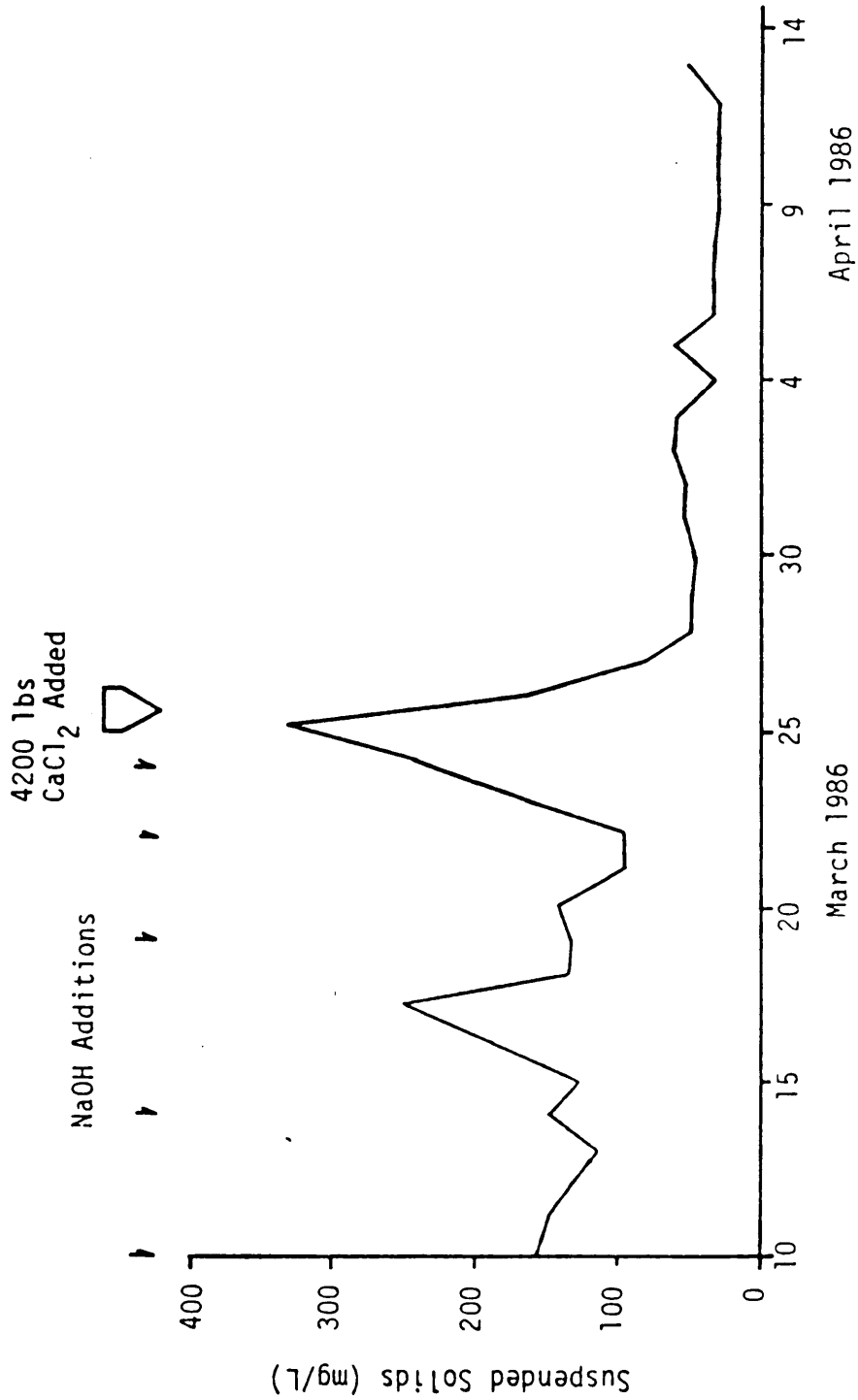


Figure 5. Variation in Effluent Suspended Solids for Celanese Wastewater Treatment Plant (Novak and Randall, 1986).

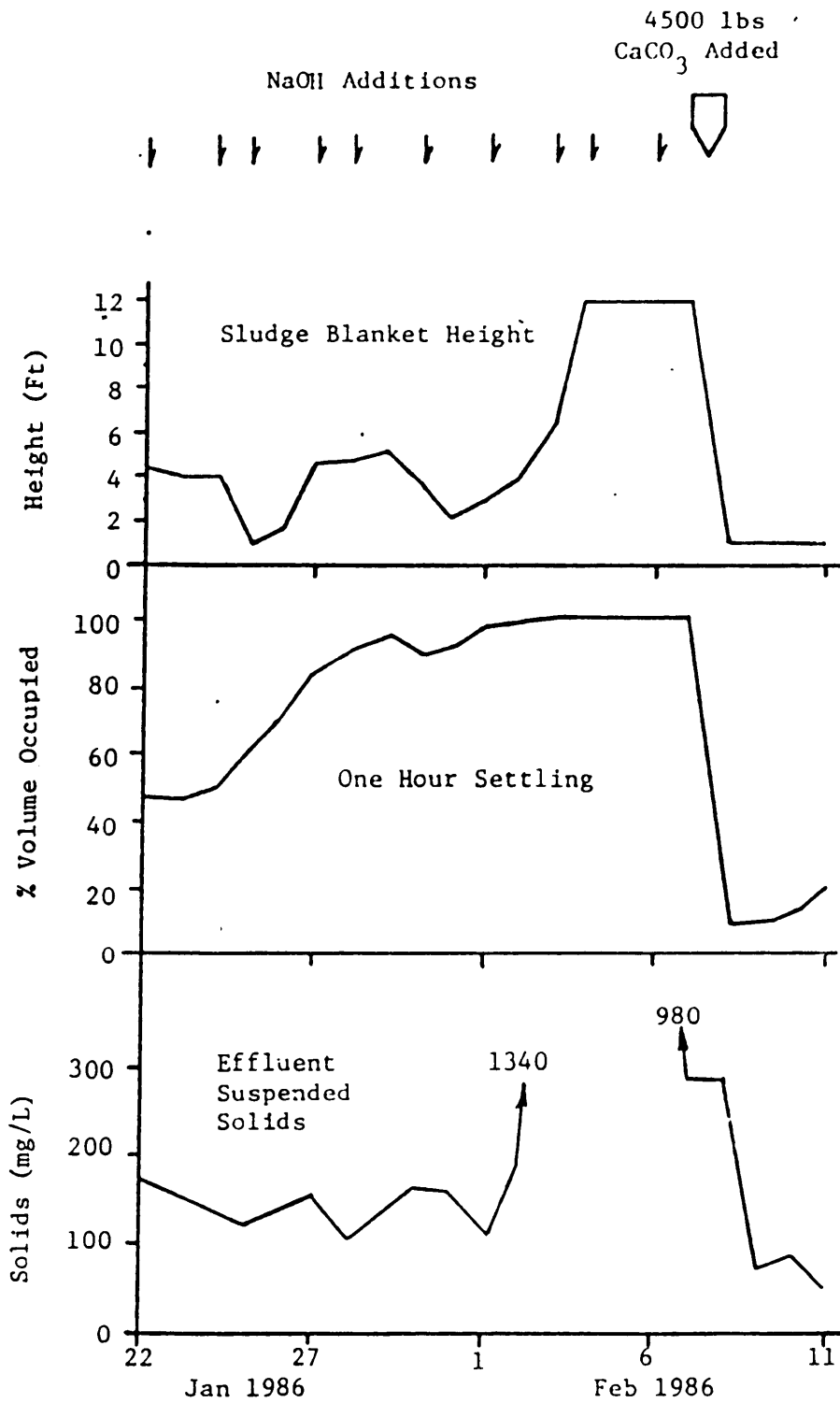


Figure 4. Operating characteristics of the Celanese Wastewater Treatment Plant (Novak and Randall, 1986).

direct result of the sodium ion or instead, by compounds formed from the reaction of sodium hydroxide with constituents in the wastewater. The third topic addressed was whether there was a specific concentration where sodium caused detrimental effects to the system. The fourth topic was to find if there was an optimum concentration of divalent cations where the best operational parameters could be maintained.

In order to accomplish the objectives of this research, two continuous flow, completely mixed, activated sludge reactors were operated and monitored for approximately twenty months. Wastewater used was collected from the Celanese plant, salts were added to each reactor and data collection was started after approximately two days or one hydraulic detention time. The performance data which were collected for each salt addition have been tabulated and can be found in the appendix.

METHOD OF ANALYSIS

The nature of the wastewater used in this research from the Celanese Wastewater Plant was quite different from those typically encountered in municipal systems. The Celanese cellulose acetate fibers plant produces an extremely variable waste. Because of this variability, the sludge characteristics at the wastewater treatment plant are also variable. Therefore, the sludge characteristics are not comparable to those from municipal treatment studies. Effluent Suspended Solids are much higher, as is the Sludge Volume Index. In looking at the data, it must be taken into account that laboratory scale studies will also exaggerate the already unusual characteristics of the sludge.

The salts which were being fed to a specific reactor over the study period were often alternated. This makes it necessary, when analyzing the data during a specific experimental period to take the following conditions into consideration to see what effects were realized:

1. Cation of interest
2. Concentration of cation of interest
3. Cation which preceded the cation of interest.

This last condition is important because the preceding cation may have altered the system such that these effects were noted for some time after a cation change occurred.

In addition to the considerations listed above, cation concentrations preexisting in the Celanese wastewater used must also be taken into consideration. Magnesium levels from the plant were generally found to be between 800 and 900 mg/L. Calcium levels were generally around 40 mg/L. These concentrations must be added to each of the experimental salt additions when evaluating the data.

PHYSICOCHEMICAL VS. BIOLOGICAL EFFECT OF CATIONS

In the study of plant operations performed at the Celanese plant, Novak and Randall (1986) described the effect calcium had on the sludge as being a physicochemical effect and used coagulation theory to explain the observed responses. The calcium added to the activated sludge basin produced an immediate improvement in sludge flocculation and settling properties. It was assumed that similar results could be achieved in the laboratory. Sodium was added to the Celanese waste in different concentrations to try and cause deterioration of the sludge properties

as had been theorized to have occurred at the Celanese plant. Divalent cations, Ca^{++} and Mg^{++} , were put into the system to try and restore the good sludge properties. What was found in the laboratory was, rather than an immediate physicochemical response, a slower response suggestive of a biological change. The typical response to the salts added were, in most cases, characterized by the parameter immediately deteriorating and then gradually going back to its level before the salt addition or settling on a new level. These transient curves suggest more is going on than a simple physical, chemical cause and effect relationship can explain.

THE EFFECT OF PHOSPHORUS ON THE SYSTEM

The Celanese wastewater had rather low levels of phosphorus. It was not known whether the level of phosphorus present would be a limiting factor in the activated sludge growth. It was the objective of this portion of the study to see what effect, if any, the addition of phosphorus might have on the flocculation and settling of the activated sludge.

At the start of the experiments, one reactor was run with the addition of 50 mg/L of nitrogen and the other was run with the addition of both 50 mg/L of nitrogen and 10 mg/L of phosphorus. Approximately halfway through the experiments, the one previously receiving nitrogen alone began receiving phosphorus also (see Table 1). With the preexisting levels of nitrogen and phosphorus at 10 mg/L and 40 mg/L respectively, the experimental addition would set the new levels at 60 mg/L of nitrogen and 50 mg/L of phosphorus. Comparing the two different

reactors at the beginning, the Effluent Suspended Solids were quite different. Looking at Figure 6, the reactor receiving nitrogen had an Effluent Suspended Solids of approximately 289 mg/L. The other reactor, being fed both phosphorus and nitrogen (Figure 7), had an Effluent Suspended Solids of approximately 436 mg/L towards the end of the experiment. Looking at the SVI for the nitrogen only reactor, a value of approximately 60 was typical (see Figure 8) and for the nitrogen/phosphorus reactor the equilibrium SVI was approximately 80 (see Figure 9). These numbers might lead to the conclusion that phosphorus caused some deterioration in the system, but examining data from the first reactor when phosphorus was added, a number of 150 mg/L for the Effluent Suspended Solids is seen (see Figure 10). Only the first set of data points in this experimental period have been used in the analysis, as the reactor exhibited a period of intense filamentous growth which disrupted the system and which resulted in a new seed sludge being required. The average SVI of this reactor was about 80 (see Figure 11). The Oxygen Uptake Rates for the two experimental periods which received phosphorus were approximately the same at 7.5 and 8.0 as shown in Figures 12 and 13, which suggests that some reproducibility was maintained.

Because of the difference in values between the two reactors, a conclusion as to the effects of phosphorus on the parameter of Effluent Suspended Solids cannot be made. This outcome may have been caused by some biological aspect not readily apparent in the system. Pavoni et al. (1972) concluded in a study that flocculation does not occur unless

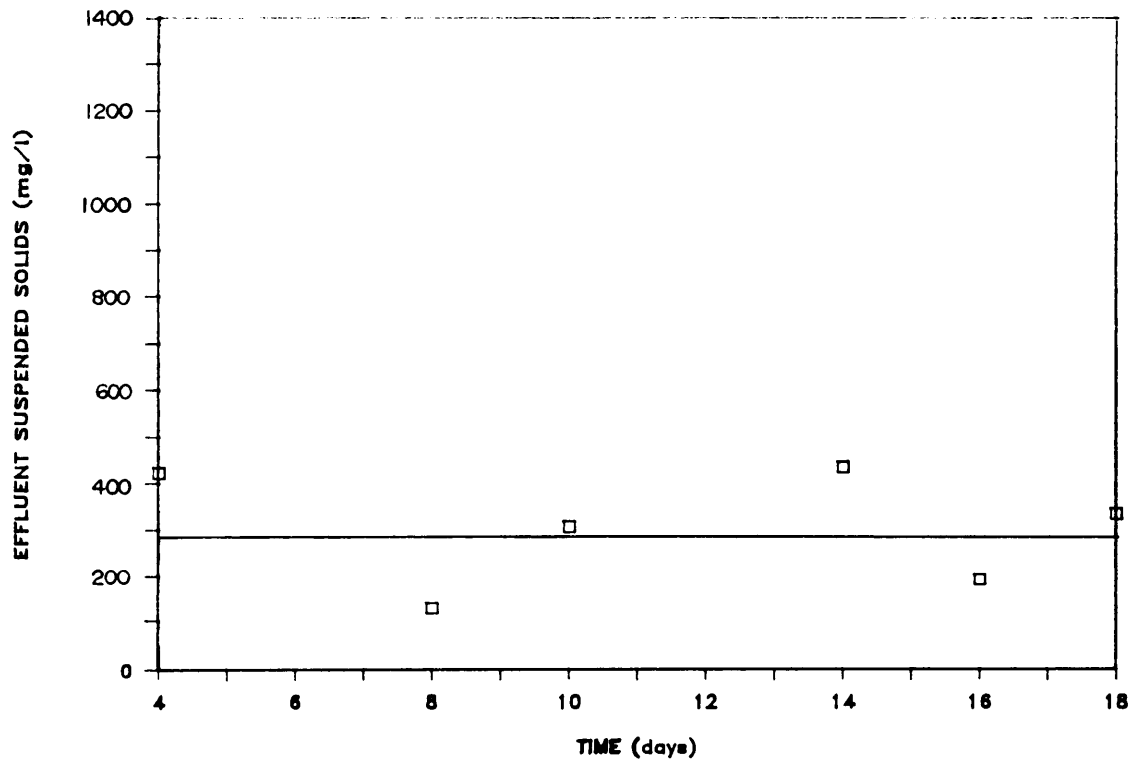


Figure 6. Effluent Suspended Solids for experimental period A1 - 50 mg/l Nitrogen.

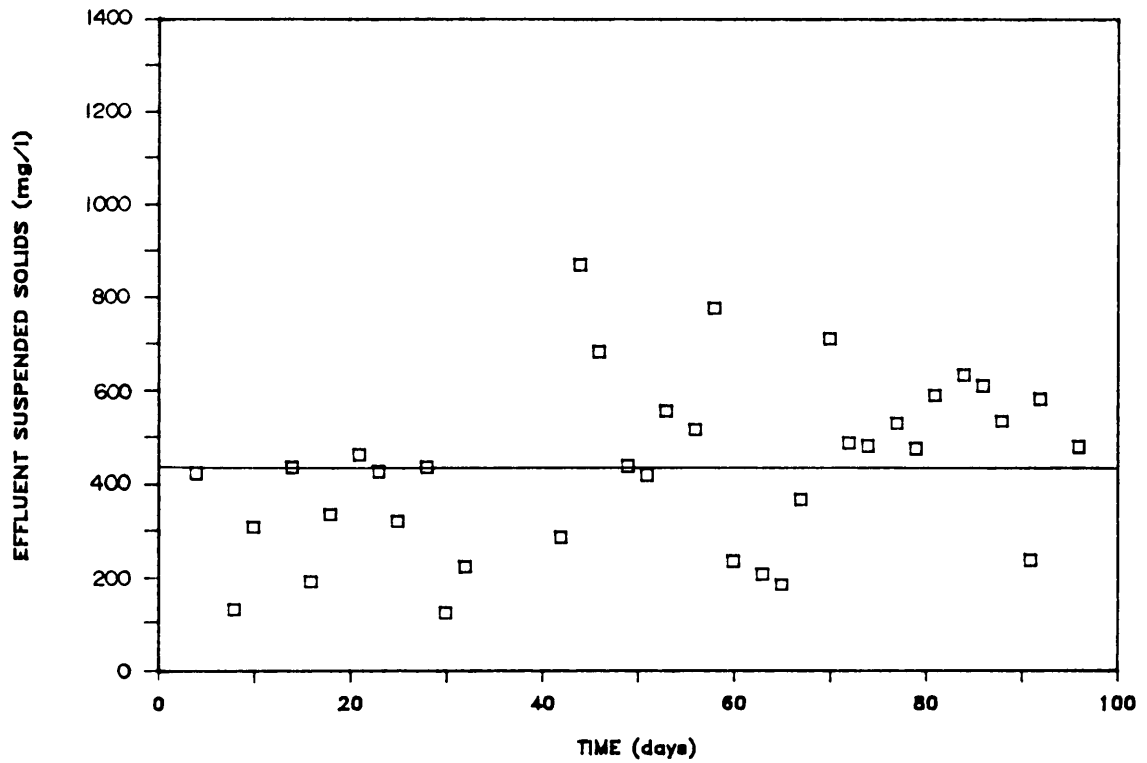


Figure 7. Effluent Suspended Solids for experimental period B1 - 50 mg/l Nitrogen, 10 mg/l Phosphorous.

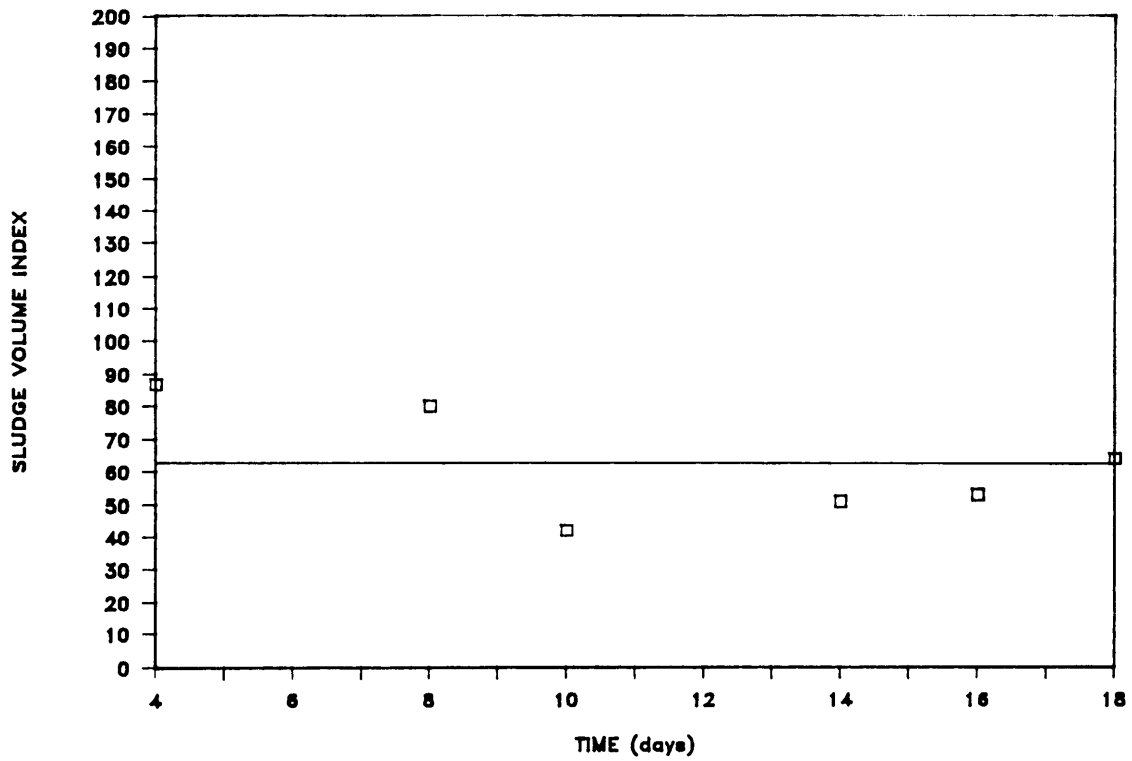


Figure 8. Sludge Volume Indexes for experimental period A1 - 50 mg/l Nitrogen.

