

THE EFFECT OF LIME TREATMENT OF SEWAGE ON  
OXYGEN UPTAKE BY ACTIVATED SOLIDS

by

RALPH L. FLOURNOY

B. S., Kansas State University, 1970

5248

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Civil Engineering

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1971

Approved by:

Lawrence A. Schmid  
Major Professor

LD  
2663  
TH  
1971  
F55  
C.2

## TABLE OF CONTENTS

INTRODUCTION . . . . .	1
LITERATURE REVIEW . . . . .	5
Lime Treatment of Sewage	
Manometric Methods	
Factors Involved in Organic Biodegradation	
PROCEDURES . . . . .	20
Analytical Procedures and Equipment	
Experimental Procedure	
Part I--Preliminary Tests	
Part II--Manometric Measurements	
RESULTS . . . . .	34
Part I	
Part II	
Accuracy Data	
DISCUSSION . . . . .	67
Part I	
Part II	
Accuracy Data	
CONCLUSIONS . . . . .	77
RECOMMENDATIONS FOR FURTHER RESEARCH . . . . .	79
BIBLIOGRAPHY . . . . .	80

## LIST OF TABLES

Table	Page
1. BOD and COD Removals with Lime Treatment . . . . .	5
2. Pilot Plant COD Removals . . . . .	6
3. Characteristics of Highland Park Sewage Samples . . . . .	10
4. Contribution to Sewage Fraction of Certain Strength Parameters in Percent of Recovered Strength Parameter . . . . .	10
5. Summary of Part I . . . . .	35
6. Summary of Data for Run 1a . . . . .	41
7. Summary of Data for Run 1b . . . . .	43
8. Summary of Data for Run 1c . . . . .	45
9. Summary of Data for Run 2a . . . . .	48
10. Summary of Data for Run 2b . . . . .	50
11. Summary of Data for Run 2c . . . . .	52
12. Summary of Data for Run 3a . . . . .	55
13. Summary of Data for Run 3b . . . . .	57
14. Summary of Data for Run 3c . . . . .	59
15. The $k_1$ Reaction-Rate Constants . . . . .	61
16. COD Accuracy Data . . . . .	64
17. Uptake Accuracy Data . . . . .	65
18. Factors of Relative Stabilization Ratios of Lime-Sewage $k_1$ Values to Settled Sewage . . . . .	69

## LIST OF FIGURES

Figure	Page
1. Schematic of Proposed Phosphate Removal Process . . . . .	3
2. BOD Curves for the Particulate Fractions of Sewage . . . . .	14
3. Observed BOD for Synthetic Organic Materials Seeded with Sewage . . . . .	16
4. Oxygen Uptake Curves for Run 1a . . . . .	42
5. Oxygen Uptake Curves for Run 1b . . . . .	44
6. Oxygen Uptake Curves for Run 1c . . . . .	46
7. Oxygen Uptake Curves for Run 2a . . . . .	49
8. Oxygen Uptake Curves for Run 2b . . . . .	51
9. Oxygen Uptake Curves for Run 2c . . . . .	53
10. Oxygen Uptake Curves for Run 3a . . . . .	56
11. Oxygen Uptake Curves for Run 3b . . . . .	58
12. Oxygen Uptake Curves for Run 3c . . . . .	60
13. Calculation of $k_1$ Reaction-Rate Constants . . . . .	62
14. Calculation of $k_1$ Reaction-Rate Constants . . . . .	63

### ACKNOWLEDGMENTS

I wish to sincerely thank Dr. Lawrence A. Schmid for his assistance and support during this study. I am grateful to Dr. Jack Blackburn, Head of the Department of Civil Engineering, Dr. Larry Erickson, Dr. Richard Marzolf, and Dr. Frederick Oehme for serving on the review committee.

This research was supported by a traineeship from research grant 170050 DCC, Environmental Protection Agency.

## INTRODUCTION

The problem of wastewater treatment has been compounded in recent years by the growing number of synthetic organic compounds in use. As Hunter and Heukelekian (1) point out, ". . . many of these new and economically important compounds are partially or wholly resistant to microbial attack." This resistance has increased the interest in the biodegradability of compounds (see literature review) and caused a re-evaluation of existing tests and methods of analysis. Tests such as the BOD test, which have been used for a long time, no longer are completely adequate (1, 2). While it still has obvious value in sanitary engineering, its slowness and remoteness from conditions existing in aerobic treatment chambers gives rise to a certain amount of dissatisfaction. Only the employment of more sophisticated analysis will permit the determination of the extent of organic contaminants and the character and nature of these. A more complete picture is important in determining the overall effect of a given treatment on that fraction that shows evidence of being highly persistent in the environment (particularly aquatic ones).

The primary methods of dealing with wastewater come under either chemical, physical or biological classifications. Most conventional plants include sedimentation (physical) and aerobic stabilization (biological). The primary interest in such plants is centered on insuring that adequate treatment is present to reduce BOD and turbidity--the quantities easiest to measure. Good removals of BOD do not give a complete picture of the total organic removal. New areas of waste treatment must be perfected to remove the growing class of materials that is not now effectively treated and whose persistence in natural

aquatic systems is undesirable.

One such system formed the basis for this research. This process originally was conceived by Schmid (3), (Fig. 1), who determined the performance parameters in extensive bench-scale tests for the lime-biological treatment system. The system involves lime treatment of raw sewage followed by conventional settling and activated sludge systems. This overall system was conceived as a means of complexing phosphates and removing them from raw sewage. The process was transferred to pilot plant scale for further testing. The idea for this thesis was conceived from data accumulated here at Kansas State University. The data indicated high COD (chemical oxygen demand) removals that seemed to merit investigation. The basic process differed radically enough from processes lacking initial chemical treatment to merit more tests anyway.

The research itself consisted of two parts. The first part consisted of preliminary bench-scale tests. These tests were to analyze the effect of lime treatment of sewage on the removal of soluble organic material. This part was to determine whether any significant data could be gathered at this scale. To accomplish this, the aeration chamber of the pilot plant was modeled down to a 2 liter graduated cylinder that held, as a portion of total volume,  $2/3$  activated sludge and  $1/3$  sewage. Two identical units were established--one using settled sewage and one using sewage coagulated with lime solution before settling. Both units used activated sludge from the pilot plant and were simultaneously aerated. Testing the solutions for soluble COD at intervals indicated (crudely) the rate and extent of removal of soluble organic matter for each type of sewage.