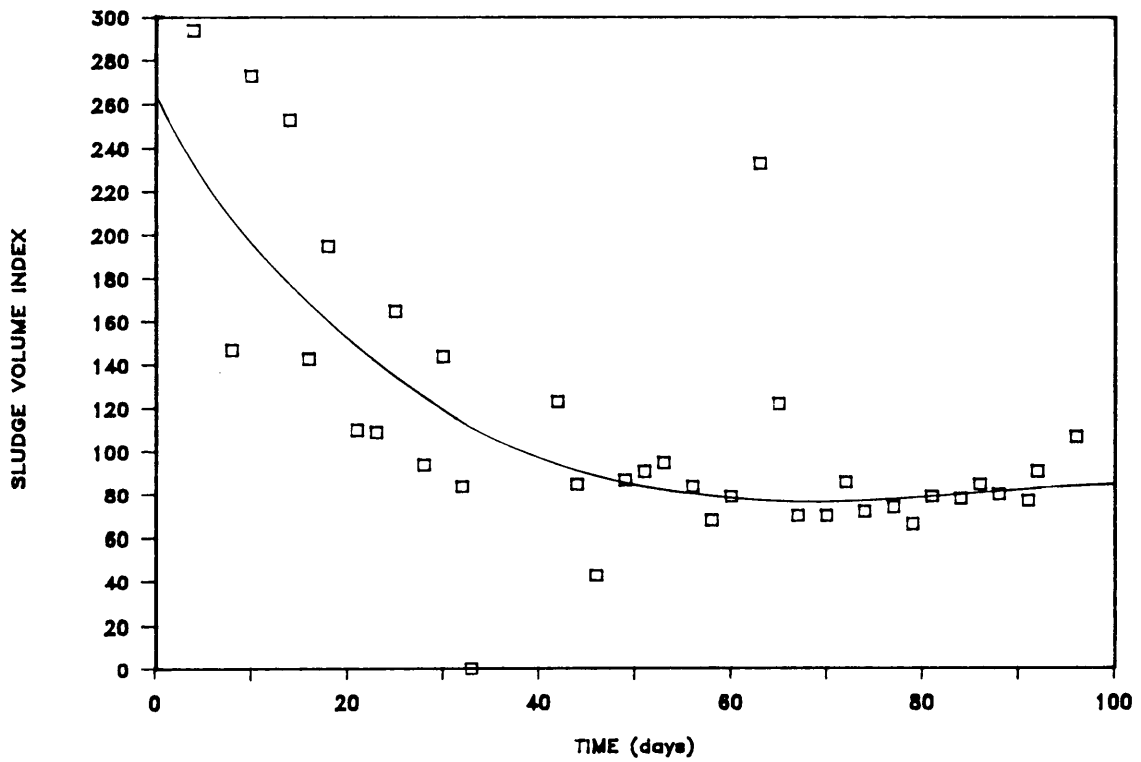


Figure 9. Sludge Volume Indexes for experimental period B1 - 50 mg/l Nitrogen, 10 mg/l Phosphorous.

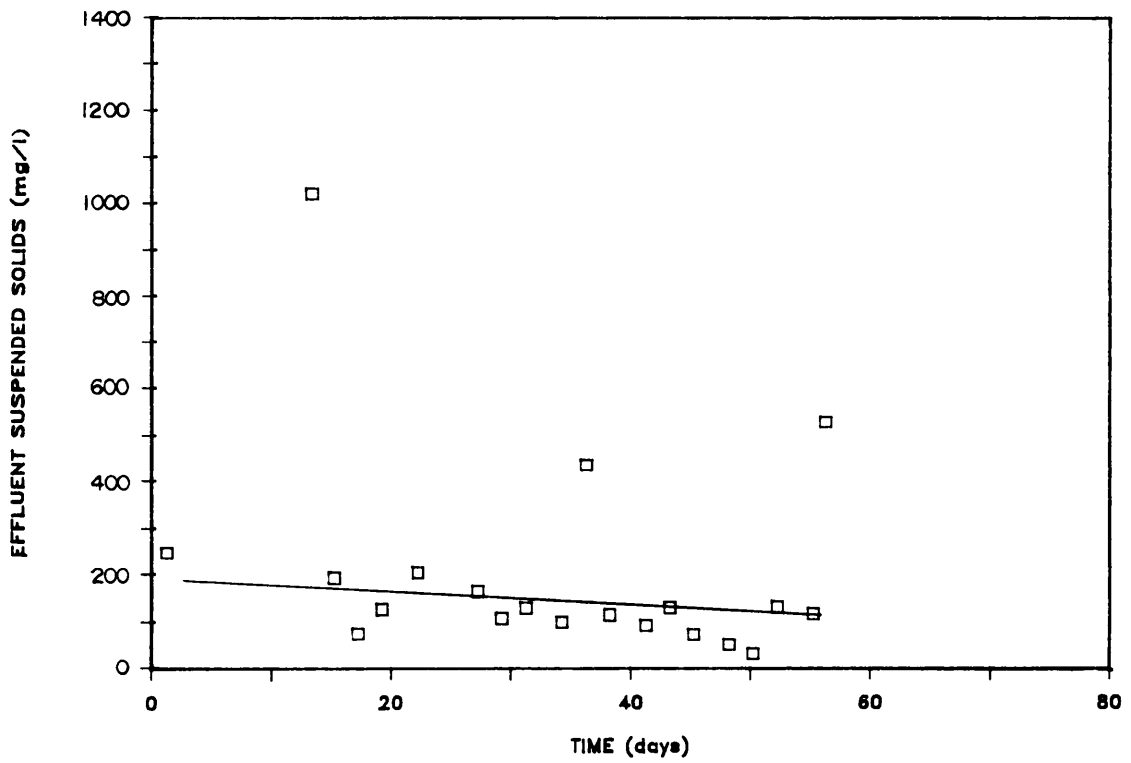


Figure 10. Effluent Suspended Solids for experimental period A7 - 50 mg/l Nitrogen, 10 mg/l Phosphorous.

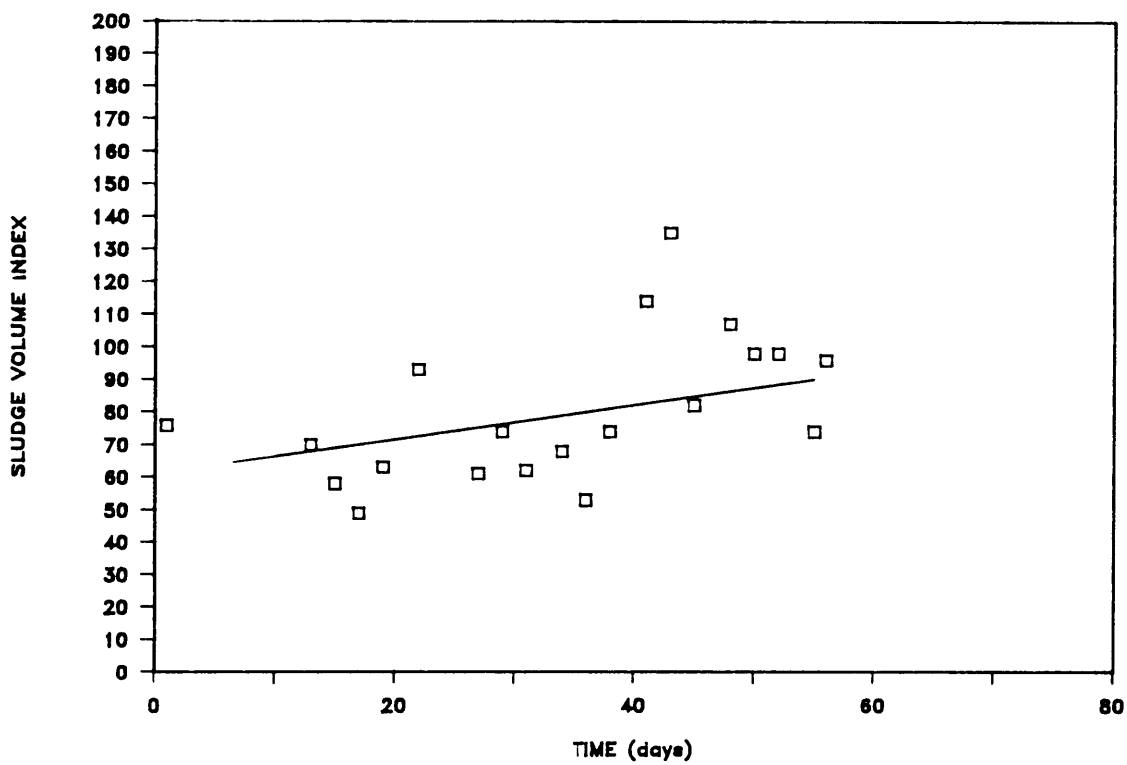


Figure 11. Sludge Volume Indexes for experimental period A7 - 50 mg/l Nitrogen, 10 mg/l Phosphorous.

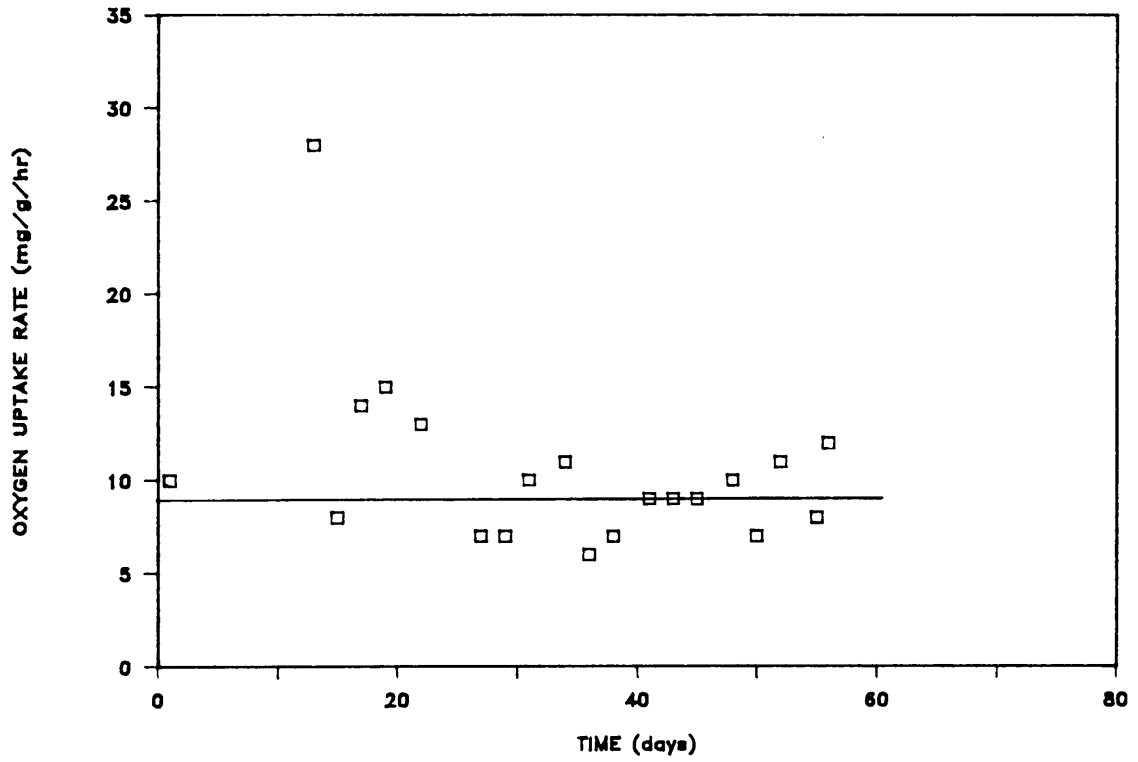


Figure 12. Oxygen Uptake Rates for experimental period A7 - 50 mg/l Nitrogen, 10 mg/l Phosphorous.

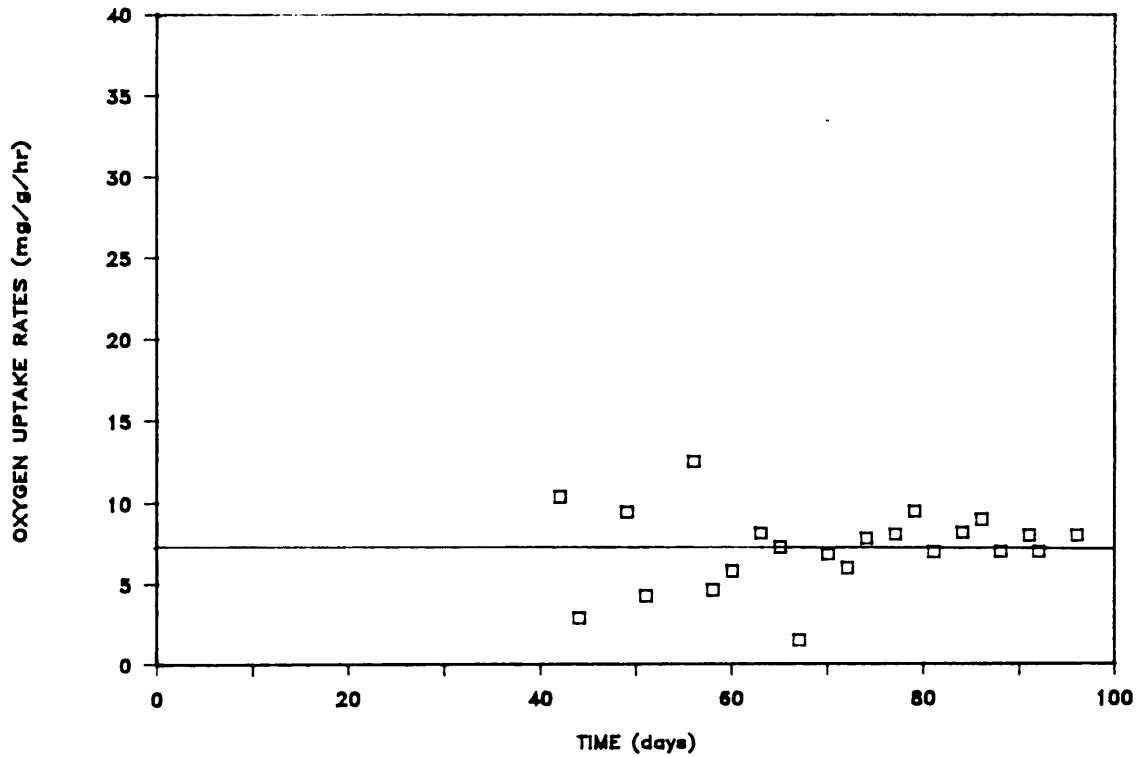


Figure 13. Oxygen Uptake Rates for experimental period B1 - 50 mg/l Nitrogen, 10 mg/l Phosphorous.

growth of the organisms within the sludge is in the endogenous phase. Perhaps what is being seen is a stimulation of the growth due to phosphorus which would promote dispersion of the microorganisms thus producing a higher Effluent Suspended Solids. The differences between the nitrogen only and the nitrogen with phosphorus reactors were small but it appears that there was a general trend which suggests that the phosphorus affected the SVI negatively.

THE EFFECTS OF MAGNESIUM ON THE SYSTEM

Studies in the past have suggested that divalent cations can improve the flocculation and settling of sludges. The full-scale study by Novak and Randall (1986) used calcium and showed marked improvement to the sludge. It was the objective of this research to see if a divalent cation other than calcium would create beneficial effects on the system.

An addition of 500 mg/L MgCl-Mg^{++} to reactor #1 was begun after a period of time where the reactor was receiving 50 mg/L nitrogen and 10 mg/L of phosphorus. The phosphorus and nitrogen continued to be fed into the system in addition to the magnesium. Because of preexisting levels of approximately 800 mg/L Mg^{++} , the total concentration would be 1300 mg/L Mg^{++} .

Figure 14 shows the Effluent Suspended Solids which averaged around 200 mg/L. Figure 15 shows the SVI dropped to approximately 60 which is an improvement over the 80 held before the addition of the magnesium. The Oxygen Uptake Rate of approximately 13 mg/g/hr (Figure 16) does rise well above the 7.0-8.0 mg/g/hr given in the baseline

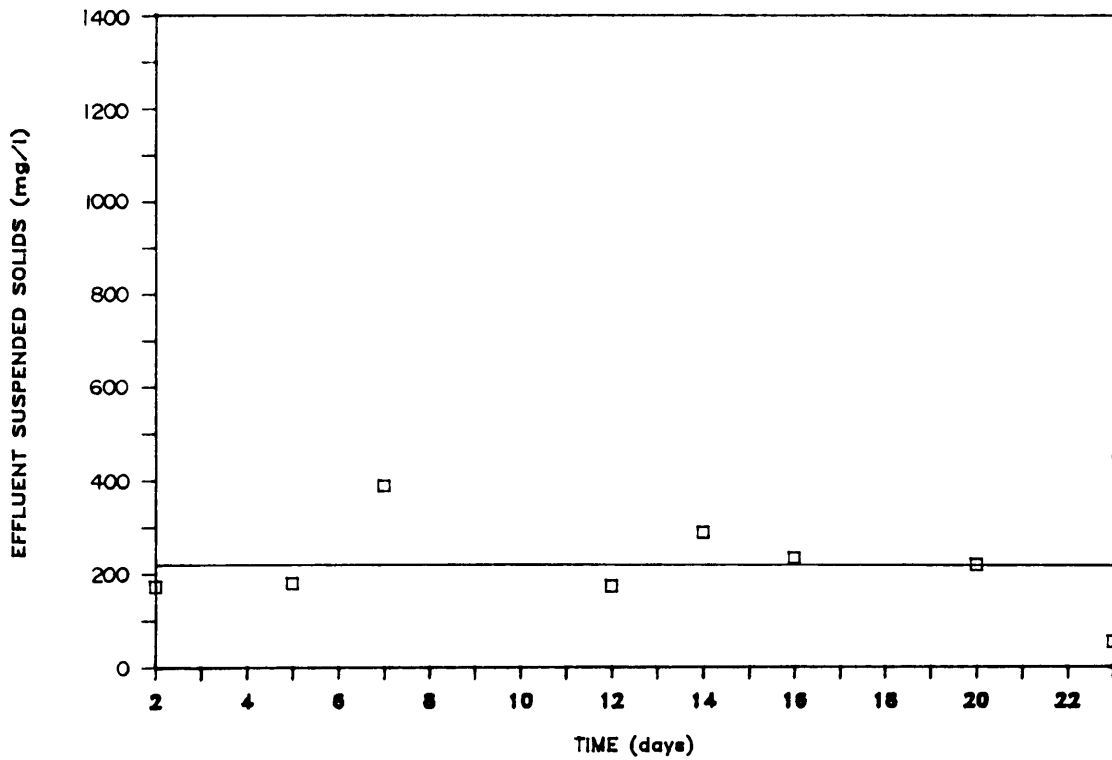


Figure 14. Effluent Suspended Solids for experimental period A8 - 500 mg/l Magnesium.

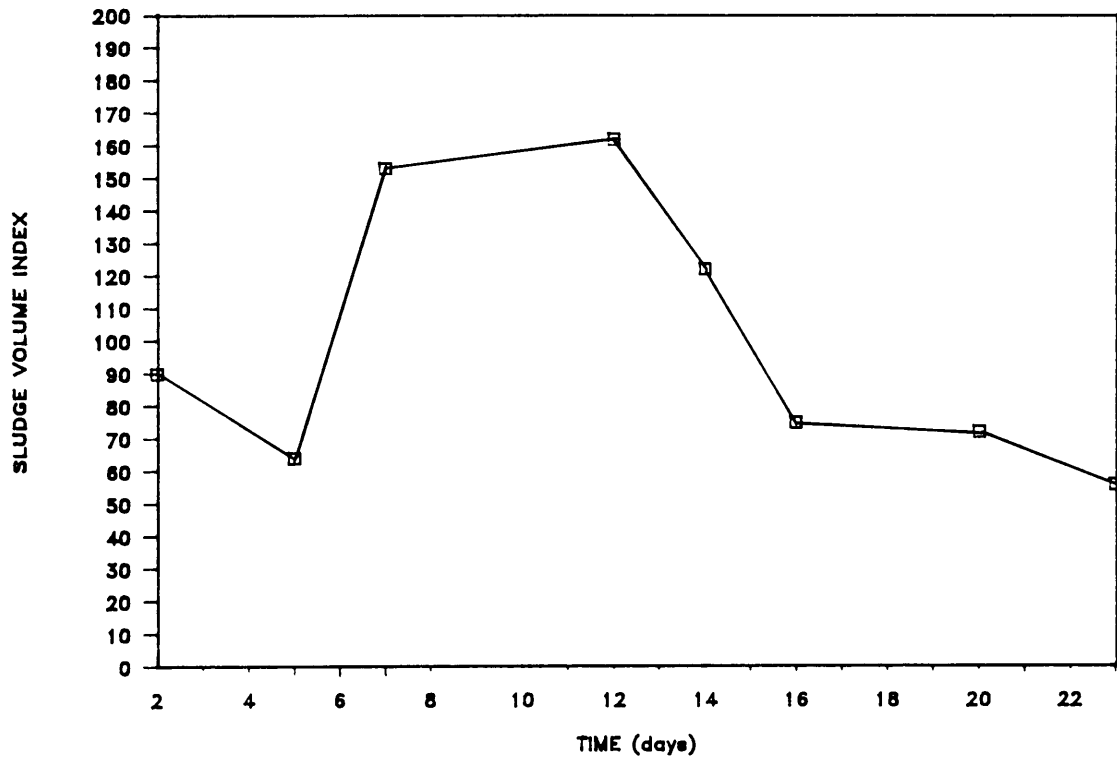


Figure 15. Sludge Volume Indexes for experimental period A8 - 500 mg/l Magnesium.

nitrogen phosphorus experiments but it is not known how this parameter would affect the sludge properties. Capillary Suction Times and Zone Settling Rates remained approximately the same at about 10 seconds and 1.5 cm/min, respectively. Conclusions as to whether these numbers represent true improvements are rather tenuous, but during the experiments, a distinct change in the visual characteristics of the sludge could be recognized. Prior to magnesium addition the sludge did not settle with a distinct sludge/supernatant interface, however when magnesium was added this interface became very well defined.