The second part of this research involved the use of a Warburg manometric apparatus. Building on the data from Part I, the scope was expanded.

**THIS BOOK  
CONTAINS  
NUMEROUS PAGES  
WITH DIAGRAMS  
THAT ARE CROOKED  
COMPARED TO THE  
REST OF THE  
INFORMATION ON  
THE PAGE.**

**THIS IS AS  
RECEIVED FROM  
CUSTOMER.**

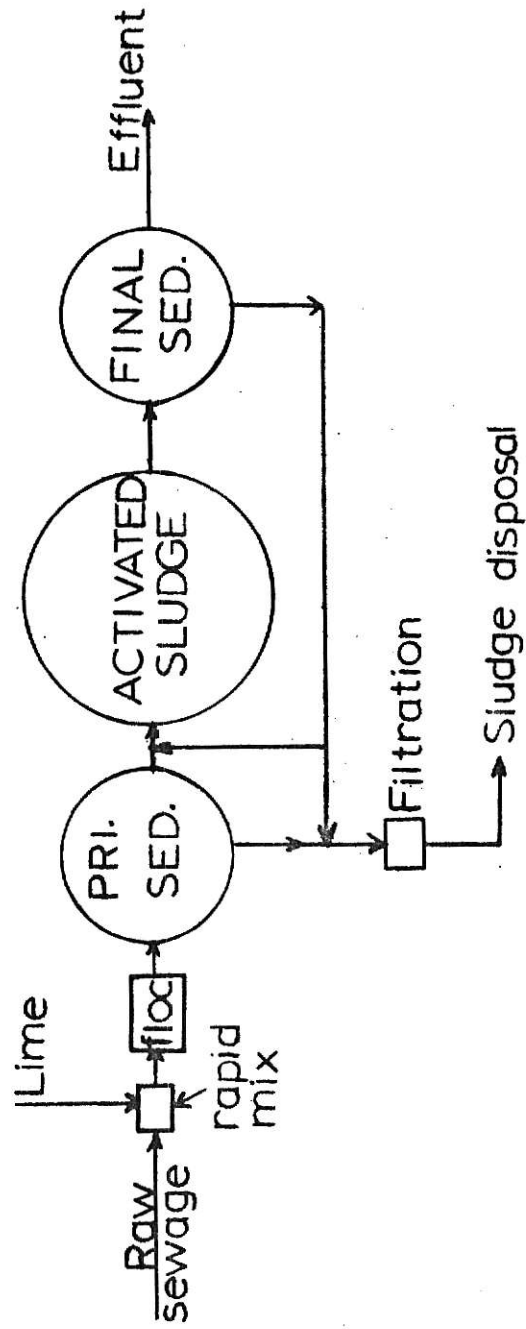


Fig.1 Schematic of proposed phosphate removal process

Units were set up in the lab to maintain activated sludge grown on lime-treated sewage and settled sewage. Using the activated sludge solids from these units and the two types of sewage, more complete and precise data could be gathered. Further variations involving different levels of lime treatment and solids concentrations meant that a more complete picture of the lime-biological process could be attained. The manometric data would be used to plot oxygen uptake curves and calculate reaction rates ( $k_1$ ) for first-stage aerobic oxidation.

## LITERATURE REVIEW

### LIME TREATMENT OF SEWAGE

Schmid (3) investigated the potential of a lime-biological treatment process in removing phosphates. This process consists of lime clarification of sewage followed by a conventional secondary treatment process.

The data compiled by Schmid (3) included a series of jar tests<sup>1</sup> run on raw sewage from the Lawrence, Kansas, treatment plant. The results for BOD and COD removal, taken from the appendix, are summarized in Table 1. They are based on runs 3, 5, 6, 7, 12, 16 and 27, and give some idea of the removals that can be attained for various lime dosages.

TABLE 1. BOD and COD Removals with Lime Treatment (3)

Dosage	Average % COD removal from raw sewage	Range of COD removals	Average pH	Average % BOD removal from raw sewage	Range of BOD removal
0	33	24 - 42	7.1	25	4 - 36
100	52	41 - 63	9.0	50	40 - 56
200	56	49 - 64	9.7	52	45 - 59
300	56	50 - 65	10.5	52	40 - 59
400	61	54 - 67	11.0	61	---

The results for no dosage, which represents settling for 1/2 hour, is presented to show the additional removal by lime treatment. The pH shows the smallest variation and gives some idea of the effect of certain dosages.

---

<sup>1</sup>These tests were done by adding lime to the sewage, mixing at 100 r.p.m. for 1 min. and at 30 r.p.m. for 15 minutes, followed by settling for 1/2 hour.

This research led to the development of a pilot plant for researching the process on a larger scale. Data gathered from this plant indicated an efficiency at removing the COD material higher than expected. This is due partially to the domestic character of Manhattan sewage and to the increased efficiency realized in transferring the process to a larger scale operation. The lime was fed in at a rate high enough to maintain a constant pH of 9.8. Tests were run about twice a week. These tests were based on samples taken every 6 hours for 24 hours (3 p.m., 9 p.m., 3 a.m., 9 a.m.) of the 1) raw influent sewage from the Manhattan treatment plant primary settling basin, 2) the effluent from the primary settling basin of the pilot plant following lime treatment and sedimentation and 3) the final effluent from the pilot plant. At times the samples were composited for a daily average and at other times individually tested and prorated according to flow records.

After about four months the data compiled indicated good purification and phosphate removals (4) (5). The important results are summarized in Table 2. They indicated consistently high COD removals reaching 97% and BOD removal reaching 98%.

TABLE 2. Pilot Plant COD Removals (4) (5)

Date	Flow	Primary pH	COD removals				
			Raw	Primary	% Removal	Final	% Removal
7/ 6- 7	10,000	9.8	485	151	69	15	96
7/ 8- 9	8,000	9.8	300	170	43	10	97
10/26-27	12,250	9.3	507	164	68	16	97
2/18-19	10,000	10.6	359	202	44	40	89

As will become clear in this review, COD removals generally do not reach this level, there being a certain amount of hard or refractory material in any sewage effluent. In addition to this data, detailed and sensitive tests of biological oxygen uptake of various facets of the process are important. The detailed analysis is important in describing any important distinction from conventional treatment.

Humenick and Kaufman (6) noted in their literature review that chemical and biological systems in various optimized combinations can effect a high degree of degradable carbon removal. They also pointed out that biological suspensions can assimilate soluble organic compounds, especially those of low molecular weight, although they do not attempt to define any limits for a low weight classification. As they mention, chemical coagulants are primarily effective in removing suspended and colloidal matter. The process investigated consisted of high-rate activated sludge treatment followed by coagulation-precipitation with lime. They reported removals of BOD in excess of 90% and COD in excess of 80% at a lime dosage of 280 mg/l as CaO (370 mg/l  $\text{Ca(OH)}_2$ ) in the process.

Given the removal of particular fractions of sewage by coagulation-precipitation and activated sludge, it might be advantageous to discuss briefly the composition of raw sewage and secondary effluents.

Hunter and Heukelekian (7) have done a fairly recent study on the composition of domestic sewage. They first separated the sewage into soluble and particulate fractions. The particulate fraction was further separated into settleable, supracolloidal and colloidal fractions. Some of the results are given in Tables 3 and 4.

Conclusions arrived at by testing composited samples over two six-month periods include:

1. The particulate fraction solids are approximately 80% organic matter; the soluble fraction solids are 30% organic.
2. There appears to be some pattern in the general distribution of organic matter among fractions; no set pattern is apparent for nitrogenous matter.
3. The soluble organic matter was found to be composed largely of ethyl-ether extractable matter, the organics acids (lactic, gallic and citric) being the primary constituents followed by neutral compounds. A small fraction was contributed by amphoteric and basic.

This study is correlated with other studies (8) (9) and contains much more data than could be presented conveniently here. A detailed analysis of each fraction is given.

Bunch, Barth and Ettinger (10) have presented a concise analysis of secondary effluents from five different cities (seven plants). They concluded that:

1. Suspended solids account for 20-30% of the total effluent COD.
2. The ratio of volatiles to COD is about 1.5.
3. The majority of constituents giving COD are dialyzable but 40% of the material is indicated to be of high molecular weight (protein or other polymeric substances), because it resists dialysis.

Helfgott, Hunter and Rickert (11) analyzed effluents from primary, secondary and tertiary treatment plants. They reviewed other papers including the above two and tried to fill in gaps. They report from their readings and research that:

1. Incomplete hydrolysis and oxidation treatment can create compounds more refractory than those existing in the influent waters. This is because the greater the degree of partial oxidation, the more resistant is the compound to further oxidation steps. The effluent may have a low BOD but a high COD

that is more detrimental environmentally in terms of persistence.

2. The combined colloidal-soluble fraction of raw sewage is significantly more refractory than the settleable-supracolloidal fraction (separation by centrifugation at low and high speed).
3. The soluble fraction is the single most refractory of all.
4. The residual colloidal fraction in secondary effluents is largely parts of microorganism's cell walls.

Returning to the effect of lime treatment, Molof and Zuckerman (12) (13) have described the effect of high dosages on raw sewage. They started with bench-scale tests and then transferred the process to a pilot plant set-up. The process consists basically of treating wastewater with lime to a high pH (11.5), neutralizing it and filtering it through sand and then activated carbon. The results indicate that retention of the chemically treated wastewater for about 80 minutes will affect the chromatographic molecular weight distribution. The bench-scale tests they ran show the soluble organic fraction to have two molecular weight distribution peaks, one at <400 and one >1200, with little between the peaks. According to their research:

1. Conventional biological treatment results in a distribution with a single peak at >1200 mw, that is unsuitable for carbon adsorption. (Helfgott, et al., (11) points out that high molecular weight hydrocarbonaceous non-polar organics can foul ion exchange resins and membranes.)
2. Chemical treatment with lime results in wastewater that contains soluble organics showing a chromatographic curve with one large peak at <400 mol. wt. This results from either removal or hydrolysis of large molecules larger than 1200 mol. wt. into smaller fragments.

#### MANOMETRIC METHODS

The most important source of information in any study of this kind is Manometric Methods by Umbreit, et al. (14). This describes the procedures used in setting up the apparatus. It served along with Burkhead's research

TABLE 3. Characteristics of Highland Park Sewage Samples (7)

Characteristic	Winter-Spring, 1959			Fall-Winter, 1959-60		
	Maximum	Mean*	Minimum	Maximum	Mean*	Minimum
Flow (mgd)	2.29	1.46	0.87	3.59	1.97	1.00
pH	7.5	7.2†	6.8	7.5	7.2†	6.7
Settleable solids (mg/l)	6.1	3.3	1.8	10.6	6.7	2.4
Total solids (mg/l)	640	453	322	676	481	294
Volatile total solids (mg/l)	388	217	118	336	249	148
Suspended solids (mg/l)	258	145	83	236	146	58
Volatile suspended solids (mg/l)	208	120	62	174	125	54
Chemical oxygen demand (mg/l)	436	288	159	443	282	97
Biochemical oxygen demand (mg/l)	276	147	75	216	136	46
Chloride (mg/l)	45	35	25	83	41	28

\* Arithmetic  
† Modal value

TABLE 4. Contribution of Sewage Fractions to Certain Strength Parameters in Percent of Recovered Strength Parameter (7)

Sewage Fraction	Organic Nitrogen		COD		Total Solids		Volatile Solids	
	Wint Sprg 1959	Fall Wint 1959 60	Wint Sprg 1959	Fall Wint 1959 60	Wint Sprg 1959	Fall Wint 1959 60	Wint Sprg 1959	Fall Wint 1959 60
Settleable	28	38	34	40	18	18	28	31
Supra-colloidal	36	32	27	23	13	10	22	18
Colloidal	12	10	14	14	7	7	11	9
Soluble	24	20	25	23	62	65	37	42

(15) as the primary sources of procedure. This has been standardized enough so that no further explanation is given.

Montgomery (2) has given a very complete and thorough review of respirometric techniques and factors affecting oxygen demand. Applications are not reviewed, although some are mentioned to illustrate points. This review is an excellent starting point in any study using respirometric methods.

A series of articles by Corbet and Wooldridge (16) and Wooldridge and Standfast (17-19) done back in 1936 give a great deal more information. Their research (using Barcroft manometers) covered a wide range of topics. Some of the most important findings were:

1. A method of rejecting faulty results (leaks, condensation in tubes) by plotting on double log paper the pressure change vs. time and rejecting those that tend to be parabolic.
2. Proof that carbon dioxide and  $O_2$  were the only gases evolved in significant quantities.
3. Application of respirometric methods to studies of activated sludge and sewage--alone or in combination--with accuracy.