A second experiment with magnesium was carried out on reactor #2. At a point where 3000 mg/L of sodium was being added, 500 mg/L of magnesium was also added to see if the two additions at one time might have any marked effect. Effluent Suspended Solids remained the same at about 150 mg/L and Oxygen Uptake Rates remained relatively constant at about 10 mg/g/hr. However, three of the parameters became very sporadic suggesting some sort of upset to the system. The Zone Settling Rate varied from 4 to 1 cm/min as shown in Figure 17. The Sludge Volume Index became very sporadic as shown in Figure 18 as did the values for Specific Resistance which oscillated between 0.9 and 0.1×10^{12} m/kg.

The analyses did not show that magnesium had any effect on the system except to improve the Sludge Volume Index slightly. What could be seen in this experiment was a visual change in the characteristics of the settling sludge. The improvement of the sludge/supernatant interface could be considered a beneficial effect if it was indeed

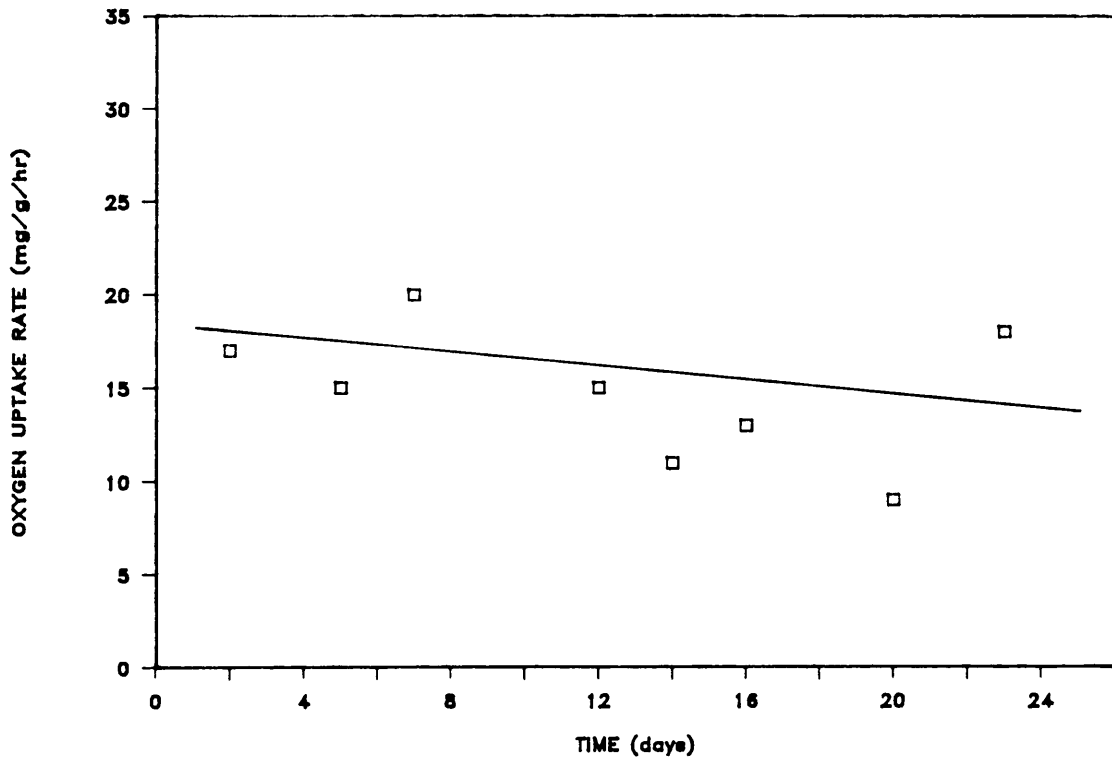


Figure 16. Oxygen Uptake Rates for experimental period A8
- .500 mg/l Magnesium.

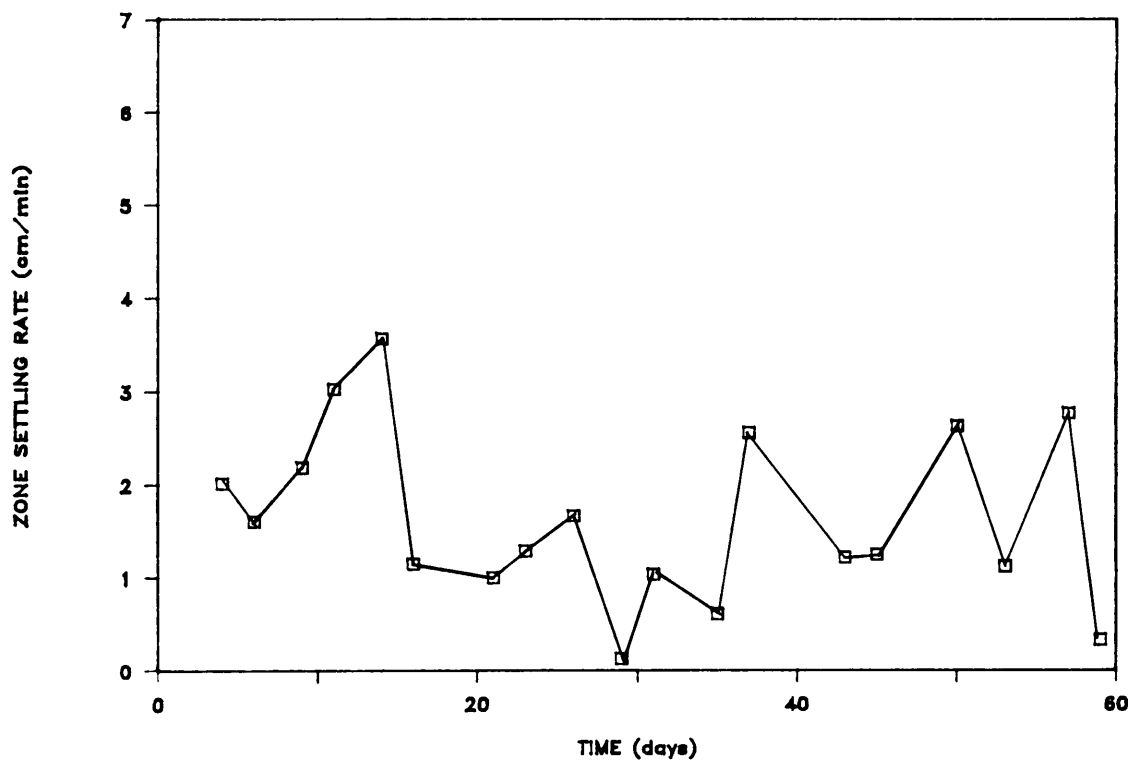


Figure 17. Zone Settling Rates for experimental period B5
- 3000 mg/l Sodium, 500 mg/l Magnesium.

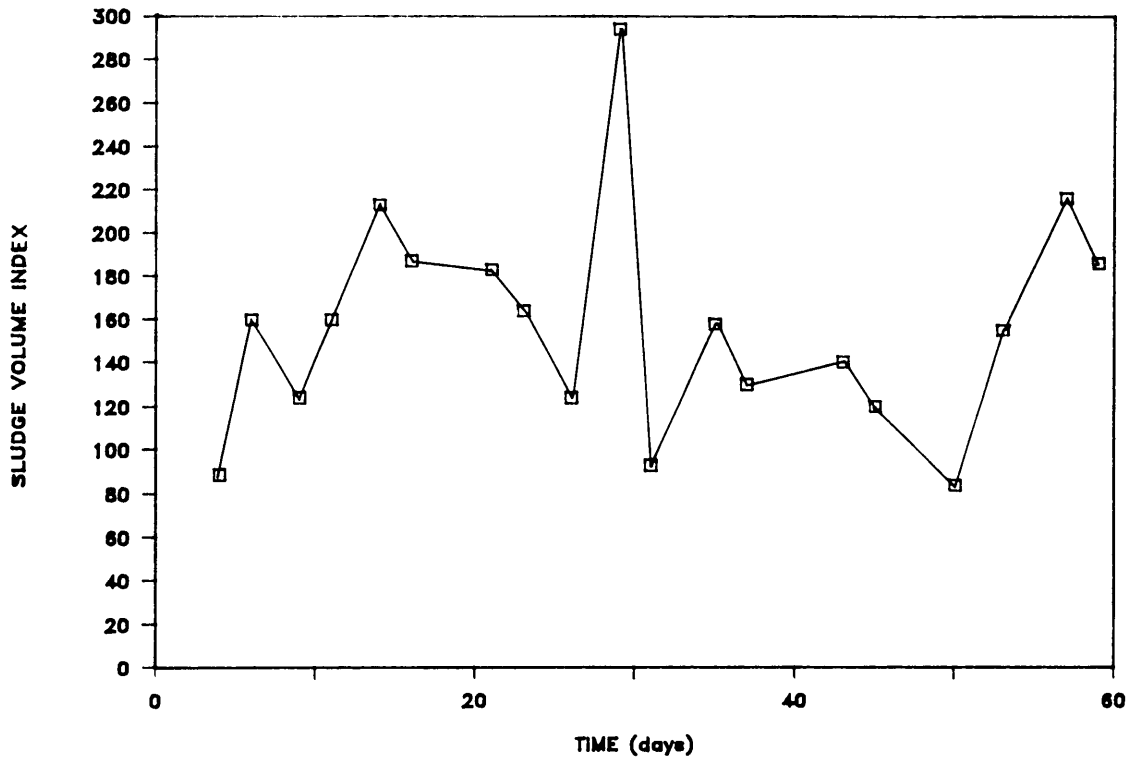


Figure 18. Sludge Volume Indexes for experimental period B5 - 3000 mg/l Sodium, 500 mg/l Magnesium.

caused by the magnesium. The upset of the system when both sodium and magnesium were added together may show that there were some competing reactions going on which caused unstable conditions for the sludge.

THE EFFECT OF CALCIUM ON THE SYSTEM

In the plant study conducted by Novak and Randall (1986) they added calcium chloride to the wastewater stream at which time the Effluent Suspended Solids were reduced from approximately 300 mg/L to 100 mg/L in one study and 300 mg/L to 40 mg/L in another study. They documented that at the 1.5 MGD plant, they added approximately 4200 lbs which would come to an addition of about 336 mg/L calcium chloride or about 127 mg/L of calcium. The following experiments were designed to duplicate these conditions. Experimental periods with additions of 50 mg/L, 1000 mg/L and 2500 mg/L of calcium were monitored and the results are presented in this section.

In the first experiment, 50 mg/L calcium was added to reactor #1, which had previously been receiving 50 mg/L of nitrogen. This addition of 50 mg/L calcium to the already preexisting concentration of 40 mg/L brought the level up to 90 mg/L calcium. Nitrogen was continued throughout this experimental period so the nitrogen only condition will be used as the baseline upon which the effects of calcium will be evaluated. Looking at both the Effluent Suspended Solids and SVI no quantifiable changes can be seen. Effluent Suspended Solids and SVI for the nitrogen experimental period were 275 mg/L and 60 respectively. Examining Figures 19 and 20 for the experimental period for 50 mg/L Ca^{++} , Effluent Suspended Solids and SVI were 300 mg/L and 60. It would

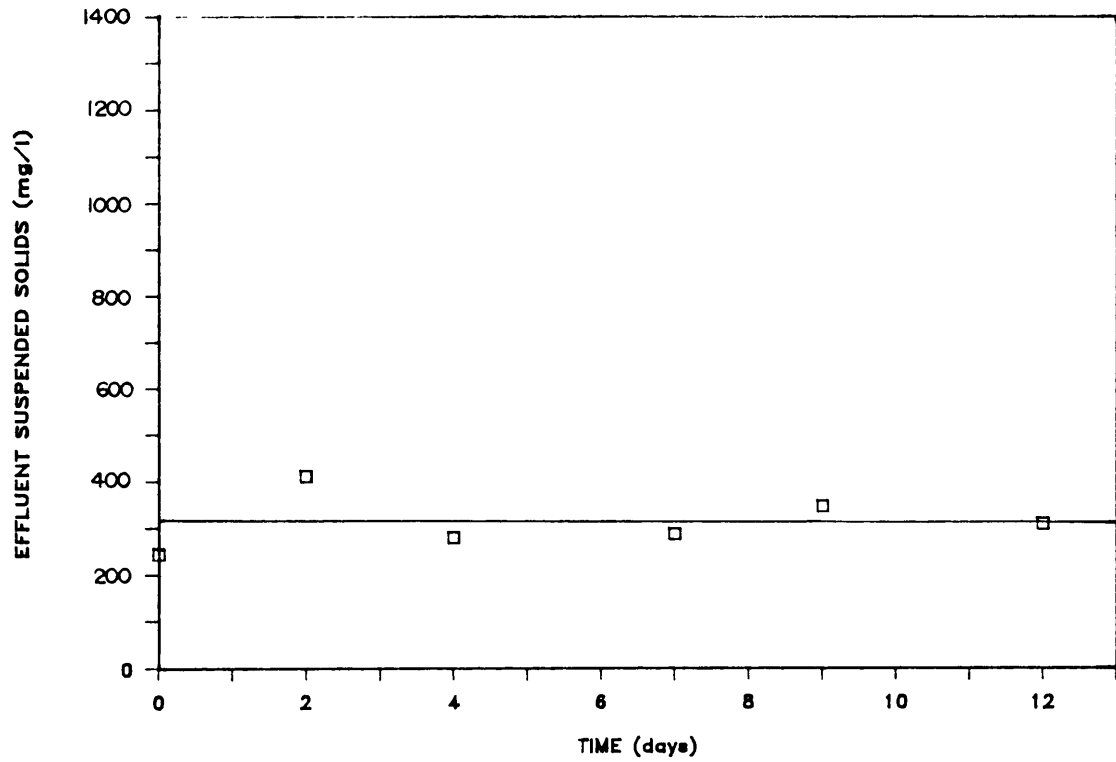


Figure 19. Effluent Suspended Solids for experimental period A2 - 50 mg/l Calcium.

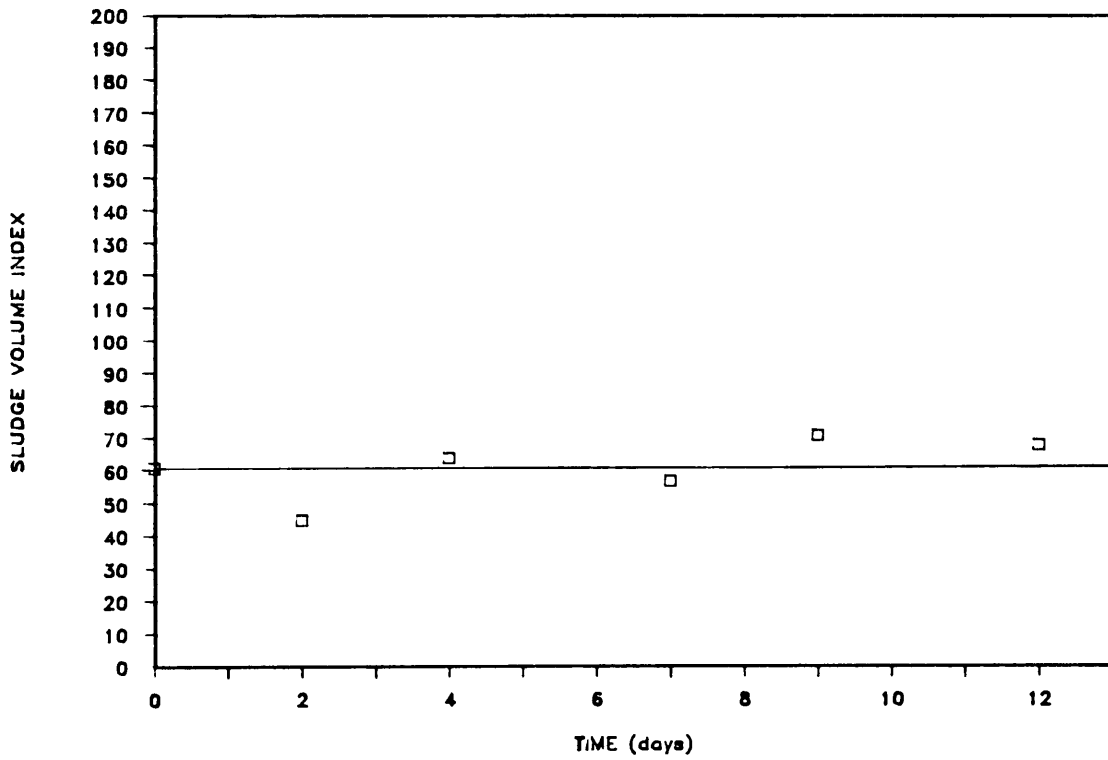


Figure 20. Sludge Volume Indexes for experimental period A2 - 50 mg/l Calcium.

appear that a 50 mg/L Ca^{++} addition is not sufficient to produce any changes in the system.

An experimental study was then conducted where 1000 mg/L of calcium was added to Reactor #2. The total calcium concentration was at 1040 in the system. In this system both nitrogen and phosphorus had been added in the period preceding so that this condition will be used as the basis for comparison. The last half of the 1000 mg/L Ca^{++} experimental period was characterized by filamentous growth so only the first half of the data will be used in the comparisons. Comparing the Effluent Suspended Solids of the two periods it is seen that the preceding period was around 436 mg/L (see Figure 6) and although at the end of the calcium period the general trend was downwards, the time period was very long suggesting that the calcium was not effective in reducing the Effluent Suspended Solids at this concentration (see Figure 21). Effluent Suspended Solids averaged 400 mg/L. The SVI of the preceding period had been approximately 80 (refer to Figure 9), SVI during the 1000 mg/L Ca^{++} period dropped to approximately 60 and stayed at that value until the filamentous growth began to affect the system (see Figure 22). Oxygen Uptake Rates stayed relatively consistent with the preceding period at a value of about 7.5 mg/g/hr.

Lastly, an experimental period was carried out where 2500 mg/L calcium was fed to reactor #1. This is a particularly noteworthy experiment as it followed an experiment where 2500 mg/L of sodium was used. The results can be compared to the study of Novak and Randall (1986) which showed marked effect upon the system when calcium was added

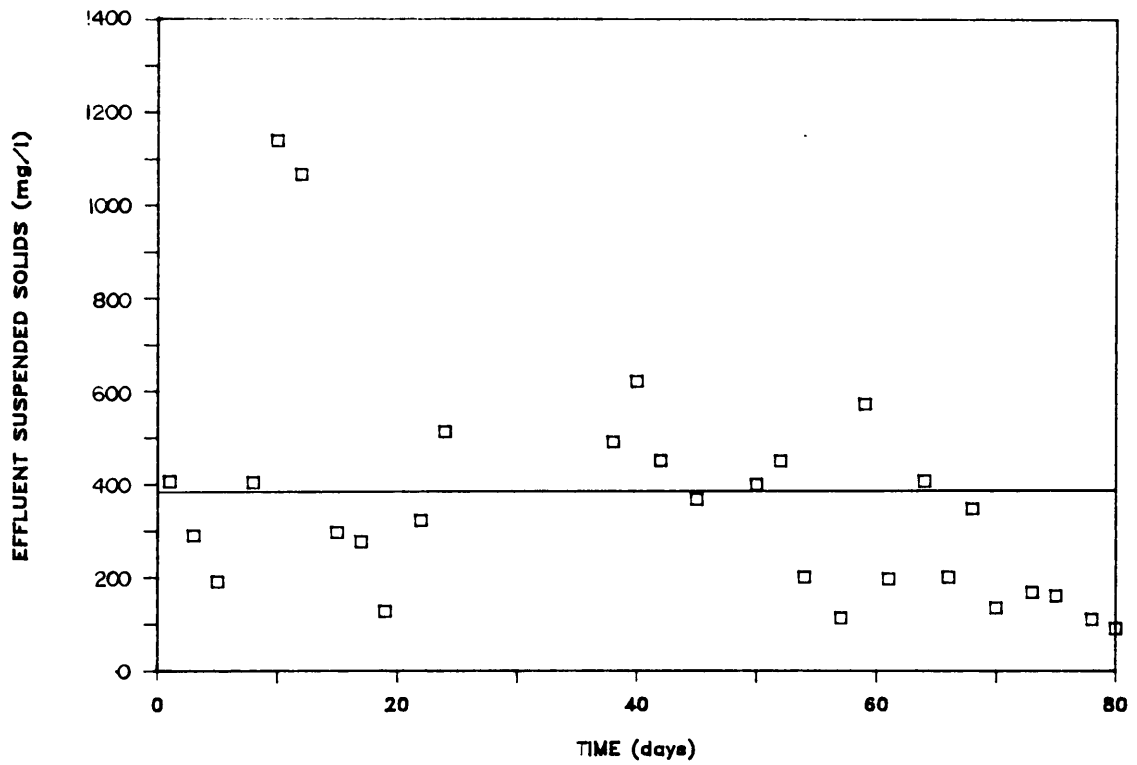


Figure 21. Effluent Suspended Solids for experimental period B2 - 1000 mg/l Calcium.