#### Determining Biodegradability

The use of manometers in determining biodegradability has been described by Schulze and Hoogerhyde (20), who used a differential manometer. The method consisted of calculating the specific growth rate ( $k_1$ ), by computing the slope of a plot of  $dO_2/dt$  versus time on log paper, for the exponential growth phase of the oxygen uptake curve and using it as a quantitative measure of degradability. The research indicated that sewage with a high proportion of industrial waste has a significantly lower biodegradability than one low in industrial waste.

Hunter and Heukelekian (1) discussed the difficulty in defining biodegradable. They point out that the term, in essence, implies the ability of a

compound to be oxidized by micro-organisms with production of cell matter, energy and waste products. Determining the extent that a compound must be degraded before it is considered biodegradable is more complex. Some researchers adopt the concept of "activity" loss, meaning the property that makes the compound objectionable is lost through microbial action. A more severe criterion would be to demand complete conversion to cell matter, energy,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and minerals. This distinction, they claim, could become a serious problem as organic pollution increases.

After pointing out the advantages of respirometric studies over the BOD test, a method of determining per cent biodegradability was presented. This method consists of first determining, 1) the weight of new cellular matter formed during the oxidation period and its COD equivalent and 2) the soluble COD of the solution. From these numbers (and the oxygen utilized) it is possible to calculate what per cent of the compound was oxidized, what percentage was not oxidized, and what percentage was converted to cell growth. The per cent biodegradation is obtained by adding the percentages representing oxidation and growth. Excellent results were reported with replication allowing an even more complete analysis.

Vath (21), states that, ". . . when the net oxygen uptake at the inflection point of the plot . . . equals or exceeds 35 to 40 per cent of the theoretical oxygen demand (COD) of the contained organic substrate, degradation can be assumed to be complete." He then claims that oxygen uptakes will exceed 35-40% of the surfactant COD when oxidation, not assimilation, is the major mechanism of initial biodegradation.

#### Accuracy

Caldwell and Langelier (22) found that replicate Warburg tests had an

average (not standard) deviation of 1.7 per cent for raw sewage and 2.3 per cent for settled sewage. The results when compared to the standard BOD test revealed the manometric results to be consistently and appreciably higher.

Lee and Oswald (23) also reported this. Their research indicated first-stage demands about 15 per cent higher for the Warburg.

Dawson and Jenkins (24), echoing research by Corbet and Wooldridge (16) pointed out that replication was important. The best accuracy they were able to obtain involved an error of 4-5 per cent with duplicates or triplicates.

#### Factors in Measuring Oxygen Uptake by Sewage and Activated Solids

Montgomery and Gardiner (25) suggested that the oxygen requirements of different batches of activated sludge growing on a given substrate might not always be the same. They attributed this partially to the unspecified mixture of microorganisms existing in an activated sludge unit. In conjunction with this they pointed out that the role of protozoa in oxygen demand tests is not completely understood. The review indicated that information on protozoan activity varies. Some researchers claim that no special effect is felt for 1.5 days, while others suggest that they excrete a substance which stimulates bacterial respiration.

Dawson and Jenkins (24) tested the uptake of washed activated solids up to a volume of 5 ml and with concentrations ranging from 500 to 15,000 mg/l. Tests run at a concentration of 2375 mg/l (suspended solids) and at various volumes showed that oxygen uptake was directly proportional to the volume of sludge. The plots were straight lines of increasing slope for increasing volume.

Wooldridge and Standfast (18) did some fairly complete and thorough work showing how the presence of sludge with the sewage to be tested greatly

3. The BOD exerted by individual components, measured singly, may not apply to an aqueous mixture of these compounds.

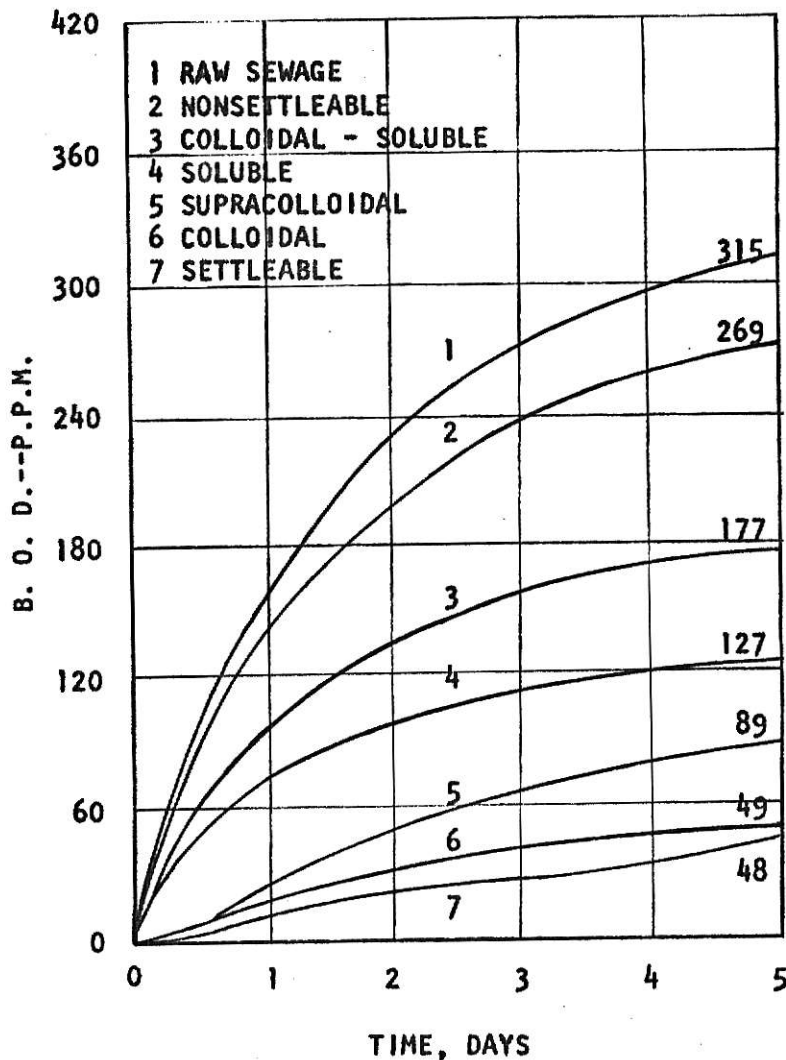


Figure 2.--B.O.D. curves for the particulate fractions of sewage (26).

Increases the initial rate of oxidation although the ultimate demand is scarcely influenced. This research demonstrated (for the first time) that activated sludge could serve to reveal marked differences in the oxygen demand of sewages. The method was capable of discerning primary and secondary effluents from each other and from raw sewage effectively.

Balmat (26), studied the uptake of various sewage fractions (soluble, supracolloidal, colloidal and settleable in order of increasing size) using a Warburg apparatus. Each fraction was suspended in BOD mineral dilution water containing 1% sewage seed. The data indicates that the  $k_1$  (BOD rate) decreases with the increasing particle size as listed above. This is shown in Fig. 2.

#### FACTORS INVOLVED IN ORGANIC BIODEGRADATION

Mills and Stack (27) classified the BOD curves of synthetic organic compounds into four classes:

1. Type I: those materials that are readily biologically oxidized. Most compounds fall into this classification and include most esters, sugars, straight chain alcohols, organic acids and aldehydes.
2. Type II: those materials slow in exerting BOD with or without an initial lag phase.
3. Type III: those materials having a characteristic lag phase when sewage seed is used. Included here are allyl alcohol, diethyl ketone and ethylene glycol.
4. Type IV: those materials exerting no significant BOD over extended incubation periods. Isopropyl ether is an example.

These curves are illustrated in Fig. 3. Testing was done on many compounds (synthetic) with the following generalizations:

1. Oxidation is related to chain structure, molecular size, and functional groups present.
2. Atoms other than carbon in the main chain of a compound may interfere with carbonaceous aerobic oxidation.

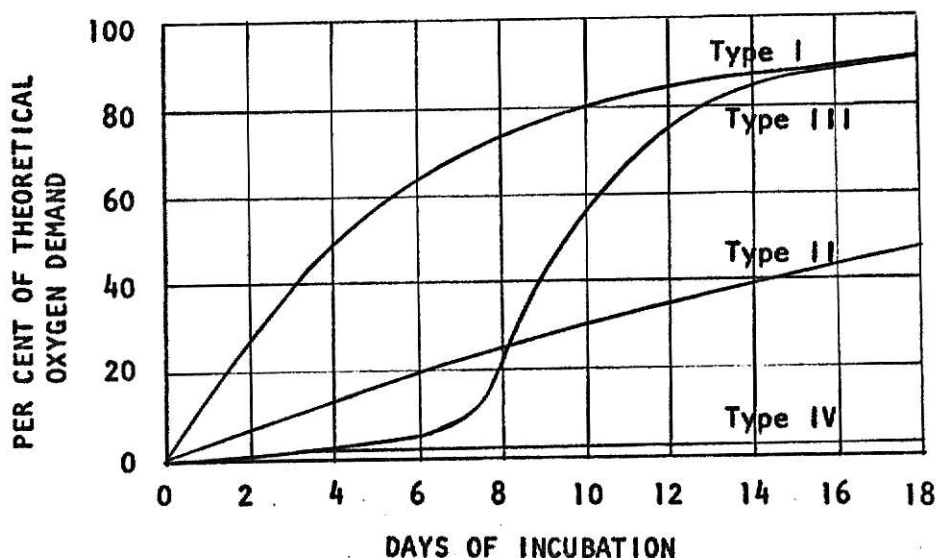


Figure 3.--Observed B.O.D. for synthetic organic materials seeded with sewage (27).

Ludzack and Ettinger (28) did an extensive compiling of data on the assimilation of a wide assortment of compounds. They generalize from the data that:

1. High molecular weight materials and tertiary-branched structures do not appear susceptible to metabolism at a significant rate.
2. Substitution of all the hydrogens on a carbon atom by alkyl or aryl groups generally results in a resistant material.
3. Agreement with Mills and Stack (26) on the chronic effect of atoms other than carbon in the chain.
4. Structures that limit enzyme approach or ability to diffuse through cell membranes contribute to resistance.
5. Acids, salts, esters, aldehydes, alcohols, amino acids, and cyanides can be relatively easily assimilated (with exceptions) under proper conditions. This list is in roughly increasing order of resistance.
6. Ethers, hydrocarbons, ketones, phenols and oxy compounds are relatively resistant with significant variation among themselves and in groups.

7. Phenols, nitrogen compounds and compounds with vinyl groups showed a great deal of variability.

McKinney, et al. (29) did work on phenol and other aromatic compounds. The results indicated stabilization by beta oxidation in activated sludge systems possible.

Leigh (30), defining degradation as a measurable chemical change (corresponding to Hunter and Heukelekian's "activity" loss), investigated the degradation of insecticides. He briefly reviewed the biological degradation of insecticides and pesticides and found that most chlorinated materials were inert (not necessarily toxic either), while some organophosphates such as malathion could be effectively removed in activated sludge systems.

Lamb and Jenkins (31) tested many of the same compounds as Mills and Stack (27) with comparable results, pointing out the need for longer BOD tests (up to 20 or 30 days length) when industrial compounds are tested.

Vath (21) briefly outlined the basic mechanisms involved in biological degradation for aerobic and anaerobic processes. He described the differences between the two as being, 1) the source of the hydrogen acceptor for enzyme regeneration, 2) the end productions, and 3) the rate and efficiency of substrate removal. The use of various tests (in determining extent of biodegradation) such as Warburg, river-die-away, activated sludge and anaerobic die-away was discussed. The compounds tested were linear anionic surfactants. Vath's bibliography contains a number of references to the degradation of detergents which has been discussed to such a large extent that they are not mentioned here.

Young, et al., (32) and Irvine and Busch (33) describe tests that are major modifications of the BOD test to estimate biodegradability of compounds.

Irvine and Busch (33) present a summary of the various chemical and bio-

logical factors involved in biological waste treatment. The goal of waste treatment processes is given as the ". . . transformation of dilute soluble or colloidal materials into a more concentrated insoluble mass." This is accomplished by biochemical conversion of organic compounds into cell mass and other metabolic compounds. As pointed out, the general class of compounds which are not biodegraded easily is termed either hard, recalcitrant or refractory--all terms for the same thing. These compounds are not removed in a set time period by organisms. The authors point to evidence that materials normally degraded exist without degradation for thousands of years when conditions are limiting for microbial action.

The acceptance of high COD values and low BOD values by pollution enforcement agencies is mentioned along with a statement that modifications of present treatments systems must be made to degrade these hard materials.