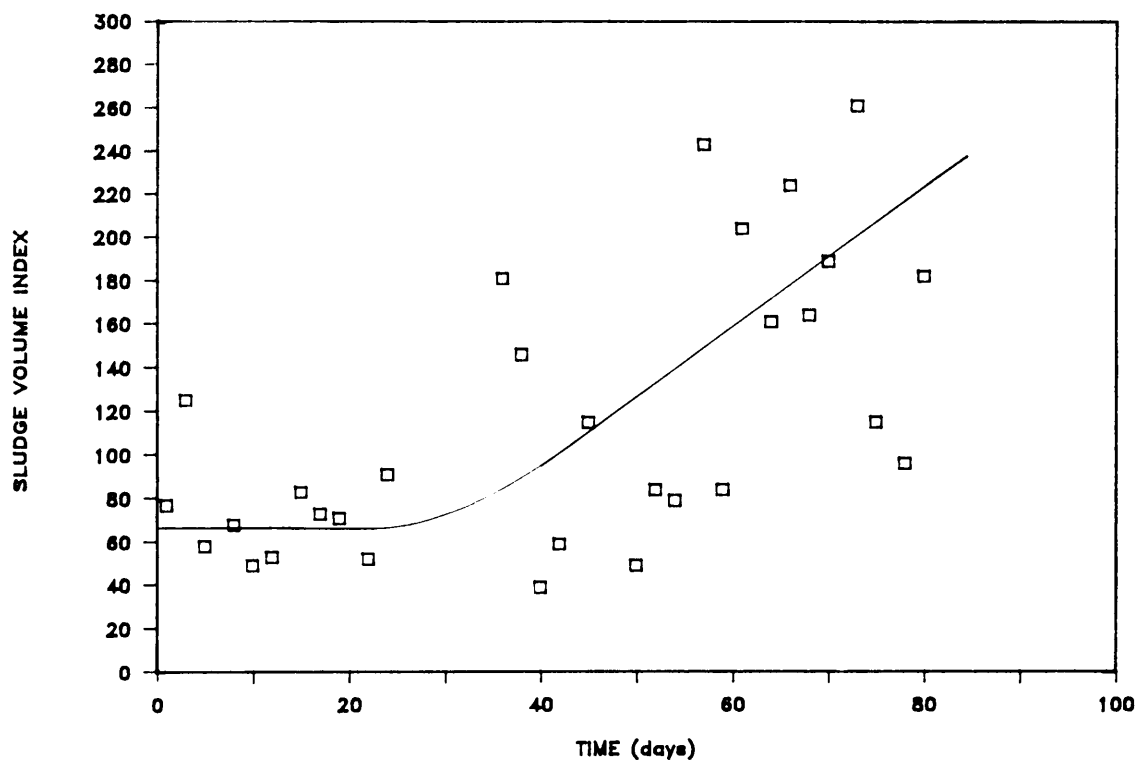


Figure 22. Sludge Volume Indexes for experimental period B2 - 1000 mg/l Calcium.

after sodium hydroxide had caused deterioration of the system. It was theorized that the laboratory scale system would also exhibit this effect. Looking at a plot of Effluent Suspended Solids through the periods of 2500 mg/L Na^+ and 2500 mg/L Ca^{++} addition, it can be seen that a decrease in the solids can be reproduced in the laboratory with the addition of Ca^{++} as the divalent ion (see Figure 23). The other parameters were not changed quite so drastically. SVI stayed approximately the same at 30 (see Figure 24) and the Oxygen Uptake Rate increased slightly to 8 mg/g/hr. It should be noted that towards the end of this experimental period, there was obviously an upset in the system where all parameters deteriorated and then returned to previous values.

The main conclusion gained from this analysis is that laboratory units did not produce as dramatic an affect as was achieved in the full-scale study but a decrease in suspended solids was seen with calcium additions. Other parameters did not seem to be significantly affected. The addition of amounts of calcium less than 2500 mg/L Ca^{++} did not cause the sludge properties to improve. It must be noted here that this was the only concentration where calcium was added immediately after an experimental period with sodium addition. Also, the Effluent Suspended Solids during the preceding sodium period was very high at approximately 900 mg/L prior to addition and this may also account for the pronounced effect.

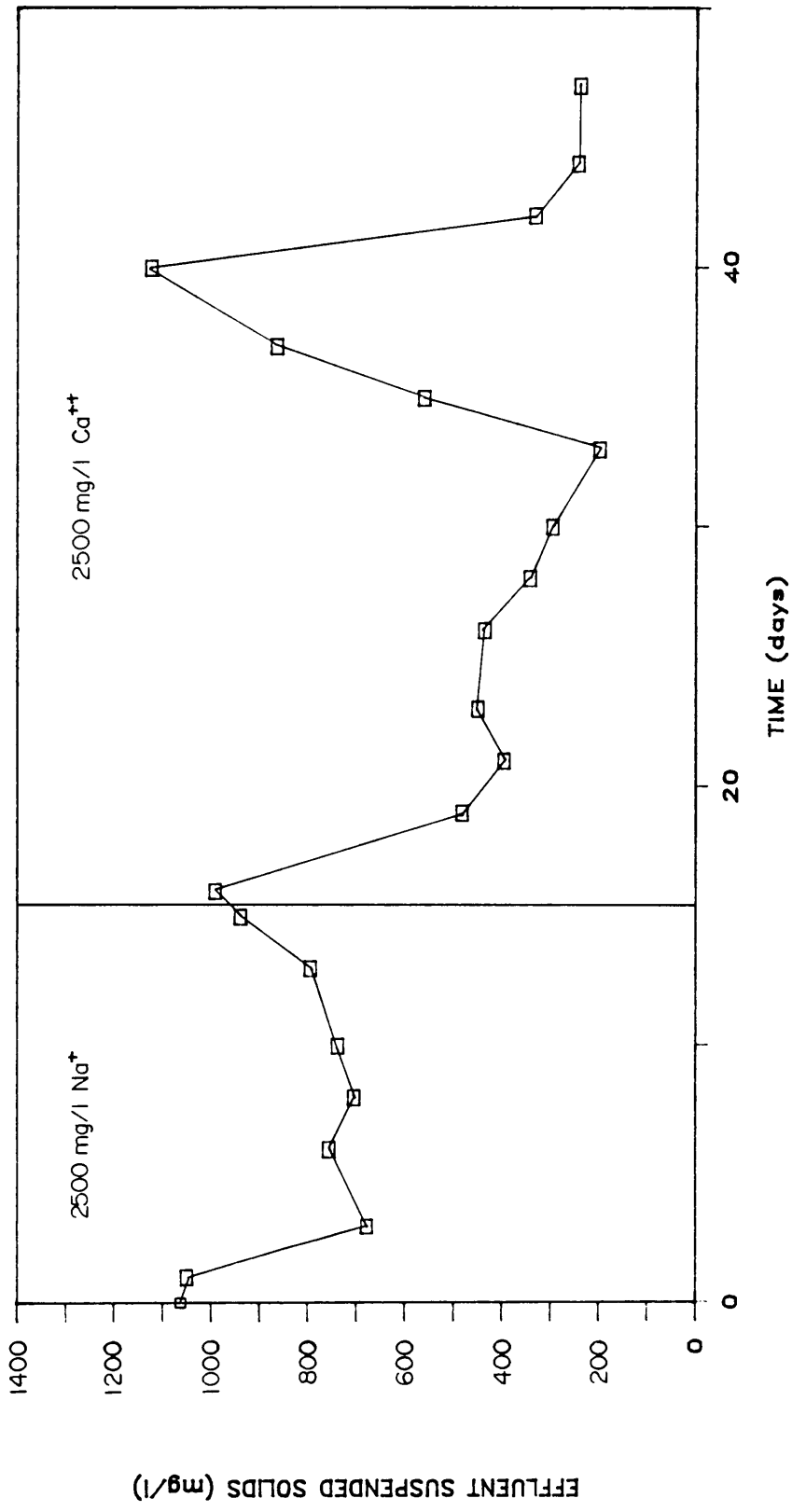


Figure 23. The effect of 2500 mg/l Calcium on Effluent Suspended Solids after deterioration of system by 2500 mg/l Sodium.

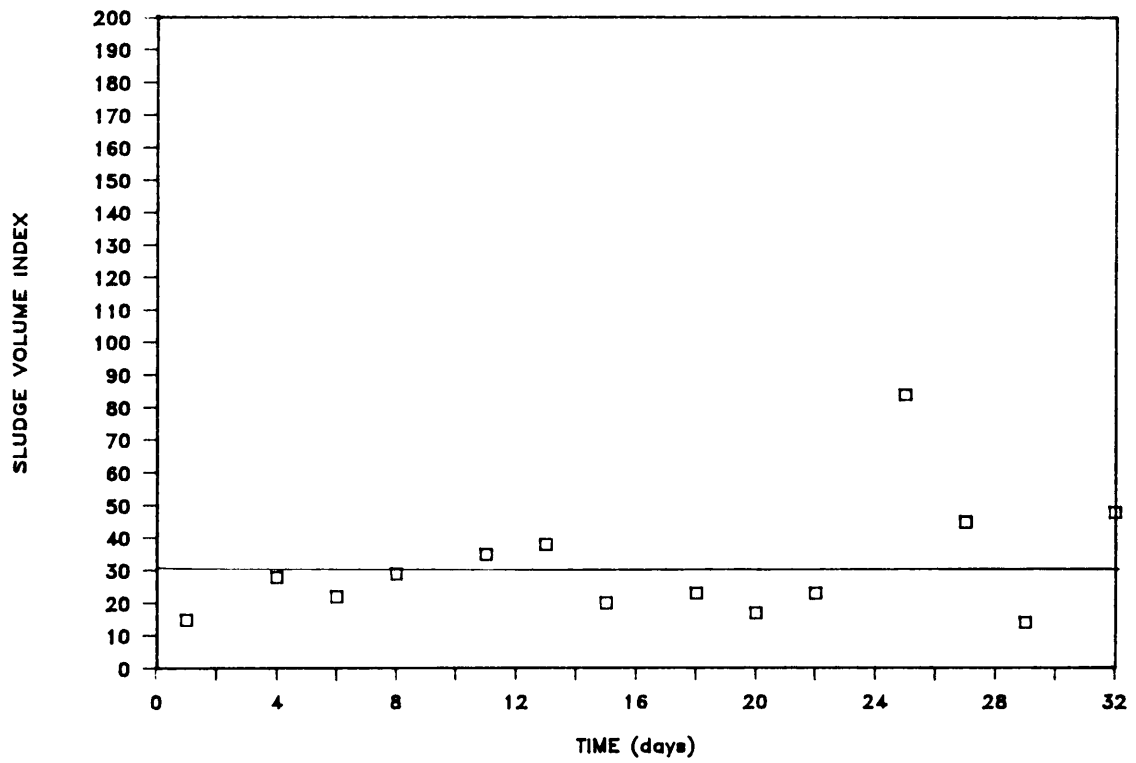


Figure 24. Sludge Volume Indexes for experimental period A6 - 2500 mg/l Calcium.

THE EFFECT OF SODIUM ON THE SYSTEM

In the study at the Celanese Treatment Plant by Novak and Randall (1986) it was suggested that the sodium ions being introduced into the waste stream during pH control caused deflocculation of the sludge floc matrix. During this research it was hoped that this effect could be simulated in the laboratory. There were two different sets of experiments where several consecutive experimental periods were used to raise the concentration of sodium ions. It should be noted that the baseline sodium concentration of the Celanese wastewater was approximately 50 mg/L and therefore the following experimental concentrations are in addition to this number.

In Figure 25 there is a progression of sodium salt concentration from 50 mg/L to 500 mg/L to 2500 mg/L of Na^+ . The effluent suspended solids seem to progressively deteriorate from around 275 mg/L to 1000 mg/L. Examining another set of similar experiments where the concentration rose from 3000 mg/L to 5000 mg/L to 7000 mg/L of Na^+ , a slight increase in the Effluent Suspended Solids can be seen (see Figure 26). Solids going into the effluent started out at about 100 mg/L and ended up around 300 mg/L.

Examining the SVI of the first set of experiments (see Figure 27), the initial value starts at 50 but there is a progressive downward trend throughout the experiments to approximately 20 which is a value lower than that of the controls. The second set of experiments did not exhibit the same response (see Figure 28). The initial response was

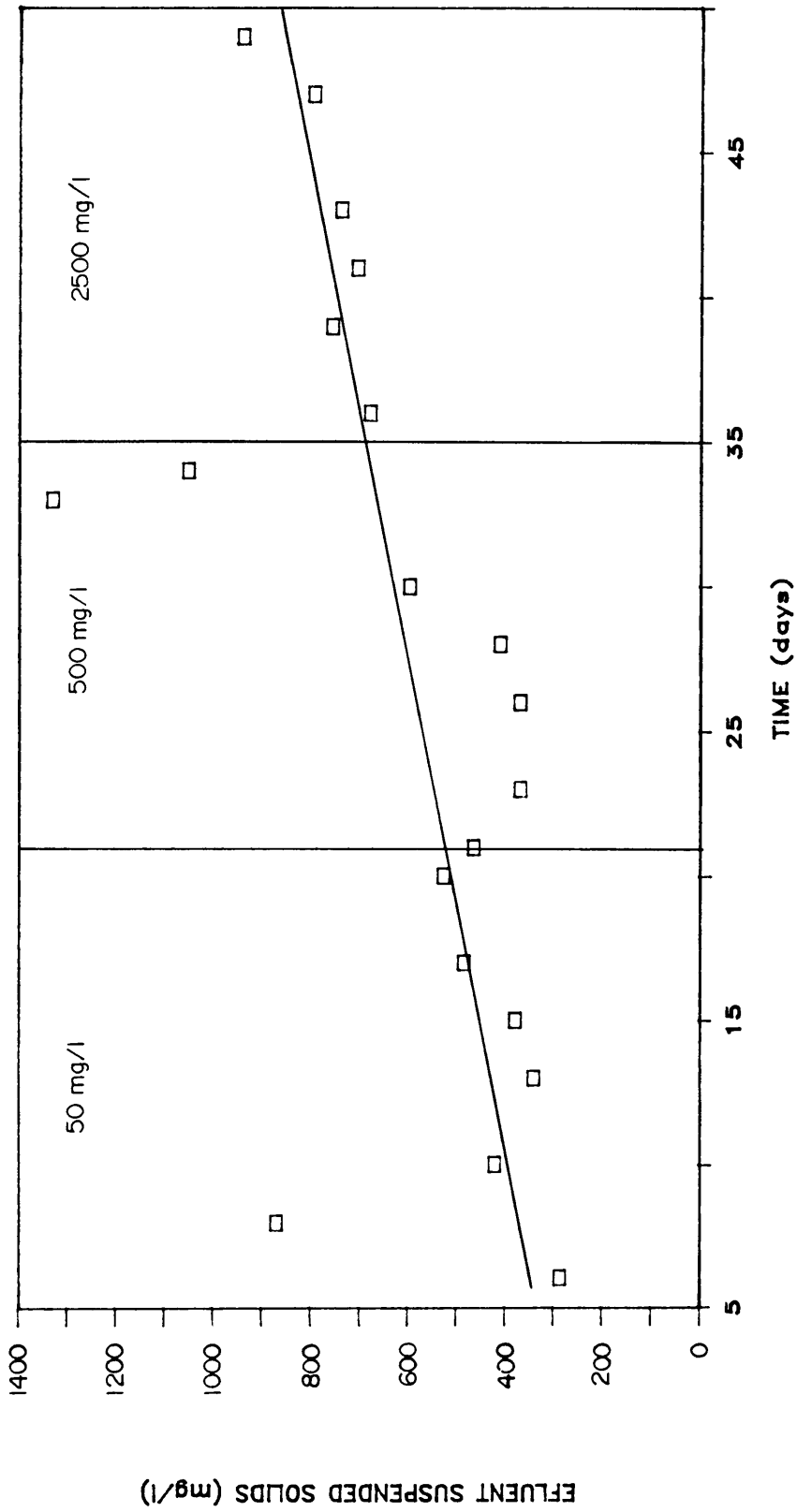


Figure 25. Effluent Suspended Solids for experimental periods A3,4 and 5 - 50, 500 and 2500 mg/l Sodium.

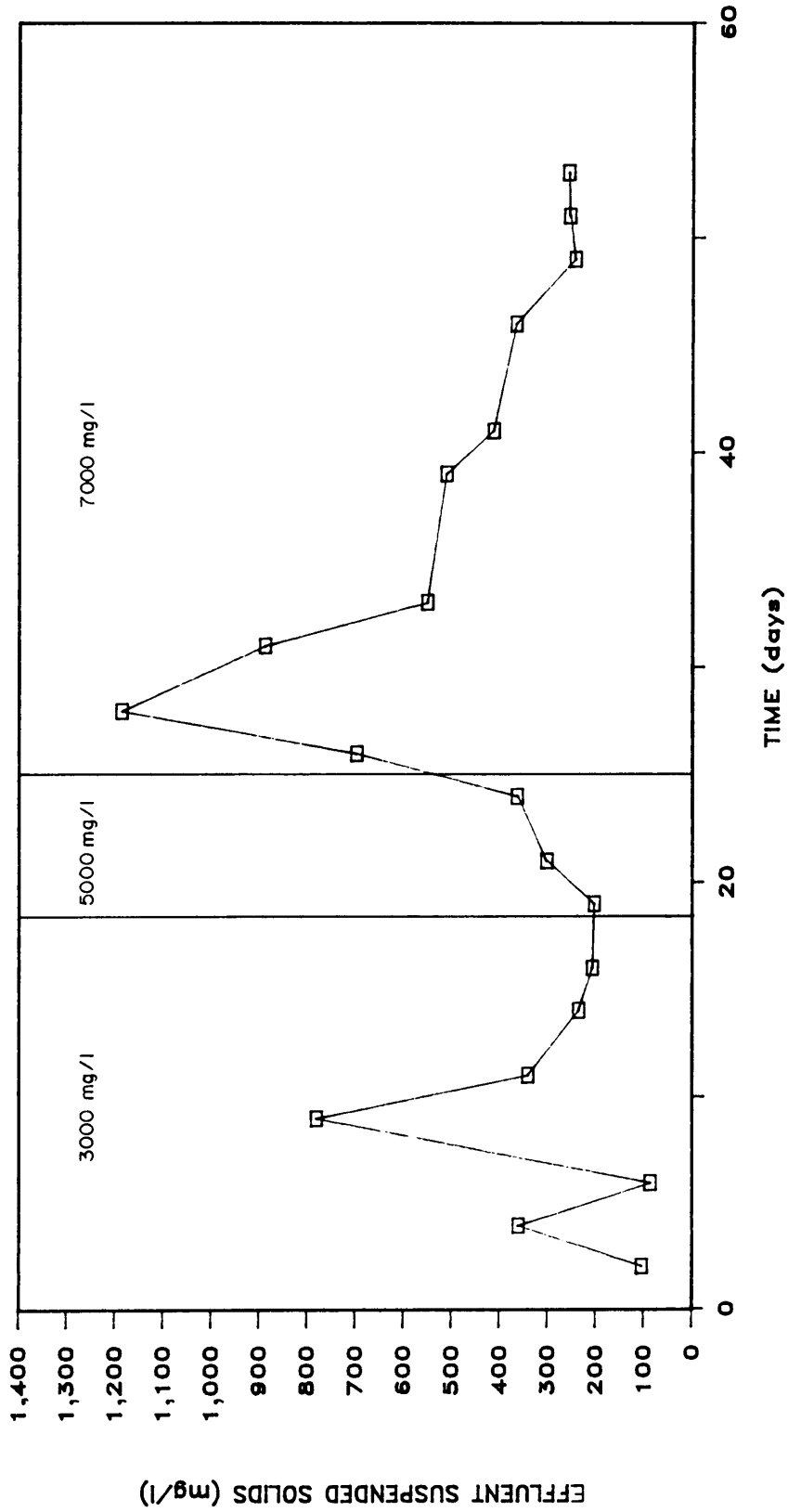


Figure 26. Effluent Suspended Solids for experimental period A9, 10 and 11 - 3000, 5000 and 7000 mg/l Sodium.