The authors then outline the function of enzymes in the assimilation of material. Permease enzymes are responsible for the transport of the substrate from the liquid medium through the cell membrane into the organism. The catabolic enzymes catalyze the formation of compounds such as pyruvate and ribose 5-phosphate. The biosynthetic enzymes catalyze the conversion of these compounds into amino acids, purines and pyrimidines. Since some molecules are too large for penetration of the cell membrane, hydrolytic enzymes exist to break the molecule into smaller fragments.

Since some compounds can cause inhibition or repression, they recommend a sequence of reactors to remove material that has been shown to cause disruption of enzyme activity and to remove separately those materials not removed in a particular biomass tank.

One important point made is that the release of intermediates and end

products of metabolic pathways, by diffusion outward, increases the COD of the effluent but does not appreciably alter the BOD. The release of cell constituents during cell lysis magnifies this situation although agglomeration and adsorption reduce the problem. In regard to adsorption it is important, they claim, to realize that this process is an important and misleading factor in assessing biodegradability.

In the use of high molecular weight compounds the concentration of hydrolytic enzymes is crucial since the hydrolysis of compounds is slow. The death of some organisms keeps the ratio of enzymes to polymeric substances higher so the removal of these compounds depends on the selection of the proper conditions.

## PROCEDURE

### ANALYTICAL PROCEDURES AND EQUIPMENT

#### pH

The pH values were obtained using a Fisher Accumet Model 320 research pH Meter. The meter was zeroed using either a pH 7.0 or 10.0 buffer solution, depending on the end pH.

#### Solids

Total suspended solids were run using the millipore filter technique. The millipore filters were placed in aluminum dishes and the dishes placed in the Thelco Model 17 oven at 103° C. After at least 3 hours they were placed in a desiccator for 5 minutes to come to room temperature and weighed on a Mettler H6 balance. This was repeated until the weight checked to the nearest one ten-thousandths of a gram. After this was done they were left in the desiccator until needed, then they were placed upon a ground glass holder with funnel. The sample was added, using a volumetric pipet, and the vacuum applied. When the moisture had been drained the filter with solids was placed back in the dish. The solids were dried at the same temperature (103° C), using the same procedure as done initially.

Total fixed solids were run using porcelain crucibles. The ash-less millipore filters with solids from the previous test were placed in the pre-weighed and dried crucible and burned at 600° C for one hour, put in the 103° oven for an hour, cooled to room temperature in a desiccator for 30 minutes. Then they were weighed on the Mettler. This was done until the weight on two

succeeding trials checked to the nearest two ten-thousandths of a gram. This procedure was also followed on the empty crucible to determine its initial weight.

### COD

The COD's, both total and soluble, were run for the most part according to the methods described in Standard Methods (34) for 10 ml samples. Some were run according to the standard approach and others using the alternate approach for dilute samples.

The only two exceptions were: 1) the soluble COD's in Part I were titrated with .025N ferrous ammonium sulfate solution, and part of the soluble COD's of Part II run using the alternate procedure were titrated with .005N solution; 2) the silver sulfate (22 g.) was added to the bottle of sulfuric acid ahead of time. The equipment consisted of 200 or 250 ml Erlenmeyer flasks, 300 mm. Pyrex condensers, and either a Linberg or Lab Con heater. The titrations were done using a 50 ml automatic buret.

### Microscopic Observations

All observations of the microbial organisms were done using a Bausch and Lomb DynaZoom research microscope at 430x or 100x. The various types of organisms and their relative abundance was recorded, as well as the general structure of the solids. The unit fed lime-treated sewage in Part II was checked at the three pH's used to determine changes in structural and organism distribution.

### Oxygen Uptake

The oxygen uptake measurements were done using a seven-unit Precision Scientific Warburg--model number 66670. This unit accommodated 7-300 mm.

manometers and 7-15 ml. Warburg reaction flasks. One flask manometer combination was used as a thermobarometer. The thermobarometer flask was filled with distilled water to the same volume as the test flask. Any change in the air pressure or temperature in the room affected all manometers equally regardless of volume (15).

The Warburg bath temp. was regulated at 25° C by means of a No. 62541 thermoregulator accurate to .1° C and the temp. constantly monitored using a thermometer.

A 10% KOH solution was added to the centerwells to adsorb carbon dioxide. The entire combination was agitated at 110-120 oscillations/minute to insure oxygen transfer.

The change in the level of the manometer fluid (Brodie's fluid) was correlated into oxygen uptake using calculated flask constants. This calibration is discussed in the following section.

A more complete description of Warburg apparatus use can be found in Manometric Techniques by Umbreit, et al. (14).

## EXPERIMENTAL PROCEDURE

### A. PART I

This part concerns the bench scale tests discussed in the Introduction. The purpose is to determine whether the removal of soluble organic matter (by bioadsorption or more importantly oxidation and assimilation by microorganisms) occurs to a greater extent and at a faster rate for lime-treated sewage than for settled sewage.

The morning of the testing, four liters of activated solids were gathered from the Kansas State University pilot plant. This pilot plant tests

phosphate removal using lime treatment prior to a conventional treatment involving settling and complete mix aeration. This process is outlined in more detail by Schmid (3) (4). Also gathered was at least two liters of raw sewage from the influent to Manhattan's primary settling tank.

Upon returning to the lab, one liter of sewage was added to each of two one-liter beakers. One of these beakers received lime treatment from a 50 mg/ml lime solution until it reached a specified level of treatment, usually either 150 mg/l or 200 mg/l. The mixture was stirred using a Phipps and Bird six paddle stirrer at 100 r.p.m. for 10 seconds, then at 20 r.p.m. for 10 minutes, and settled for 30 minutes. The untreated solution was placed on the stirrer at the same time as the treated. Total and soluble COD's were run on the supernatant. For some tests the settled sewage supernatant was diluted so its soluble COD was less than or equal to that of the lime-treated sewage.

One liter of activated sludge was placed in each of four two-liter beakers. Then about 800 ml. of warm tap water was added to each beaker. Two of the beakers were aerated using the lab air supply channeled through a water solution and then through a porous air stone. After 10 minutes of aeration the solutions were allowed to settle for 10 minutes and the other two were aerated. This washing procedure was done four times to all solutions. Total suspended solids tests were run on the activated sludge solutions--the original solution collected at the pilot plant and the final decanted, washed solution. All the solutions were intermixed to insure uniformity, and a soluble COD run on the final solution.

After completing this, 1333 ml of the final activated solids mixture was added to each of two 2000 ml graduated cylinders. Next, 666 ml of each of the prepared sewage solutions--the diluted settled sewage and the lime-treated

one--were added to their respectively marked cylinder. Aeration was started immediately thereafter.

A soluble COD test was made immediately after start-up on each unit. Thereafter a soluble COD test was run every 1/2 hour for the first two hours and every hour for the next four hours, and a final test 20 hours after start-up. The use of .025N ferrous ammonium sulfate solution instead of the .05N normally used was an attempt to increase accuracy.

## B. PART II

This part includes the maintenance of two laboratory activated sludge solids units and the use of a Warburg manometric apparatus. Using the Warburg, oxygen uptake curves and reaction-rate constants ( $k_1$ ) for the first stage BOD (biological oxygen demand) were calculated. This data is to indicate more precisely in mathematical terms the variance in treatability of the two types of sewage.

### 1. Activated Sludge Solids Units

The second phase required the maintenance of activated sludge units. Two different bench scale units were set up. One unit was fed lime-treated sewage and the other one settled sewage. Hereafter the solids will be referred to as either lime solids or settled sewage solids, depending on the type of material fed.

The sewage used was collected from the influent of the Manhattan sewage treatment plant in five gallon plastic containers and stored in the laboratory at 2-5° C.

Each day 2200 ml of the sewage was placed in each of two 2-liter beakers. After warming the sewage up to room temperature, one solution was treated with a  $\text{Ca(OH)}_2$  mixture (50 mg/ml concentration) to a given pH (either 9.8, 10.5, or

11.5). This was done using the pH meter and a magnetic stirrer.

Next, the two solutions were placed on the paddle stirrer and stirred at 100 r.p.m. for 10 seconds, at 20-30 r.p.m. for 10 minutes and settled for 30 minutes. The activated sludge units (one gallon jars) which were settling during this time were decanted of 1.5 liters (out of a total volume of 3.0 liters) of supernatant. Then the sewage solutions were added to the respective containers and aeration resumed. This once a day feeding is based on McKinney's method (28), which was adopted by Burkhead (15). It is an activated sludge system with 23 hours aeration and complete sludge return.

Aeration was accomplished by running the lab air supply through a 1000 ml flask (containing 500 ml of water) and then through porous air diffusers in the solids jars.

When a new pH for the testing was attempted solids from the pilot plant were added. The testing was first in order of increasing pH and then in order of decreasing pH.

## 2. Warburg Procedure

These tests were undertaken 1) to determine more precisely what might be responsible for the greater efficiency in COD removals experienced and 2) to obtain precision uptake data at various pH levels that might assist in defining operating procedures for this type of treatment.

To do this it was necessary to use untreated sewage and solids fed untreated but settled sewage as a control for comparison purposes. Since it is conceivable that the nature of the activated solids in a system fed lime-treated sewage could have some effect, it was necessary to have various combinations of sewage and activated solids. These tested combinations then draw upon the four following possibilities, with one from each group for a total of four.

### Sewage

1. Untreated but settled sewage.
2. Sewage that undergoes lime treatment followed by a period of flocculation and settling.

### Solids

1. Activated solids fed settled sewage.
2. Activated solids fed lime-treated sewage.

#### a. Preliminary Work

The day before any run was started, the sewage was added to the activated solids units, at least 18 hours in advance. This was to insure that the bacteria were in the endogenous phase and that sufficient time had elapsed for the units to adjust to the shock loading of 1.5-2 liters they received every day.

The night before a run (about 10:00 P.M.), triplicate tests were run on the solids content of the activated solids units using preweighed membrane filters in aluminum dishes. These measurements were not done quite as accurately as the rest of the solids tests (see analytic procedure), but the duplication afforded sufficient check. The average of the three was used as the accepted value.

The morning (9:00 A.M.) of a test about 9 liters, or enough for two preparations, of sewage was collected from the influent to the Manhattan treatment plant settling tank just as described in the procedure for activated solids units.

The day before a run the initial weight of the aluminum dishes containing the membrane filters was determined, as well as the weight of the crucibles used for the volatile solids procedure.

All glassware including the COD flasks, manometer flasks, pipettes and beakers were cleaned according to the procedure as described later in this section.

#### b. Set-Up

The first thing that was done upon returning to the lab the next morning was to turn the Warburg on so that the temperature of the bath had time to adjust to 25° C. Since most of the manometers went on the apparatus at about 11:00 A.M. and the temperature regulating device was switched on by 9:30 A.M., there was about 1-1/2 hours for the temperature of the 10 gallons of water in the bath to come to equilibrium at 25° C. This usually required about a rise of 5° C from a lab temp. of 20° C (early in the morning) to the final.

Next, the solids filtered the night before were taken from the 103° C oven and placed in the dessicator, and then weighed 5 minutes later. The values for both the lime solids unit and the settled sewage solids unit were then calculated. These values were used to calculate the volume of unit solution that would be needed to make up a final 75 ml solution at a given solids concentration using the formula:

$$kx = 75 c$$

where:

$k$  = conc. of solids in solids unit in mg/ml

$c$  = desired concentration of solutions in prepared solution

(thousands of mg/l = 1, 2, 3)

$x$  = amount of solution that should be decanted.

The solution decanted was then centrifuged and some of the supernatant in the centrifuging tubes decanted. The tubes were marked in increments of 10 ml so that 40 ml (total) of supernatant for each type of solids was

retained. This was to insure that a sufficient microbial population was present so that long lag periods would be avoided and also to insure that everything in the preparation of the activated solids solutions was comparable.

After pouring the 40 ml of supernatant into a graduated cylinder, the solids in the centrifuge tubes were put into solution by rinsing with distilled water. This rinsing was done until a volume of 75 ml was reached. This solution was then poured into a specially marked 100 ml beaker and 4-8 drops of BOD nutrient solution [see Standard Methods (34)] was added. The amount added varied. Higher solids levels (3000 mg/l) received 8 drops and lower solids levels (1000 mg/l) received 4.

At about the same time, the sewage preparation was also undertaken. This involved exactly the same procedure as that in making up the solutions for the activated sludge solids units each day. After completing this, about 300-400 ml of the supernatant was poured into the properly marked plastic bottles.