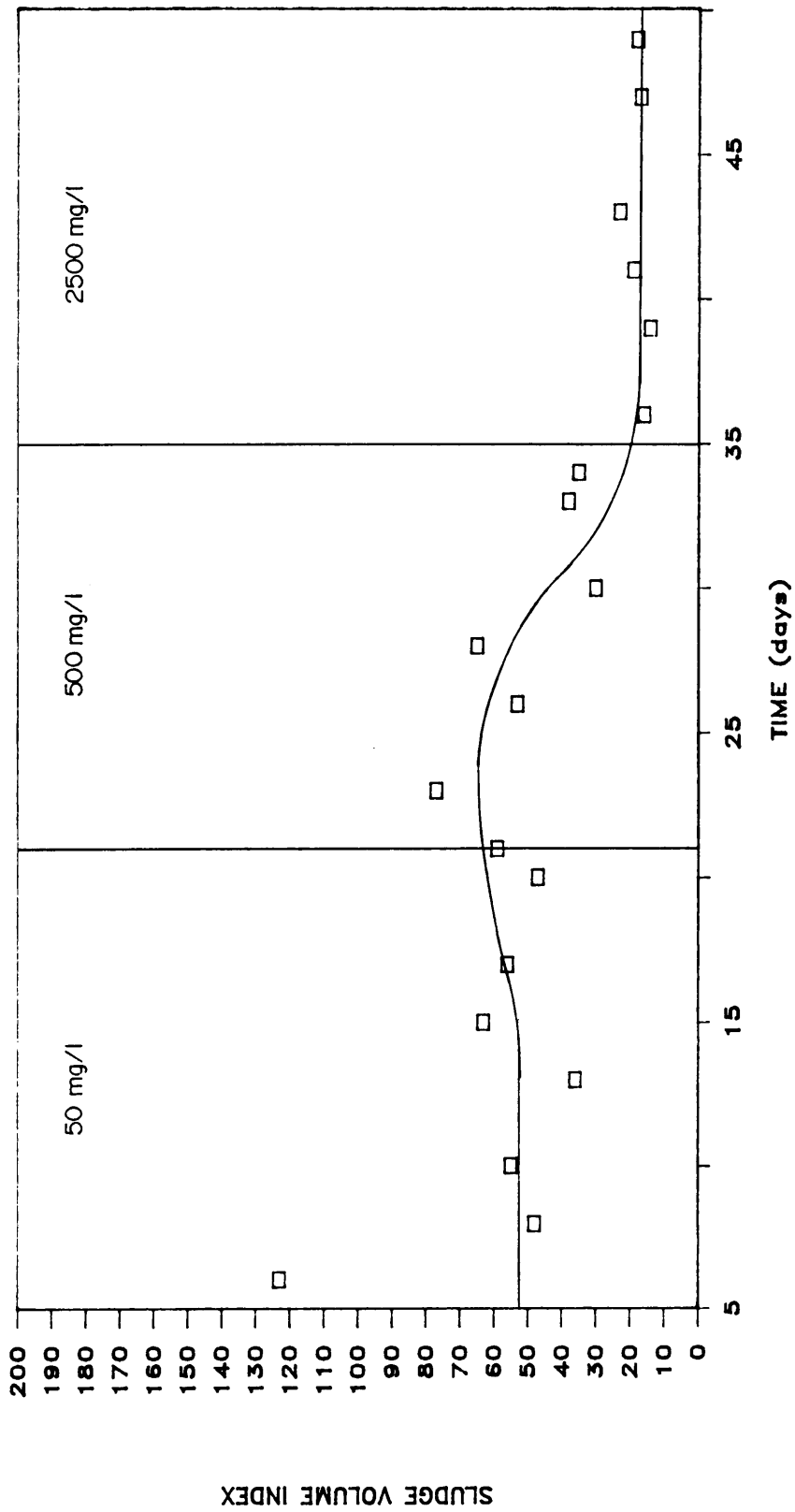


Figure 27. Sludge Volume Indexes for experimental periods A3, 4 and 5 - 50, 500 and 2500 mg/l Sodium.

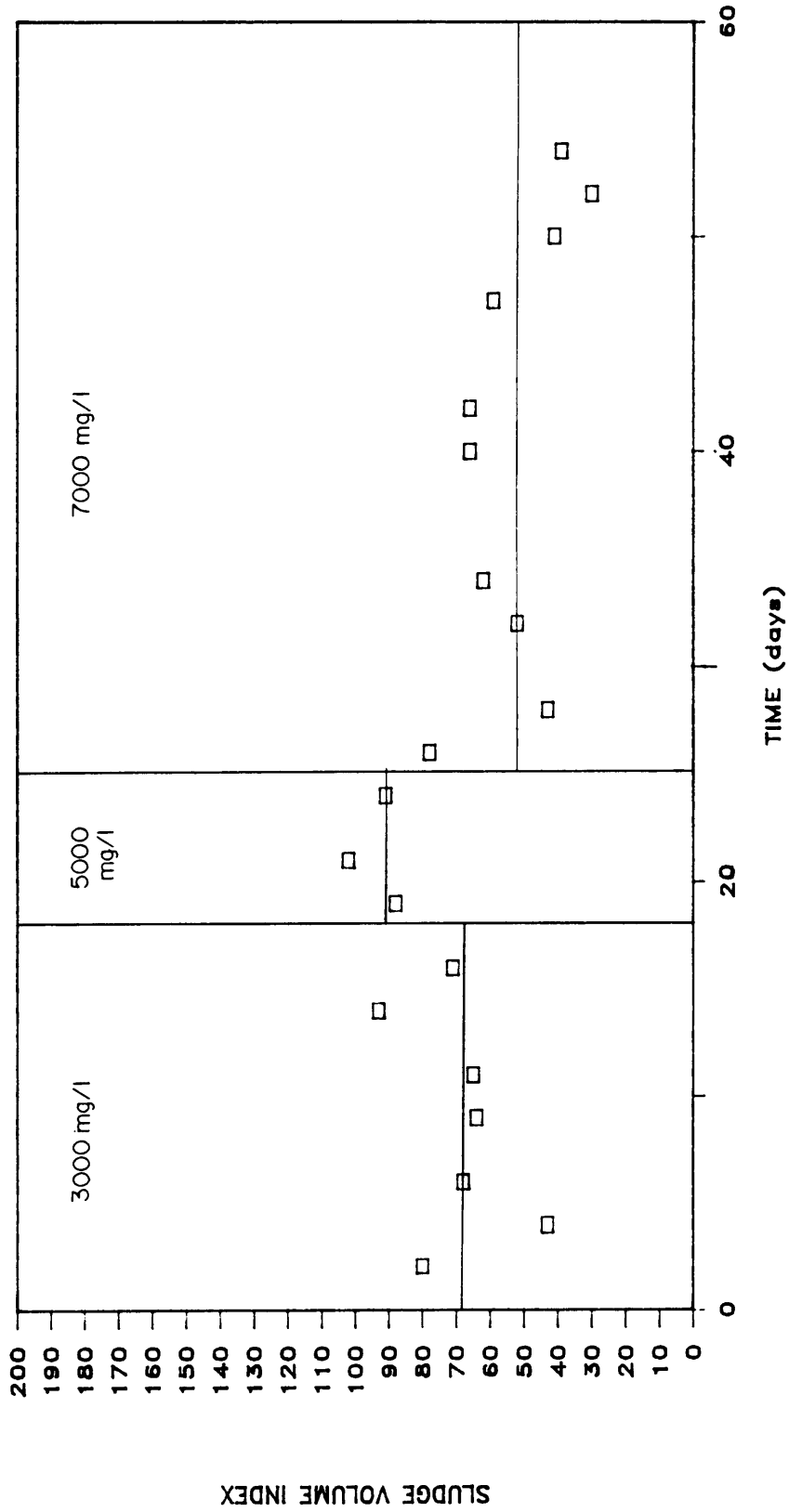


Figure 28. Sludge Volume Indexes for experimental periods A9, 10 and 11 - 3000, 5000 and 7000 mg/l Sodium.

downward to 70, followed by a slight upward trend to 90 until the 7000 mg/L Na^+ was added and it fell back down to 50.

Oxygen Uptake Rates did not appear to be affected by sodium ions, staying between 10 and 20 mg/g/hr for the duration of both experiments. Zone Settling Rates did not seem to be affected either, staying around 3 cm/min consistently.

Some general statements about the effects of sodium can be made. It can be shown that sodium affects the Suspended Solids creating a higher than normal Effluent Suspended Solids. SVI, however, seems to be improved by the presence of sodium ions except at concentrations of 3000 and 5000 mg/L. What is shown in these data was the inability to simulate the drastic effects caused by the NaOH in the Novak and Randall (1986) study. This suggests that it was not just the sodium ion which caused the effects. It may be a compound formed in a reaction between the sodium or hydroxide ions with the organics or whatever compounds can be associated with the pH decrease of the waste.

Another theory as to why the settling rate improved at higher concentrations of sodium may be described by the Schulze-Hardy rule. This rule states that the coagulation effectiveness of an ion decreases markedly with charge. The sodium ion being a monovalent cation would require a much higher concentration than a divalent cation but once this concentration level was met, would perform just as well as a divalent cation to destabilize the colloid (Stumm and Morgan, 1962). Perhaps what was happening in the higher concentrations of sodium was that the concentration of the monovalent cation was high enough to coagulate the

sludge and improve the settling.

REPRODUCIBILITY OF EXPERIMENTS

In this section two groups of data will be compared to see if results were reproducible. The two experimental periods were preceded by different salts thus exposing the sludges to different initial conditions. One experimental period was preceded by a period where 500 mg/L of magnesium had been added and the other after 2000 mg/L sodium. The two experimental periods considered here both had additions of 3000 mg/L of sodium added to the reactors. Looking at Figure 29, it can be seen that the Effluent Suspended Solids value of both reactors varied from 100 to 200 mg/L which was not significantly different. The SVI values start out differently but eventually leveled off at of 90 or 100 (see Figure 30). The graph for experimental period B4 starts out at a high SVI because of the preceding salt addition of 2000 mg/L sodium which had brought the value up to approximately 550.

Capillary Suction times averaged the same at 8 sec. for both experiments, see Figure 31. Both systems exhibited an average for specific resistance at 3×10^{12} m/kg, (see Figure 32).

Zone Settling Rates are comparable. Looking at Figure 33 it can be seen that even though the two reactors started out quite different they followed a very similar pattern.

It can be seen in this analysis that the equilibrium values for each of the parameters were comparable. It is interesting to note that although each reactor had been through different preceding conditions, they both show similar results under similar conditions.

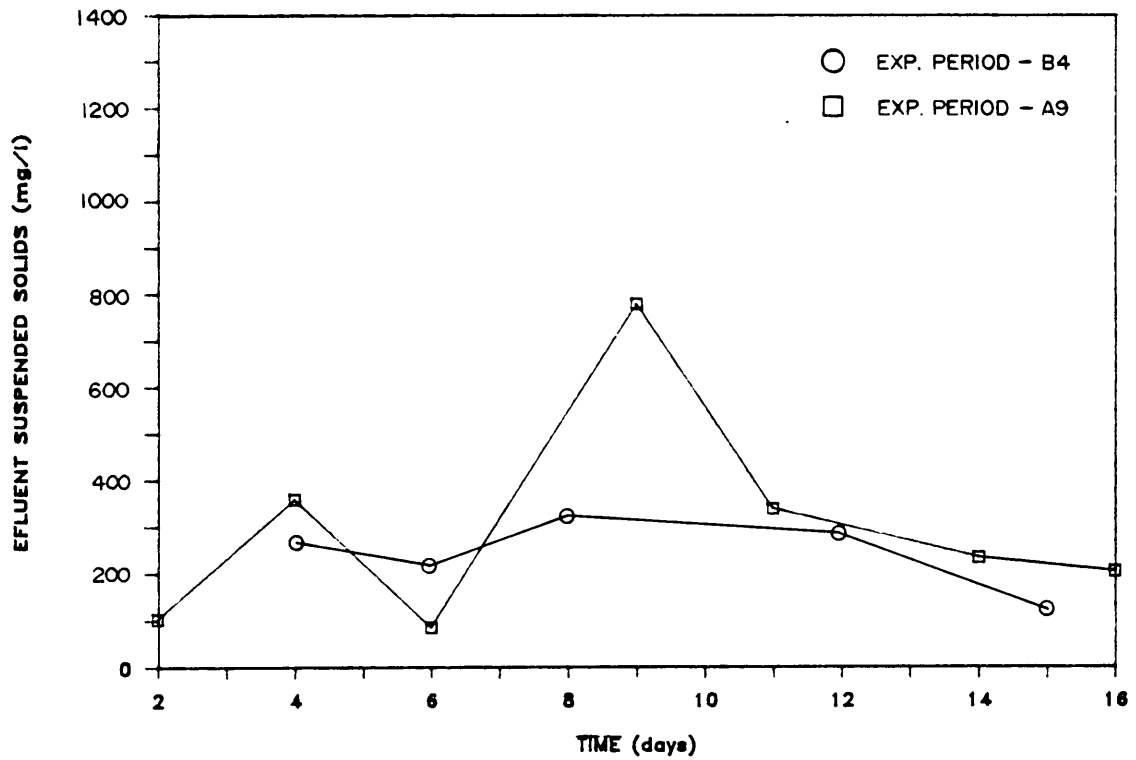


Figure 29. Comparison of Effluent Suspended Solids for experimental periods B4 and A9 - 3000 mg/l Sodium.

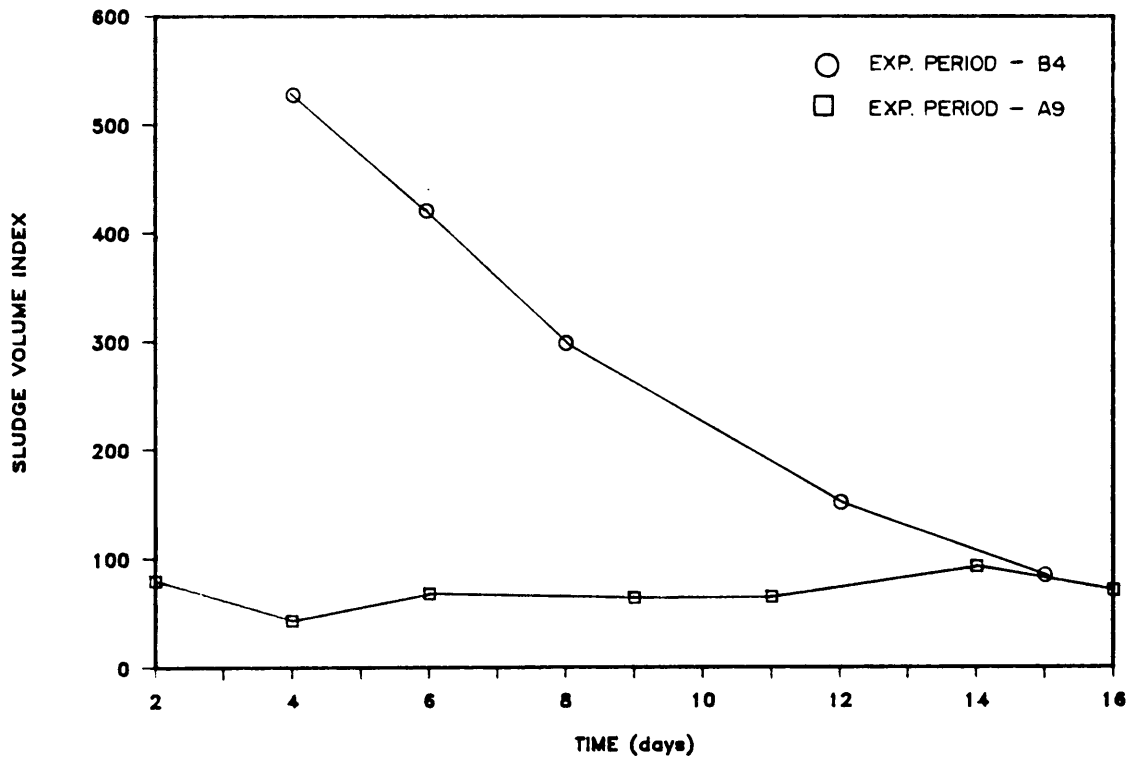


Figure 30. Comparison of Sludge Volume Indexes for experimental periods B4 and A9 - 3000 mg/l Sodium.

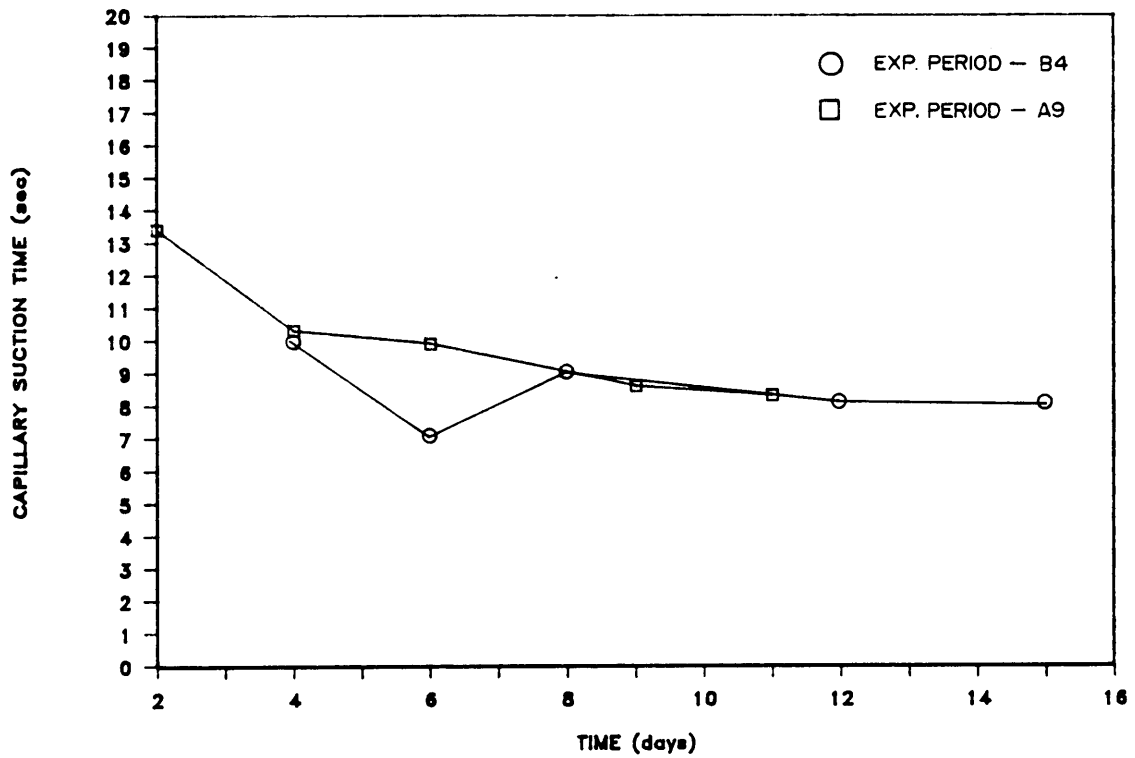


Figure 31. Comparison of Capillary Suction Times for experimental periods B4 and A9 - 3000 mg/l Sodium.

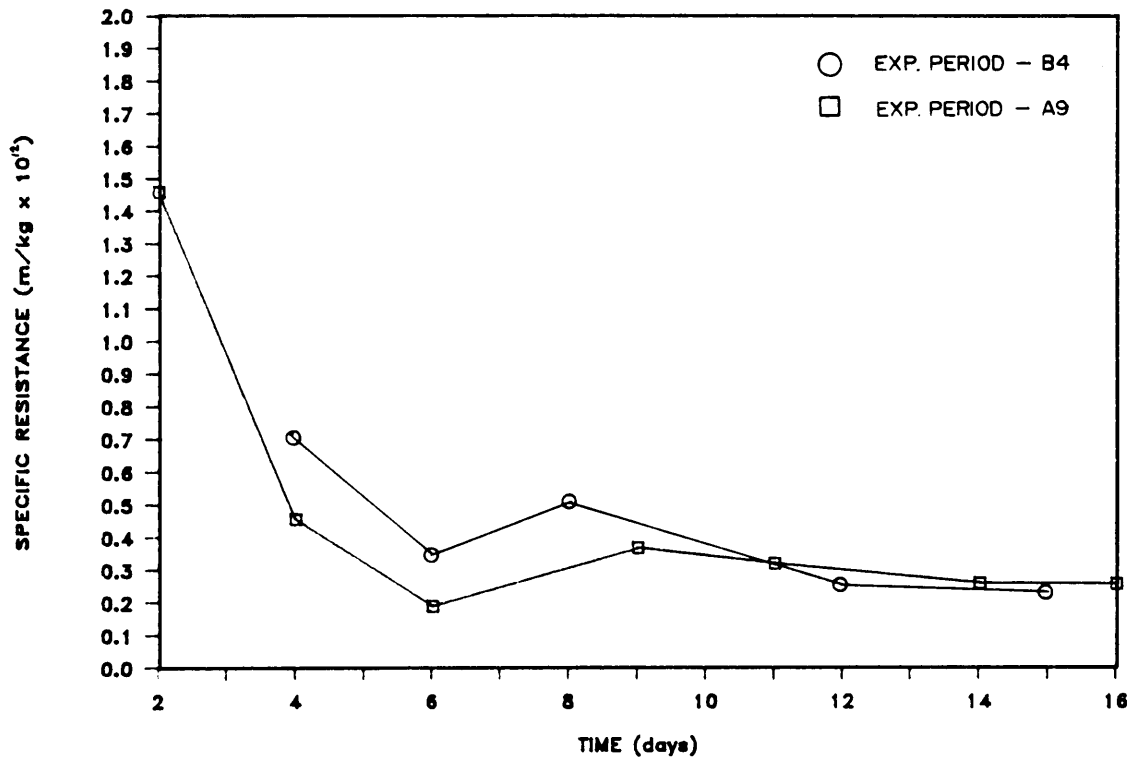


Figure 32. Comparison of Specific Resistances for experimental periods B4 and A9 - 3000 mg/l Sodium.

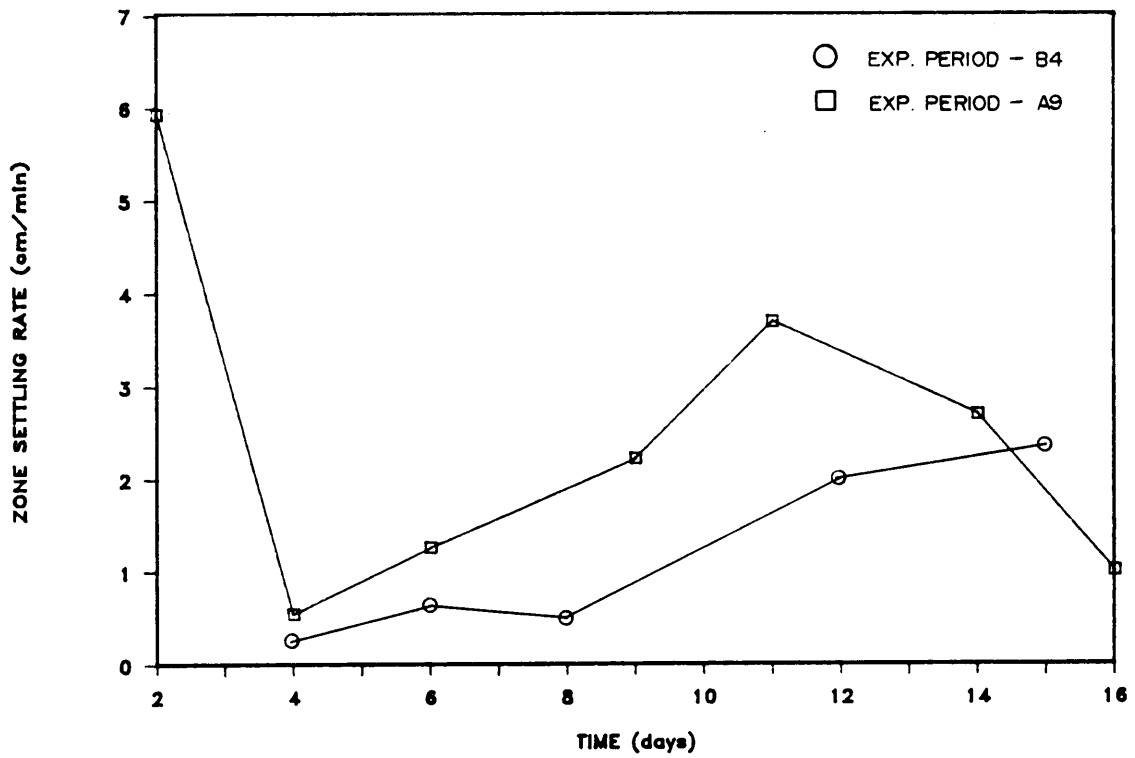


Figure 33. Comparison of Zone Settling Rates for experimental periods B4 and A9 - 3000 mg/l Sodium.

THE EFFECTS ON SUBSTRATE REMOVAL

The objective of this analysis was to see what effect, if any, the addition of salts had on Substrate Removal efficiencies, measured in COD. Looking at substrate removal over time for each experiment, a reproducible pattern begins to show throughout the data. At the start of a different salt concentration, the system is disrupted but then reaches an operational condition specific to that salt concentration. There is a notable difference between the ultimate removal efficiencies obtained with each cation.

The effects on substrate removal at concentrations of 50, 1000 and 2500 mg/L of calcium are shown on Figure 34. The average percent removal at 50 mg/L calcium is shown to be approximately 83%. It appears that there may be a trend towards improvement but there are not enough data points to substantiate this trend. The average removal efficiency at a concentration of 1000 mg/L of calcium is approximately 92% which does appear to be lower than the baseline experiment with just nitrogen and phosphorus (see Figure 35) which is at 96 to 98% efficiency. A calcium concentration of 2500 mg/L shows an average substrate removal efficiency of approximately 90% but a trend towards 98% is also seen suggesting an initial upset but then recovery. It appeared that the removal efficiency was not permanently affected by the calcium addition.

Examining the results of the sodium and magnesium experiments, the data do not show as good a recovery. Figure 36 shows the removal efficiency for 500 mg/L Mg^{++} . This system never did get above 90 to 95% removal again. Figure 37 shows the effects of sodium ion concentration

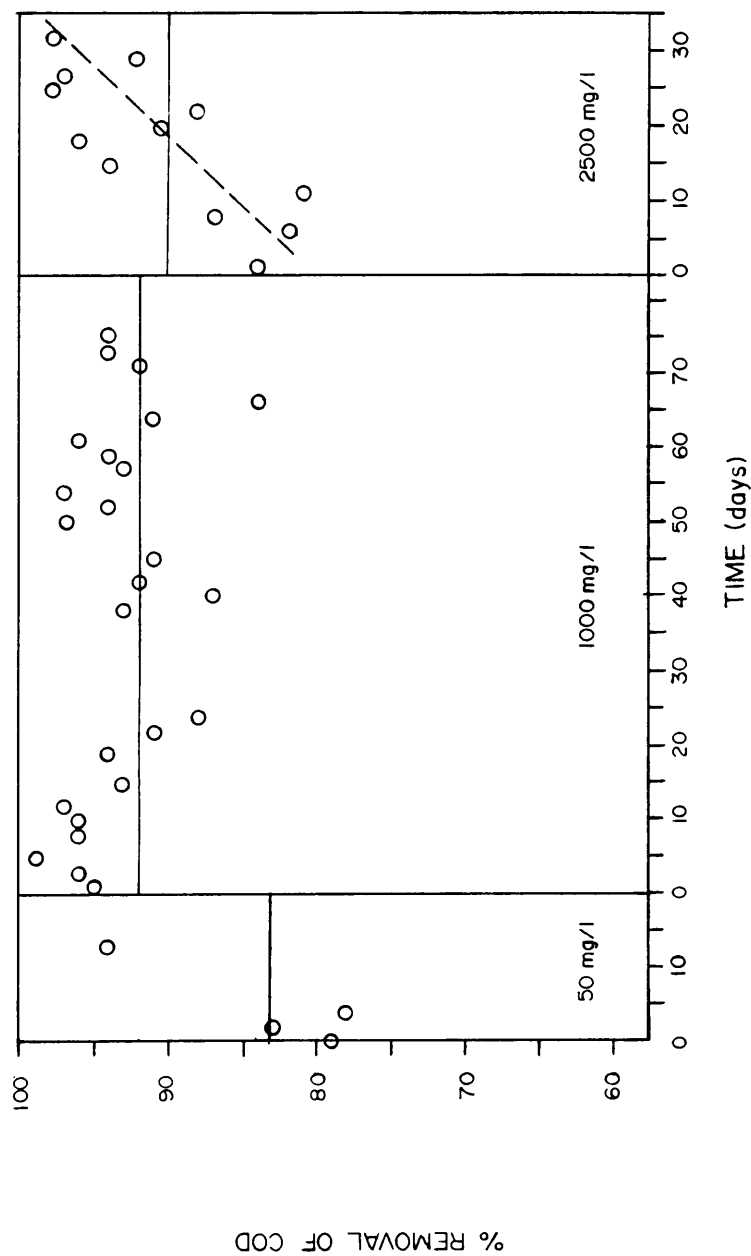


Figure 34. Substrate removal efficiencies, measured in COD, for Calcium concentrations of 50, 1000, and 2500 mg/l.

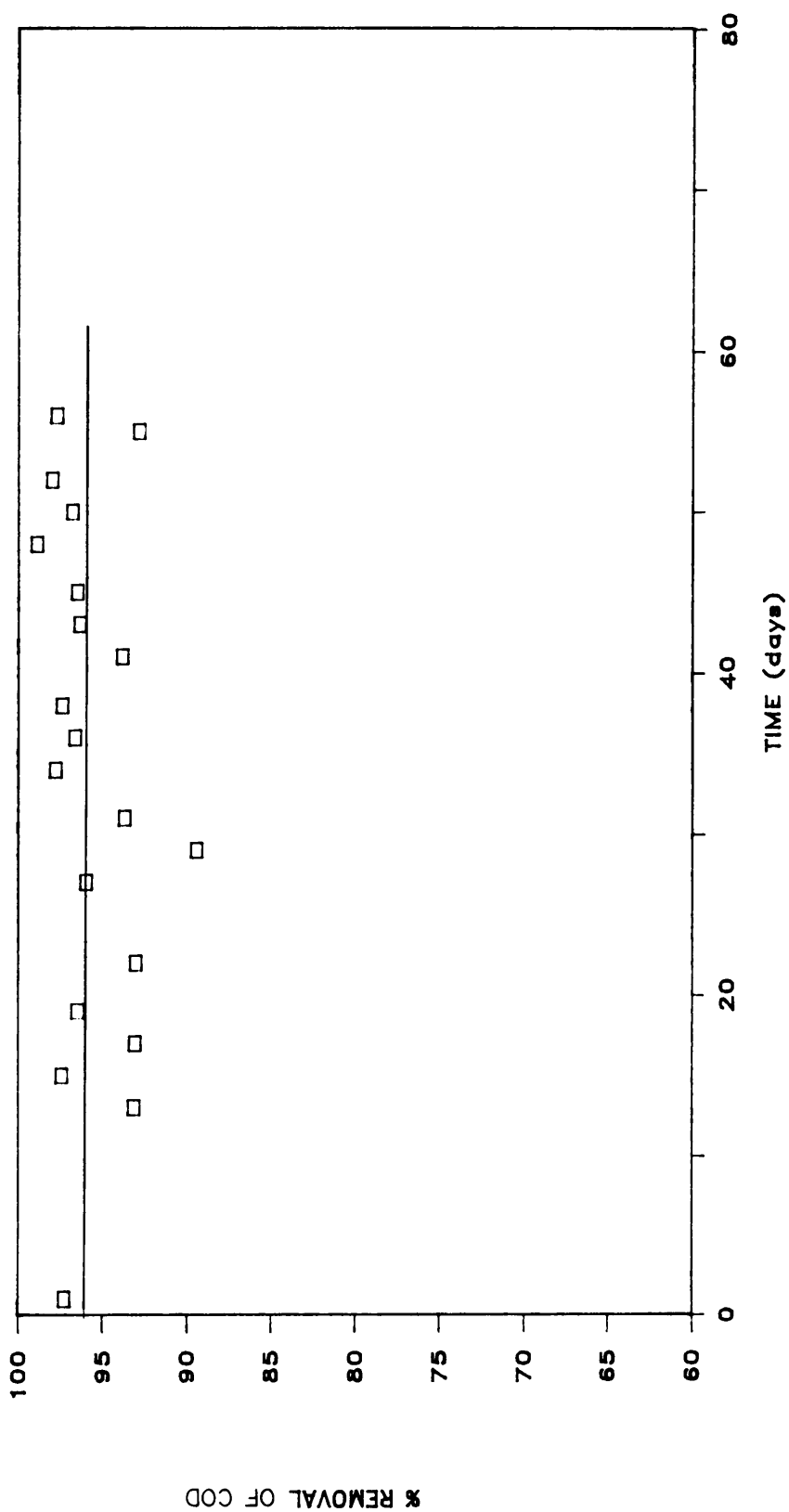


Figure 35. Substrate removal efficiencies, measured in COD, for experimental period A7
50 mg/l Nitrogen, 10 mg/l Phosphorous.

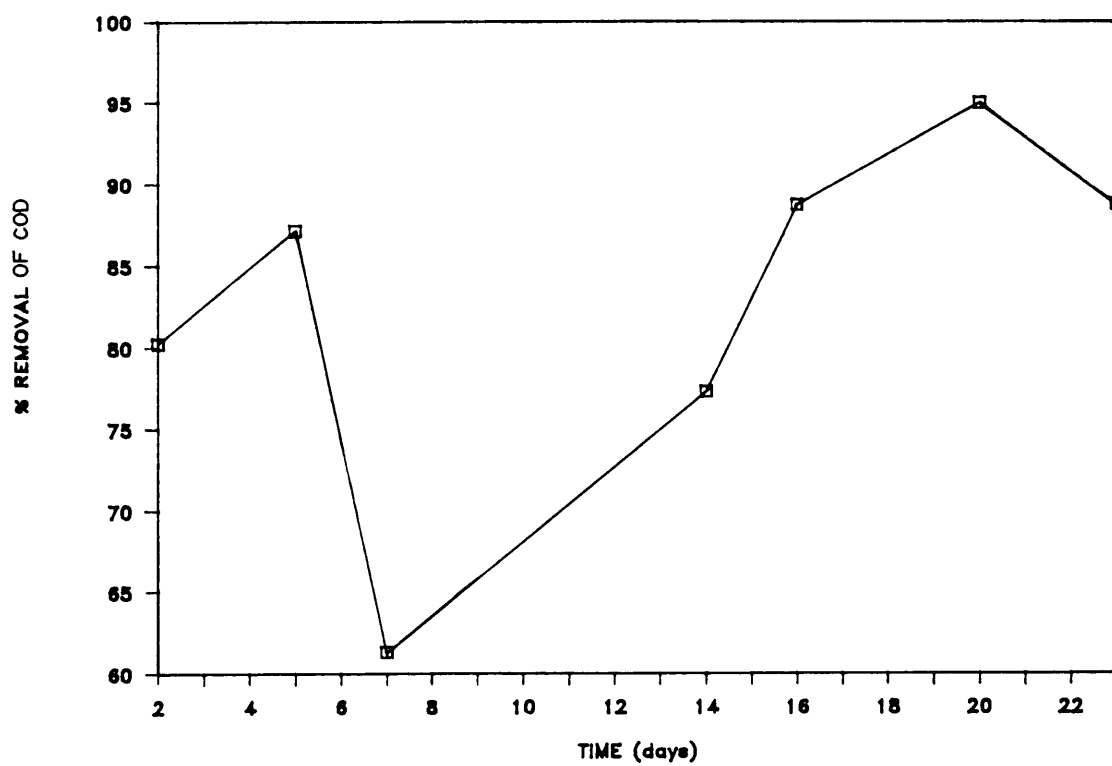


Figure 36. Substrate removal efficiencies, measured in COD, for experimental period A8 - 500 mg/l Magnesium.

on removal efficiency. For the majority of time, removal was below 90% except during the period when a concentration of 2500 mg/L was added to reactor #1. A trend did appear in the 2500 mg/L sodium data. Although the average substrate removal efficiency was close to 90%, a trend towards improvement can clearly be seen, suggesting that there was a recovery after an initial upset. In the final period of 7000 mg/L Na⁺, there was a final and drastic decrease in removal efficiency going from almost 90% to approximately 40%. This would seem to be the point where the system began to deteriorate due to excessive salt additions.

The experiment where 500 mg/L Mg⁺⁺ was added along with 3000 mg/L Na⁺ showed the initial dip, a move back to 90% removal efficiency but then drops erratically back down towards 70% removal (see Figure 38).

Conclusions gained from this analysis might be that 2500 mg/L calcium is the only salt concentration which did not affect the substrate removal efficiency in a permanent way.

ANALYSIS OF ATOMIC ABSORPTION DATA

Atomic absorption analysis was performed on several samples as seen in Tables A-3 and A-4 in the Appendix. The results were unexplainable. Although the cations had been added in known concentrations to the influent, when measured by atomic absorption, often both the influent and effluent concentrations were considerably less than that which was added. For example, on August 25 in Table A-3, where 7000 mg/L of sodium was being added to the influent. Measured concentrations in the influent were 3920 mg/L and in the effluent were 5580 mg/L. There were also many instances where the effluent concentration measured 10 to 25%

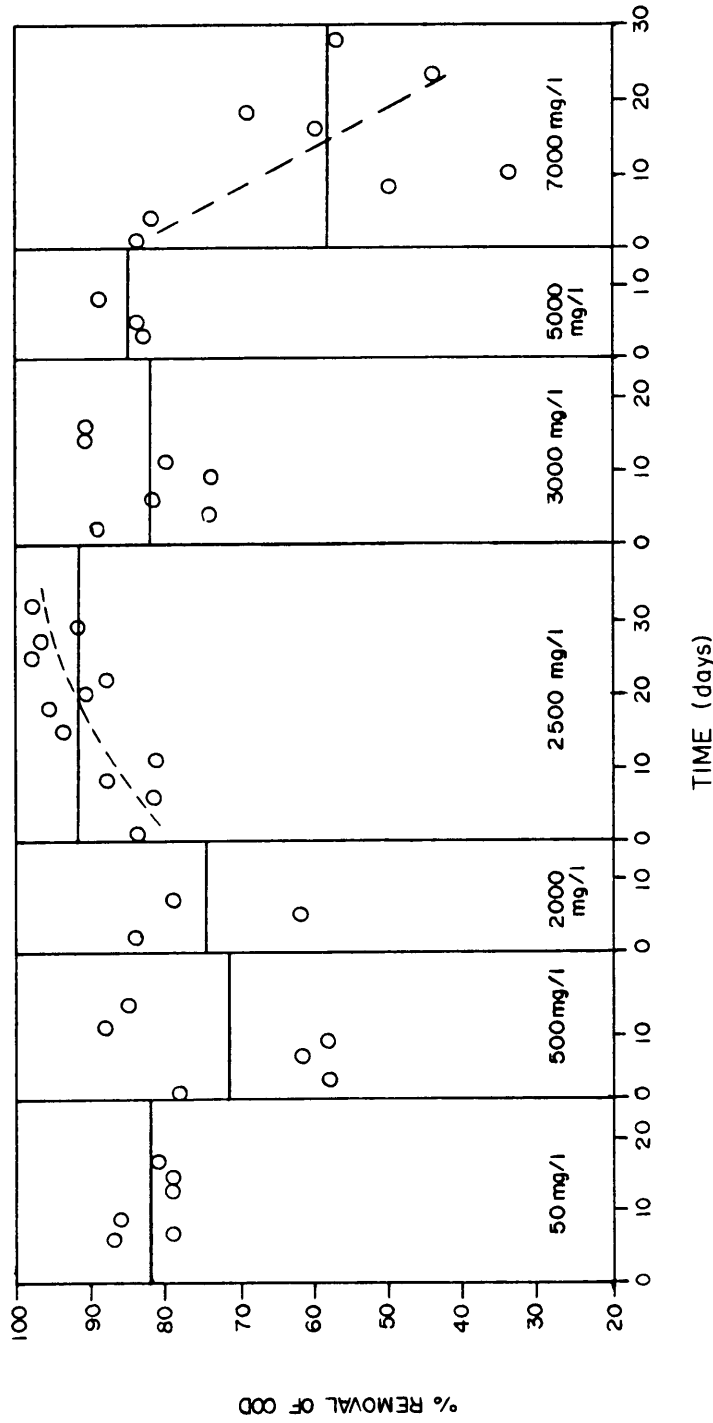


Figure 37. Substrate removal efficiencies, measured in COD, for Sodium concentrations of 50, 500, 2000, 2500, 3000, 5000 and 7000 mg/l Sodium.

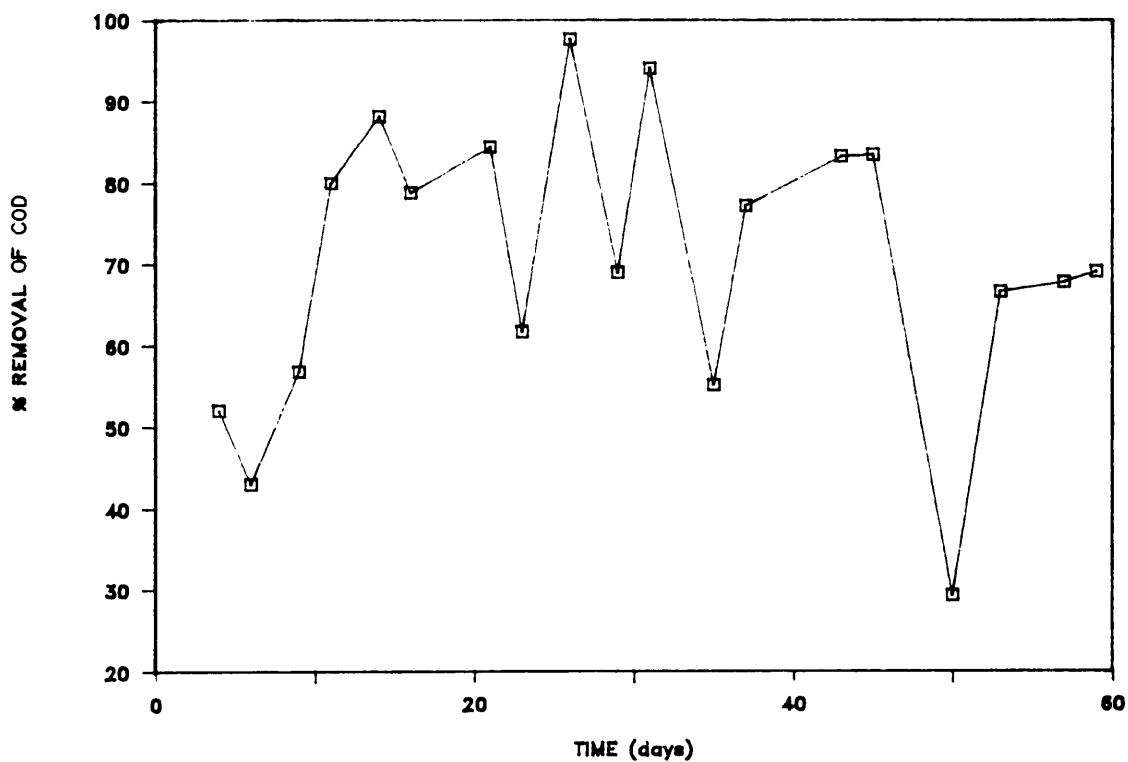


Figure 38. Substrate removal efficiencies, measured in COD, for experimental period B5 - 3000 mg/l Sodium, 500 mg/l Magnesium.

more than the influent concentration. For example on August 17, in Table A-4, reactor #2 was receiving 3000 mg/L of sodium. The Atomic Absorption readings for the influent measured 2660 mg/L and for the effluent measured 3320 mg/L, about 24% higher than the influent. Explanations such as instrument and dilution error could not be used because a conservative estimate for such errors is $\pm 5\%$. Atomic Absorption analysis measured ions in all forms, even those that are complexed, therefore no ions would have been in an unmeasurable form. Some ions may have been taken up into the organism or adsorbed onto its surface so that a loss may have occurred when the sample was filtered. Some amount may have also been lost in aerosols created by the reactor's air diffusion. Sampling error may also explain some of the discrepancy.

RELATIONSHIPS BETWEEN PARAMETERS

In hopes of finding some relationship between parameters, averages were taken of each experimental period towards the end of those periods when the reactors were relatively steady. These numbers were then plotted and can be seen in Figures 39, 40 and 41. No correlations or trends were evident.

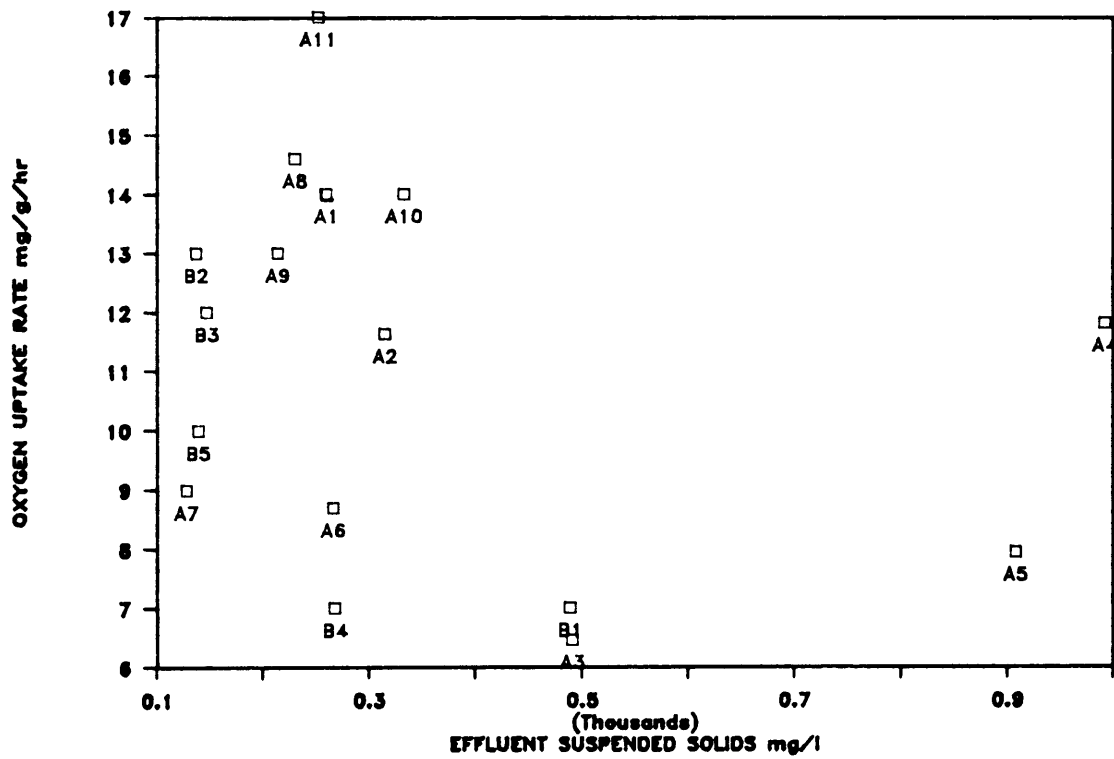


Figure 39. Relationship between Oxygen Uptake Rates and Effluent Suspended Solids for all experimental periods.

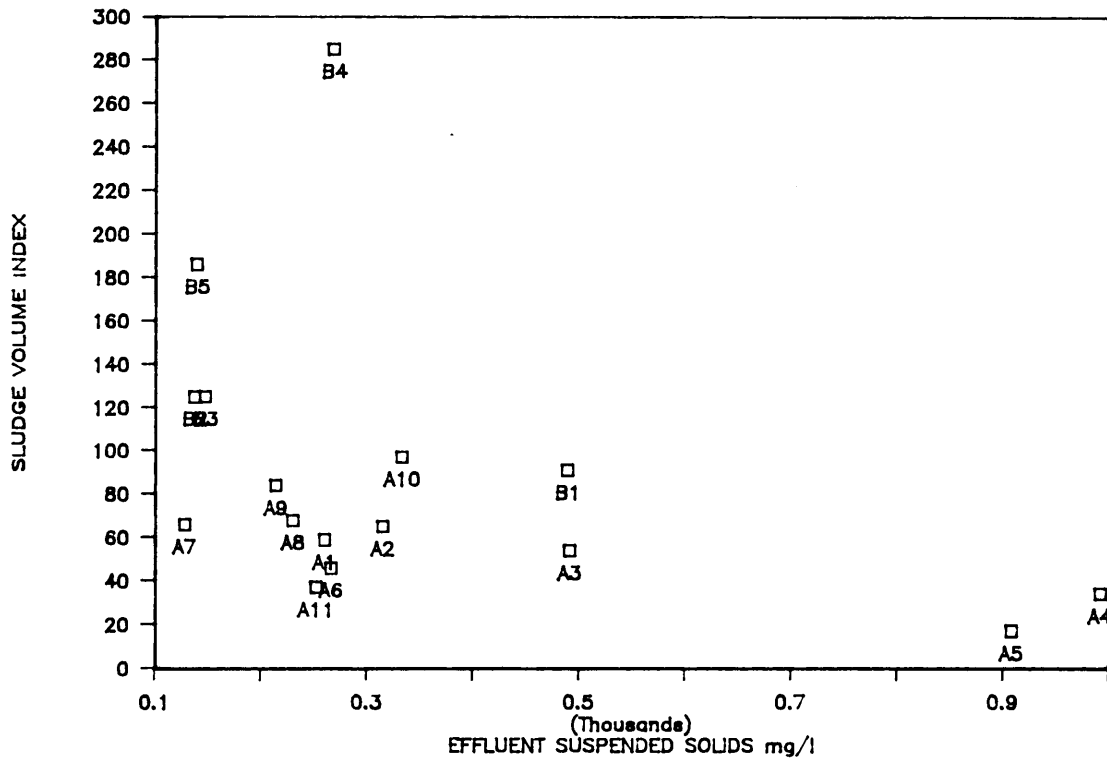


Figure 40. Relationship between Sludge Volume Indexes and Effluent Suspended Solids for all experimental periods.

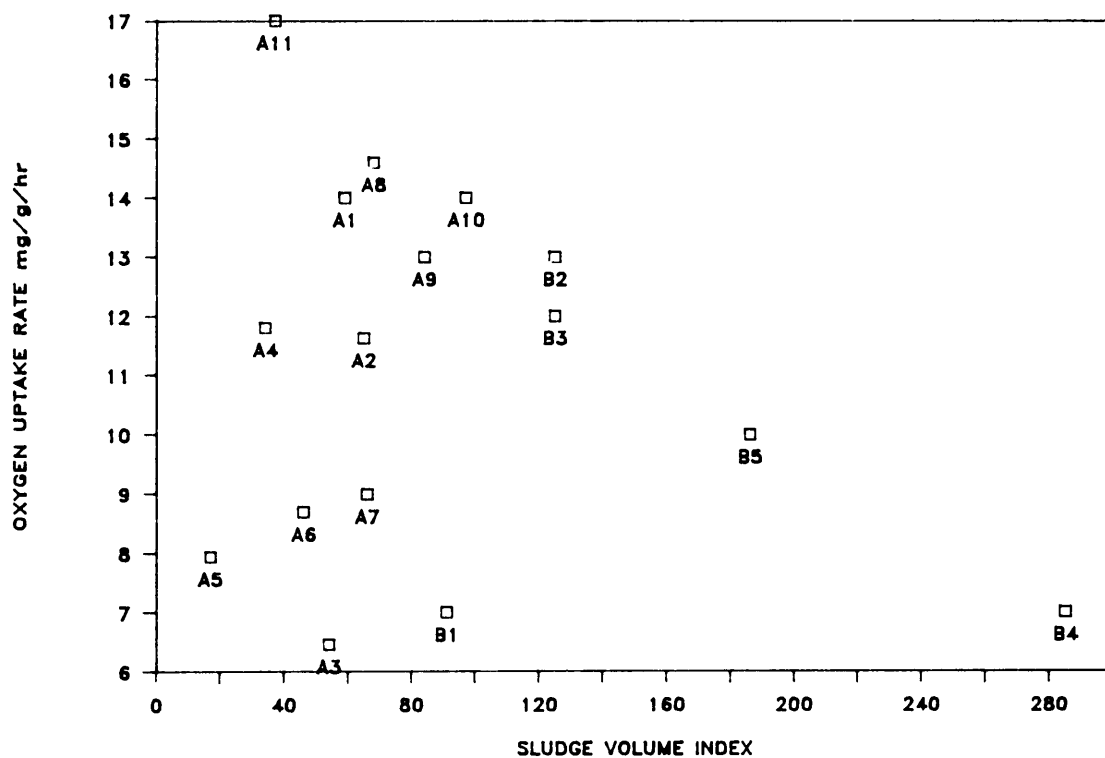


Figure 41. Relationship between Oxygen Uptake Rates and Sludge Volume Indexes for all experimental periods.

V. SUMMARY AND CONCLUSIONS

Lab scale, completely mixed, continuous flow reactors were set up to model the Celanese Corporation Wastewater Treatment Plant. Actual Celanese wastewater was used in these laboratory experiments. The main purpose of this study was to take the results obtained in the full-scale plant study conducted by Novak and Randall (1986) and better define the salt levels where these effects occurred. In the full-scale plant study, sludge characteristics deteriorated when sodium hydroxide was introduced into the waste stream for pH control. Calcium, added as a divalent cation, improved the sludge characteristics dramatically. In the laboratory study, experiments were performed to see whether the deterioration at the plant associated with the sodium hydroxide additions was due to the sodium ion or to some combination of pH, organic additions or sodium. Another set of experiments attempted to determine whether the characteristic improvements could be attributed to just the divalent cation, calcium, or to all divalent cations. Other experiments were intended to define a concentration or optimum dosage of each salt.

The results of the sodium ion experiments can be summarized by saying that the ions did cause some deterioration but did not cause the magnitude of deterioration that had been seen in the full-scale plant study. Because of this outcome, it must be concluded that the effect of the sodium hydroxide must be due to other compounds perhaps in combination with sodium hydroxide. The organics may have been present

at the time of the full-scale study but not present during the laboratory study.

Both calcium and magnesium were added as divalent cations to try and simulate the improvements noted in the full-scale study. Different concentrations were added of each to see if an optimum dosage could be found. Results showed almost no improvements with magnesium and only a small improvement with calcium. The effects from the salts were not as dramatic as in the full-scale plant. It becomes evident that there is probably something much more complicated going on in the system than just a chemical reaction with the cations that were being fed into the system. A logical conclusion is that compounds are being formed with the organics in the system which in turn affect the system in either a detrimental or beneficial way. This makes it difficult to simulate these effects in the laboratory because the organics present at any one time are not fully defined.

The following specific conclusions were derived from the experimental studies.

1. Divalent cation additions caused an improvement in sludge characteristics but not as dramatic as expected from full-scale results.
2. The slow rate of reaction which the cations had on sludge characteristics suggests that there may be biological effects occurring in addition to chemical responses.

3. Sodium ions caused a deterioration in the sludge characteristics but did not affect the system as markedly as the sodium hydroxide in the full-scale study. A concentration of 2500 mg/L Na^+ showed the most deterioration.
4. Calcium caused an improvement in the sludge characteristics but did not affect the system as markedly as the calcium chloride in the full-scale study. A concentration of 2500 mg/L Ca^{++} produced the greatest improvement.

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A P P E N D I X

Table A-1. Raw Data for reactor #1.

SAMPLE DATE	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g/hr)	CST (sec)
Feb 14	1610	1110	428	87		
18	2000		140	80	23	
20	2360	1455	412	42	11	
24	2045	2160	218	51	11	
26	2705	1960	344	53	31	
28	2700	2330	192	64	7	
Mar 3	3080	2565	246	61	4	
5	2770	2315	412	45	6	
7	2500	2075	280	64	8	
10	2615	2195	288	57	9	
12	2240		348	71	15	
14	2415	1945	310	68	12	
15						
24	2900	2305	286	123	4	
26	2870	2260	870	48	3	
25						
27						
28	3485	2885	420	55		
31	2235	1725	340	36	6	
Apr 2	2380	1885	378	63	10	
4	2670	2090	484	56		
7	3205	2510	526	47	4	
9	2180	1640	464	59	9	
11	1680	1580	368	77	10	
14	1510	1165	368	53	12	
16	2015	1600	410	65	12	
18	2015	1255	596	30	16	
21	2321	1300	1330	38	6	
23	1710	1065	1050	35	13	
25	1915	1190	678	16	19	
28	2265	1360	756	14	14	
30	1540	535	704	19	7	
May 2	1315	645	738	23	5	
5	1740	890	794	17	10	
7	2255	1340	939	18	8	
9	2020	1045	992	15	6	
12	1055	735	482	28	10	
14	1355	1010	396	22	7	
16	1205	825	450	29	7	
19	1420	890	436	35	7	
21	775	475	342	38	5	
23	1000	620	296	20	5	
26	1716	1074	198	23	16	
28	2345	1365	560	17	7	

Table A-1. Raw Data for reactor #1 (continued).

SAMPLE DATA	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g /hr)	CST (sec)
30	2170	1125	864	23	8	
Jun 2	1780	1320	1124	84	6	
4	1320	755	332	45	49	
6	3425	1520	244	14	8	
9	4545	2900	240	48	8	
11	2760	1705	250	76	10	
23	1990	714	1022	70	28	
25	2375	1190	194	58	8	
27	2020	1365	76	49	14	
29	2200	1585	128	63	15	
Jul 2	2135	1590	206	93	13	
7	2790	2055	166	61	7	
9	2675	1960	110	74	7	
11	3020	2135	132	62	10	
14	2765	1825	102	68	11	
16	3730	2535	438	53	6	
18	2650	1850	118	74	7	
21	2800	2060	96	114	9	
23	2950	2040	134	135	9	
25	3020	2495	76	82	9	
28	1860	1488	54	107	10	10.5
30	2240	1828	34	98	7	12.0
Aug 1	2350	1825	136	98	11	11.6
4	2680	2150	122	74	8	8.2
6	2290	1870	534	96	12	10.3
8						9.5
Oct 30	2245	1865		420		83.0
31						83.0
Nov 4						42.6
5						38.0
6						38.7
7						44.6
8						81.6
11						39.4
12						30.0
13						42.3
14						32.1
17						30.2
18						20.6
19						15.5
20						15.6
Jan 19	3555	995	344	273	226	118.6
21	2830	792	90	318	184	73.1
23	3160	884	225	278	150	56.6

Table A-1. Raw Data for reactor #1 (continued).

SAMPLE DATE	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g /hr)	CST (sec)
26	2910	814	82	189	204	45.4
28	3020	904	140	149	174	92.2
30	3600	1008	235	130	221	50.8
Feb 6	3180	2226	68	163	8	29.8
9	2885	2019	130	107	6	22.1
11	2425	1698	398	103	7	16.6
13	2921	2045	106	92	6	32.5
17	1915	1340	216	130	11	33.7
19	2090	1463	180	86	10	15.7
22	2365	1656	78	59	9	9.8
Apr 3	1462	1023	188	246	14	
21	2195	1537				
24	1620	1134	340	185	16	
27	1925	1348	292	259	10	
29	1395	977	310	415	14	
May 4	1590	1113	209	238	13	9.7
8	1450	1015	210	280	13	12.4
Jun 17	2050	1435	205	82	13	11.0
19	1885	1320	175	90	17	9.5
22	1880	1316	182	64	15	8.3
24	1955	1369	390	153	20	7.1
29	1480	1036	175	162	15	9.5
Jul 1	1820	1274	290	122	11	8.3
3	1738	1217	235	75	13	8.3
7	1670	1169	220	72	9	7.9
10	1785	1250	55	56	18	10.9
15	1760	1232	104	80	18	13.4
17	3455	2420	360	43	15	10.3
19	2360	1652	86	68	10	9.9
22	2515	1761	780	64	14	8.6
24	2460	1722	340	65	12	8.3
27	1865	1306	235	93	12	
29	2410	1687	206	71	12	
Aug 3	2720	1904	202	88	16	
5	2265	1586	302	102	20	
8	2085	1459	363	91	8	
11	2555	1789	697	78	10	
13	3060	2142	1185	43	8	
17	2315	1621	887	52	11	
19	1940	1358	550	62	12	
25	2420	1694	510	66	7	
27	2410	1687	412	66	12	

Table A-1. Raw data for reactor #1 (continued).

SAMPLE DATA	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g/hr)	CST (sec)
Sep 1	2350	1645	365	59	14	
4	2920	2044	243	41	16	
8	3280	2296	255	30	14	

SAMPLE DATE	SPEC RES (m/kgx10 ¹²)	COD IN (mgO ₂ /l)	COD OUT (mgO ₂ /l)	ZONE SET (cm/sec)	pH	D.O. (mgDO/l)
Feb 14						7.6
18						8.0
20		1000	334			8.1
24		1935		0.16	7.62	8.0
26		2469	320	2.72	7.54	8.2
28		1535	334	4.60	7.32	8.1
Mar 3		1888	391	1.33	7.56	8.1
5		2711	460	1.19	7.58	8.1
7		2505	556	2.75	7.70	7.8
10				1.78	7.50	7.9
12				2.40	7.63	
14				2.24	7.75	7.9
15		1914	124			8.0
24				1.28	8.04	
26				3.24	8.26	8.0
25		1928				8.2
27		1913	253			8.4
28				2.34	8.31	8.2
31		1462	306	3.82	8.30	8.3
Apr 2		1392	292	3.55	8.43	8.3
4		2745	506	4.03	8.30	8.3
7		1760		2.59	8.32	8.2
9		2182	478		8.31	8.2
11		1620	687		8.33	8.1
14		1944	740		8.30	8.2
16		1620	673	6.07	7.90	8.3
18		2182	268		7.82	8.3
21		1549	225	10.00	7.65	8.3
23		2816	197	8.12	7.83	8.2
25		1984	292	3.30	7.83	8.0
28		1347	195		7.62	7.9
30		2096			7.50	7.8
May 3		1472	44		7.77	7.9
5		1840	147		7.78	7.9

Table A-1. Raw Data for reactor #1 (continued).

SAMPLE DATE	SPEC RES (m/kgx10 ¹²)	COD IN (mgO ₂ /l)	COD OUT (mgO ₂ /l)	ZONE SET (cm/min)	pH	D.O. (mgDO/l)
	7	1509	191	0.00	7.90	7.9
	9	1197	183	0.00	8.00	7.9
	12		141	0.00	8.04	7.9
	14	1126	211	0.00	8.50	7.9
	16	1095	137	0.11	8.21	8.0
	19	890	178	0.11	8.30	8.0
	21		95	8.00	8.32	7.8
	23	915	63	3.40	8.10	7.9
	26	985	42	5.60	8.17	7.8
	28	774	70	5.60	7.95	7.9
	30	822	96	6.00	7.97	7.9
Jun	2	1369	27	7.00	7.80	7.9
	4	1232	41	8.20	7.80	7.8
	6	1760	140	5.40	7.96	7.6
	9	1689	28	3.50	7.97	7.5
	11	1548	42	3.10	7.82	7.2
	23	2041	140	0.23	7.54	7.2
	25	2182	56		7.70	7.4
	27	1619	112	3.45	7.81	7.8
	29	1196	42	2.75	7.80	7.7
Jul	2	1408	98	1.73	7.85	7.6
	7	1838	74	2.05	7.41	7.8
	9	1059	112	2.25	7.93	7.9
	11	667	42	0.89	8.31	7.8
	14	1898	42	1.51	8.19	7.7
	16	2028	68	1.47	8.00	7.7
	18	1860	48	1.44	8.12	7.7
	21	1170	72	1.57	8.00	7.7
	23	1320	48	1.22	8.32	7.7
	25	1294	45	1.03	7.95	7.7
	28	1370	15	2.97	7.85	7.7
	30	1408	45	4.12	7.41	7.3
Aug	1	750	15	1.78	7.71	9.3
	4	1050	75	1.60	8.31	6.5
	6	1012	23	2.38	8.04	6.9
	8			2.08	8.18	6.9
Jan	19	898	33	0.04	7.98	7.7
	21	1224	82	0.11	8.00	8.0
	23	898	293	0.15	8.00	8.4
	26	816	277	0.36	7.93	8.0
	28	898	277	1.00	8.02	8.4
	30	898	147	1.05	8.30	7.4
Feb	6	2267	320	0.67	8.30	7.8
	9	2488	395	3.03	8.36	8.4
	11	2414	261	3.33	8.40	8.0

Table A-1. Raw Data for reactor #1 (continued).

SAMPLE DATE	SPEC RES (m/kgx10 ¹²)	COD IN (mgO ₂ /l)	COD OUT (mgO ₂ /l)	ZONE SET (cm/min)	pH	D.O. (mgDO/l)
13	7.12	1455	232	3.51	8.07	7.8
17	3.08	662	33	1.40	8.30	7.5
19	4.58	330	115	5.56	8.30	7.9
22	5.39	496	99	3.82	8.40	8.0
Apr 3	22.60			0.12	7.30	7.5
21						
24	6.58			1.14	7.15	7.5
27	6.92	1548	138	0.67	7.20	7.7
29	2.07	851	0	0.20	7.85	6.5
May 4	2.20	1316	30	2.23	7.50	7.2
8	1.99	984	276	2.54	8.05	6.8
Jun 17	0.25	1144	100	1.52	8.00	8.1
19	1.36	1144	226	2.99	7.82	7.9
22	0.41	904	116	3.07	7.80	6.0
24	0.42	1182	457	2.50	7.74	7.6
29	0.41			3.32	7.53	8.1
Jul 1	0.07	1107	251	2.03	7.63	7.6
3	0.07	1182	133	5.40	7.51	7.5
7	0.16	2658	132	0.69	8.04	8.3
10	0.04	1041	117	1.13	7.85	6.3
15	1.46	1747	190	5.94	7.50	7.2
17	0.46	1494	389	0.55	7.82	7.0
19	0.19	1584	290	1.27	7.51	7.3
22	0.37	850	223	2.23	7.60	8.7
24	0.32	1035	207	3.70	7.54	6.8
27	0.26	1330	192	2.70	7.60	7.1
29	0.26	1478	206	1.02	7.00	6.9
Aug 3	0.73	1404	236	3.34	7.93	7.8
5	0.75	1398	220	2.13	7.72	7.2
8	3.15	2355	250	3.70	7.84	7.3
11	2.75	2429	382	1.03	7.24	4.2
13	2.75	2208	397	6.66	7.46	7.1
17	1.22	1009	504	6.25	7.63	9.4
19	0.80	842	559	1.59	7.28	9.8
25	0.45	960	385	1.27	7.00	6.1
27	0.51	1485	454	3.33	7.15	7.4
Sep 1	1.16	1523	858	4.20	7.16	6.6
4	0.86	1061	899	5.90	7.21	6.9
8	0.06	1523	655	5.07	7.30	6.2

Table A-2. Raw Data for reactor #2

SAMPLE DATE	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g /hr)	CST (sec)
Feb 14	2925	2095	424	294		
18	3200		128	147		
20	3445	3075	308	273		
24	3005	2865	436	253		
26	2800	2355	192	143		
28	2435	2050	336	195		
Mar 3	3125	2655	462	110		
5	3315	2740	426	109		
7	3020	2560	320	165		
10	3420	2915	436	94		
12	2770	2330	120	144		
14	3070	2545	224	84	92	
15						
24	3475	2920	286	123	10	
26	3530	2925	870	85	3	
27						
28	5240	4470	682	43		
31	3225	2610	438	87	9	
Apr 2	3065	2455	420	91	4	
4	3350	2485	556	95		
7	3220	2545	516	84	12	
9	4125	3225	776	68	5	
11	3700	3180	236	79	6	
14	3775	3040	208	233	8	
16	3110	2590	184	122	7	
18	3270	2380	368	70	2	
21	3128	2057	710	70	7	
23	2880	2205	486	86	6	
25	2505	1755	480	72	8	
28	2430	1490	530	74	8	
30	2720	1825	474	66	9	
May 2	2390	1710	590	79	7	
5	2535	1690	634	78	8	
7	2005	1425	610	85	9	
9	2270	1605	534	80	7	
12	1820	1405	238	77	8	
14	2200	1750	582	91	7	
16	2055	1575	478	107	8	
19	2335	1735	408	77	7	
21	1755	1265	291	125	8	
23	2420	1710	192	58	8	
26	2202	1574	406	68	9	
28	2650	1850	1140	49	6	

Table A-2. Raw Data for reactor #2 (continued).

SAMPLE DATE	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g/hr)	CST (sec)
30	2820	1900	1068	53	5	
Jun 2	3005	1960	298	83	5	
4	3000	1310	278	73	7	
6	2786	1985	128	71	5	
9	4200	3485	324	52	12	
11	3820	2625	514	91	388	
23	2422	1052	1662	181	20	
25	3010	2170	492	146	9	
27	2275	1470	622	39	9	
29	3280	2255	452	59	9	
Jul 2	1565	1010	370	115	25	
7	3465	1375	402	49	5	
9	2610	1845	452	84	9	
11	3645	2720	202	79	19	
14	3165	2810	114	243	7	
16	5230	3750	574	84	11	
18	4202	3765	198	204	8	
21	4035	3110	410	161	5	
23	4010	2945	202	224	8	
25	3880	2815	350	164	9	
28	3690	2680	136	189	8	20.4
30	2675	2396	170	261	7	15.7
Aug 1	2955	2085	162	115	9	15.5
4	2495	1710	112	96	7	12.5
6	3620	2595	92	182	11	11.4
8						12.4
Oct 30	2910	2445		245		17.5
31						17.2
Nov 4						30.5
5						33.0
6						36.5
7						30.0
8						26.0
11						26.9
12						26.1
13						24.3
14						23.6
17						24.5
18						18.1
19						18.2
20						19.9
Jan 19	3610	2527	920	152	173	121.1
21	3985	2789.5	282	208	176	83.5
23	3870	2709	205	232	195	123.0

Table A-2. Raw Data for reactor #2 (continued).

SAMPLE DATE	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g/hr)	CST (sec)
26	3140	2198	68	286	218	83.0
28	2910	2037	205	96	242	109.2
30	3410	2387	350	102	196	71.9
Feb 6	2575	1803	48	97	9	35.6
9	2325	1628	136	137	20	25.4
11	2350	1645	212	106	14	25.5
13	2465	1726	100	109	10	35.0
17	2365	1656	100	147	8	48.6
19	2350	1645	68	106	10	14.7
22	1965	1376	224	112	15	11.6
Apr 3	1506	1054	185	255	16	
21	1505	1054				
24	1540	1078	420	58	9	
27	1425	998	420	84	17	
29	1270	889	170	149	22	
May 4	1425	998	418	154	9	13.2
8	1250	875	150	240	15	12.0
Jun 17	2010	1407	112	124	13	11.0
19	2085	1460	120	148	14	10.0
22	2500	1750	210	104	9	9.5
24	2780	1946	415	309	8	7.2
29	2879	2015	255	522	9	10.0
Jul 1	2435	1705	215	419	7	7.0
3	2167	1516	320	290	6	9.0
7	1770	1239	270	147	7	8.1
10	2505	1754	132	88	18	7.9
15	2515	1761	114	95	16	15.7
17	3335	2335	530	89	4	10.5
19	2369	1658	176	160	6	12.0
22	2010	1407	550	124	8	8.6
24	2460	1722	212	160	10	11.9
27	2025	1418	270	213	16	
29	2335	1635	365	187	9	
Aug 3	2505	1754	260	183	14	
5	2565	1796	370	164	15	
8	2505	1754	160	124	27	
11	2820	1974	243	294	55	
13	3215	2251	240	93	7	
17	3155	2209	195	158	5	
19	2470	1729	135	130	11	
25	2960	2072	140	140	6	
27	3005	2104	142	120	6	
Sep 1	3315	2321	107	84	10	
4	2510	1757	127	155	12	

Table A-2. Raw Data for reactor #2 (continued).

SAMPLE DATE	MLSS (mg/l)	MLVSS (mg/l)	EFF SS (mg/l)	SVI	OUR (mg/g/hr)	CST (sec)
8	3320	2324	145	216	7	
10	3165	2216	145	186	10	

SAMPLE DATE	SPEC RES (m/kgX10 ¹²)	COD IN (mgO ₂ /l)	COD OUT (mgO ₂ /l)	ZONE SET (cm/min)	pH	D.O. (mgO /l)
Feb 14						8.0
18			328			7.8
20		1801	320			7.9
24		2235	240	0.07	8.20	7.8
26		1535	387	1.83	7.90	7.6
28		2054	432	0.88	8.00	1.4
Mar 3		2368	425	2.52	8.40	7.6
5		1133	515	1.20	7.85	7.8
7				0.39	7.70	8.1
10				2.40	7.78	8.4
12				1.90	7.78	8.3
14				1.90	8.20	8.3
15		1842	89			
24				0.46	6.90	8.1
26		1928	325	2.92	7.00	8.2
27		1842		2.77	7.12	8.2
28		1531		2.15	7.30	8.3
31		1322	278	2.85	7.34	8.2
Apr 2		1322	320	2.55	7.44	8.0
4		1971	506	2.63	7.45	7.9
7		2185	295		7.88	7.9
9		2041	619		7.67	7.8
11		2073	544		6.90	7.9
14		1036	635		7.12	7.9
16		2980	180	1.35	7.23	8.0
18					7.34	7.8
21				5.50	7.36	7.9
23				2.87	7.55	7.8
25		2134	15	2.60	7.44	7.6
28		1797	165		7.56	8.0
30		2246			7.40	8.2
May 2		1693	59		6.99	8.1
5		1325	59		6.90	8.2
7		662	73	3.44	7.56	8.2

Table A-2. Raw Data for reactor #2 (continued).

SAMPLE DATE	SPEC RES (m/kgx10 ¹²)	COD IN (mgO ₂ /l)	COD OUT (mgO ₂ /l)	ZONE SET (cm/min)	pH	D.O. (mgDO/l)
		3063	99	3.95	7.78	8.2
		1197	127	2.38	7.67	8.1
		1408	85	2.27	7.70	8.1
		2123	110	2.30	7.78	8.2
		2054	82	2.00	7.78	8.0
		1814	82	2.00	7.88	7.9
		1162	49	2.95	7.97	7.9
		1056	14	1.19	7.67	7.8
		1056	42	2.45	7.86	7.5
		1677	61	0.79	7.90	7.4
Jun		1027	27	1.39	7.80	7.3
		1027	69	3.59	7.83	7.5
		2112	0	2.17	7.86	7.4
		1900	98	2.12	7.89	7.3
		1689	154	1.76	7.57	5.6
		915	112	0.61	7.65	4.5
		915	239		7.67	6.8
		2323	154	3.07	7.66	6.9
		1056	140	2.80	7.98	7.0
Jul		1549	126	1.73	8.00	7.3
		1526	149	1.80	8.11	7.0
		1558	49	2.93	8.21	7.2
		667	40	1.00	8.11	7.3
		1445	42	0.27	8.23	7.2
		1445	94	0.25	8.12	7.5
		1920	108	0.08	8.00	7.2
		1170	48	0.59	7.99	7.2
		720	72	0.12	8.34	7.0
		761	121	0.35	8.22	6.9
		1142	319	0.22	8.31	7.0
		1408	106	0.77	7.71	6.9
Aug		750	45	1.64	7.31	6.9
		1050	60	1.93	7.72	6.5
		1012	52	0.57	7.31	6.7
				0.25	7.56	6.9
Jan		1387	82	0.96	7.52	7.3
		1468	262	0.26	8.03	8.2
		1060		0.08	8.15	8.8
		897	146	0.79	8.33	8.0
		897	82	1.58	8.31	8.2
		897	147	1.90	8.29	7.8
Feb		937	409	1.19	8.30	8.1
		1307	674	3.05	8.48	8.9
		2193	40	4.34	8.41	7.8
	11.40	2488	350	2.78	8.50	7.0

Table A-2. Raw Data for reactor #2 (continued).

SAMPLE DATE	SPEC RES (m/kgx10 ¹²)	COD IN (mgO ₂ /l)	COD OUT (mgO ₂ /l)	ZONE SET (cm/min)	pH	D.O. (mgDO/l)
17	8.85	662	132	1.51	8.42	7.5
19	4.20	413	82	4.00	8.50	8.5
22	3.02	744	66	2.63	8.40	7.6
Apr 3	18.00			0.07	7.48	7.0
21						
24	8.67	1161	122	7.50	6.40	7.2
27	2.25	1393	61	3.05	6.90	8.2
29	1.63	1470	92	2.42	7.33	6.5
May 4	7.60			2.55	7.34	7.3
8	0.99	1144	245	3.23	7.72	7.2
Jun 17	1.88	1304	260	2.93	7.80	8.8
19	0.69	1144	180	1.78	6.97	7.5
22	0.14	904	341	2.85	7.20	7.4
24	0.57	1107	236	1.02	7.67	8.2
29	0.72			0.18	7.43	8.2
Jul 1	0.35	1033	236	0.60	7.23	8.2
3	0.52	1107	590	0.54	7.38	8.2
7	0.26	1993	324	2.08	7.72	8.3
10	0.02	1950	697	2.52	8.10	7.3
15	0.25	1494	244	3.25	7.50	9.0
17	0.18	1000	479	2.02	7.80	7.3
19	0.68	588	335	1.61	7.80	6.0
22	0.50	517	223	2.19	7.90	7.2
24	0.62	1035	207	3.03	7.46	6.8
27	0.77	1700	200	3.57	7.45	7.8
29	0.81	1256	266	1.15	7.90	8.1
Aug 3	0.58	1330	207	1.00	7.62	8.3
5	0.12	883	338	1.29	7.83	8.5
8	.00	1251	29	1.67	7.82	7.4
11	6.45	2134	662	0.12	6.84	
13	0.87	2428	143	1.04	7.32	
17	0.38	673	302	0.61	7.93	7.8
19	0.93	842	192	2.56	7.97	9.0
25	0.49	1048	175	1.22	7.40	7.1
27	0.53	842	139	1.25	7.51	7.2
Sep 1	0.48	692	489	2.63	7.22	6.6
4	0.65	969	323	1.12	7.11	7.4
8	0.15	1061	341	2.77	7.10	7.2
10	0.24	1707	526	0.33	7.45	6.2

Table A-3. Atomic Adsorption data for reactor #1

SAMPLE DATE	Mg++ INF (mg/l)	Mg++ EFF (mg/l)	Ca++ INF (mg/l)	Ca++ EFF (mg/l)	Na+ INF (mg/l)	Na+ EFF (mg/l)
Jul 25	670	770	45.3	71	68.7	45.1
28		900		57.2		49.7
30	750	850	46.8	52.1	46.4	47.8
Aug 1						
4	790	800	53.9	48.3	51	56.3
6	862	910	48.6	75.7	56.8	56.4
8	926	938	82	70.4	38.2	59.8
Oct 30						
31						
Nov 4						
5						
6						
7						
8						
11						
12						
13						
14						
17						
18						
19						
20	952	979	58.7	437	30.2	30.3
Jan 19						
21						
23						
26						
28						
30						
Feb 6						
9						
11	1290	1400	30.8	35.2	148	71.6
13						
17						
19	1070	1560	31.2	31.8	48	71
22						
Apr 3	1000	975	40.8	38.7	31.5	52.6
21						
24						
27						
29						
May 4						
8	895	1107	39.9	45.3	68.8	76.4
Jun 17	915	1212	40.9	42.2	116	57.8
19	856	1005	37.7	39.4	110	50.6
22	1074	1120	39.4	42.6	70.2	57.8

Table A-3. Atomic Adsorption data for reactor #1 (cont.).

SAMPLE DATE	Mg++ INF (mg/l)	Mg++ EFF (mg/l)	Ca++ INF (mg/l)	Ca++ EFF (mg/l)	Na+ INF (mg/l)	Na+ EFF (mg/l)
24						
29						
Jul 1						
3						
7						
10	1020	1150	19.6	34.3	308	82.2
15	1160	1150	29.2	29.7	118	82
17	892	1000	44.6	44.9	3240	2720
19						
22	948	1350	45.6	51.7	2480	3940
24	760	922	36.3	42.2	1860	2320
27	864	940	35.2	52	25.6	2400
29						
Aug 3	1130	812	36.3	34.4	3540	3280
5	747	856	33.1	37.1	3940	4010
8	749	855	71.2	39.2	5040	3900
11	923	874	44.2	39.9	4820	5100
13	813	843	37.1	39.2	5200	4920
17	784	791	34	38.6	5980	6270
19	914	869	36.7	37.2	3580	6640
25	751	639	34.5	38.2	3920	5580
27	767	800	34.8	38.3	5580	5600
Sep 1	767	800	58.3	47.7	5820	6020
4	828	818	41.9	39.5	7470	6900
8	843	799	49	37.4	7380	7020

Table A-4. Atomic Adsorption data for reactor #2.

SAMPLE DATE	Mg++ INF (mg/l)	Mg++ EFF (mg/l)	Ca++ INF (mg/l)	Ca++ EFF (mg/l)	Na+ INF (mg/l)	Na+ EFF (mg/l)
Jul 23						
25	800	840	760	1020	49.8	74.2
28	620	820	671	940	39.4	52.3
30	700	820	700	880	45.5	52.8
Aug 1						
4	790	770	760	51.7	52.3	31.2
6	947	965	13.8	10.6	42.2	62.2
8	884	987	95.6	65.6	52.4	53.4
Oct 30						
31						
Nov 4						
5						
6						
7						
8						
11						
12						
13						
14						
17						
18						
19						
20	979	990	59.8	40.4	29.7	30.4
Jan 19						
21						
23						
26						
28						
30						
Feb 6						
9						
11	852	918	31.5	32.6	512	450
13						
17						
19	858	946	29.4	31.9	710	884
22						
Apr 3						
21						
24						
27						
29						
May 4						
8	918	986	31.1	34.9	734	2220
Jun 17	795	923	36.7	42.2	1552	942
19	859	868	38.8	38.7	1526	1402

Table A-4. Atomic Adsorption data for reactor #2 (cont.).

SAMPLE DATE	Mg++ INF (mg/l)	Mg++ EFF (mg/l)	Ca++ INF (mg/l)	Ca++ EFF (mg/l)	Na++ INF (mg/l)	Na+ EFF (mg/l)
22	807	872	36.5	40.2	1467	1836
24						
29						
Jul 1						
3						
7						
10						
15	880	910	28.2	43.1	2500	3600
17	1030	1190	42.8	48.2	2460	2940
19						
22	912	1010	37.7	48.7	2790	3180
24	996	1180	35.5	42.8	2240	2940
27	1080	1820	36	76.1	2920	5010
29						
Aug 3	826	1030	33	35	3560	3140
5	842	1080	35.4	35.4	202	3850
8	741	857	57.9	24.9	2420	3060
11	1050	1150	10.8	84.3	2840	3900
13	967	1148	35.6	42.9	2560	3450
17	970	1080	33.9	37.9	2660	3320
19	735	826	39.9	29.3	5920	3270
25	799	100	362	477	380	2036
27	754	889	444	600	272	1196
Sep 1	856	1020	45.2	312	3080	1826
4	802	965	38.4	107	2180	3180
8	1006	1040	50.5	53.2	1760	3640

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