The lime-treated supernatant was temporarily placed in a 500 ml beaker. Drops of .49 N  $\text{H}_2\text{SO}_4$  were pipetted in, while stirring, until a pH of 8.0 was reached. This step was necessary to avoid the shock loading of the higher pH's from inhibiting initial oxygen uptake, particularly since the ratio of sewage to solids was to be 4 to 1.

After preparation of all solutions, .2 ml of a 10% KOH solution was added to the centerwell of the Warburg flasks and the top edge of the centerwell was well greased with stopcock grease. Then 1 ml of the prepared activated solids solutions was added to the respective flasks based on a previously drawn up scheme, using a 1 ml volumetric pipette. The scheme for the combinations usually meant that the solids blanks were in positions 1 and 2.

The four combinations that were tested were in positions 3-6. The four combinations tested came from combinations of solids and sewage mentioned earlier.

They are:

- 1.) Lime-treated sewage and activated solids from the unit fed lime-treated sewage.
- 2.) Lime-treated sewage and activated solids from the unit fed settled sewage.
- 3.) Settled sewage and activated solids fed lime-treated sewage.
- 4.) Settled sewage and activated solids fed settled sewage.

Next, four ml of the proper sewage solution was added to the proper flask according to the scheme with a four ml volumetric pipette. Flasks 1 and 2 received four ml of distilled water and flask 7, the thermobarometer--received five ml.

Finally the folded filter paper squares for the centerwells were added. These squares were made by cutting No. 40 Whatman filter paper into 2 cm squares. They were folded accordion-style into strips 4 mm wide to insure maximum surface exposure.

After placing the manometer and attached flask on the apparatus, the stopcock was left in the open position and the set-up allowed to come to equilibrium with the water bath temperature for 15 minutes. The stopcock was then closed and the initial reading made.

Readings were taken according to a scheme that followed a set pattern but followed no absolute guidelines other than readings being more numerous during the first 12 hours. Readings generally were taken:

1. every 15 minutes for the first 1/2 hour
2. every 1/2 hour for the next 1-1/2 hours
3. every hour for the next 3 hours

4. every 2-3 hours for the next 6 hours
5. the next reading was the next morning, 8 hours later
6. readings every 3-4 hours until at least 24 hours had elapsed.

Immediately after setting up the Warburg, tests were run on the four solutions prepared. The two kinds of sewage and both types of activated solids solutions were tested for soluble and total COD and total suspended solids. The activated solids were tested for volatile solids. All the COD's were done using the standard method.

#### c. Final Work

After the last reading all the manometers were opened and the flasks removed. The stopcock grease was wiped off the inside, the filter paper was removed from the centerwell, and the excess KOH was carefully removed.

After the above procedure was slowly carried out, the contents of the flasks were carefully swished and then poured into a Nessler tube. Next, 3 ml of distilled water was added to the flasks and a spatula was employed to loosen any solids clinging to the sides or centerwell. The contents were then poured into the respective Nessler tubes. This procedure was repeated with 2 ml of distilled water. This procedure insured fairly complete cleaning and left 10 ml of solution for testing.

The 10 ml was used for testing of soluble and total COD, and total suspended solids. First, 5 ml of the solution was taken out to run a total COD test. This 5 ml was diluted with 5 ml distilled water for a total sample of 10 ml and a final dilution of four. This was run using the standard COD method. After this, the last 5 ml was filtered through preweighed millipore filters. The filtered amount was used for the soluble COD test. It was diluted with 5 ml of distilled water for a final dilution of four. These

soluble COD's were run according to the alternate COD procedure for dilute samples, Standard Methods. The filter paper gave total suspended solids.

#### d. Summary

A summary sheet was prepared from the tests run showing the initial and final conditions in the Warburg flasks and the total oxygen uptake.

These tests were run with lime-treated sewage at a pH of 9.8, 10.5, and 11.5, and activated solids solution levels of 1000, 2000, and 3000 mg/l, for a total of 9 tests. The settled sewage and related solids were always run as comparisons.

Seven trial runs were made before the technique described above was arrived at, to insure that the final method was sound. These runs involved the use of 4 ml of activated sludge and 1 ml of sewage. This ratio is the opposite of that finally arrived at. These tests showed that a much higher sewage/solids ratio was important.

#### 3. Glassware Cleaning Procedure

The COD flasks were rinsed with distilled water and soaked in chromic acid solution. After at least 12 hours exposure, the flasks were rinsed with tap water three or four times and three times with distilled water. They were stored in an inverted position.

All pipets used were soaked in chromic acid solution at least 24 hours. They were then rinsed individually with tap and distilled water twice each.

The Warburg flasks were first cleaned thoroughly using tissue. Then the flasks were soaked in concentrated KOH solution for an hour or two to remove the traces of grease remaining. Then they were thoroughly rinsed. Finally, they were soaked in chromic acid solution for a day and removed. Rinsing with tap water was done at least four times and at least five with distilled water.

They were dried in the 103° C oven in the inverted position, cooled in the dessicator, and stored in an inverted position.

#### 4. Calibration of Warburg Flasks

The Warburg flasks were calibrated according to the scheme described by McKinney (35) with some small variations. Data collected was used to calculate the flask constants. The procedure used is given:

1. The water bath temperature was brought up to 25° C.
2. One ml of demineralized water was added to each clean flask.
3. The flasks were attached to the manometers (stopcocks in open position). The flasks were allowed 20 minutes to come to equilibrium with the bath temperature.
4. The manometer fluid was raised to the 240 mm mark, the apparatus closed, and the fluid in the closed side lowered to the 150 mm mark. Readings were made of the open leg.
5. Step four was repeated twice to confirm the initial reading.
6. The flasks were removed and 8 ml of distilled water was added to each.
7. Steps 3-5 were repeated.

#### ACCURACY DATA

The accuracy of the Warburg data is important to determine. For this reason, some duplication was done in experiments where space allowed. Since the instrument held only seven manometer-flask combinations, limited duplication was possible. The most that was attempted was to run triplicate samples. The major attempt at duplication involved lime solids and lime-treated sewage combinations at a pH level of 9.8. Schmid (3) described this as the optimum conditions for the lime-biological treatment process, thus the interest in accuracy lies here.

Some COD accuracy tests were run. This was done by running COD tests

on solutions made using dextrose in distilled water. Solutions at concentrations of 2000, 500, 250, and 125 mg/l theoretical COD were run.

## RESULTS

### PART I

The results for this preliminary part are summarized in TABLE 5 for the seven runs that were made. The MLSS concentrations given (as the footnote indicates) are the final levels attained after washing and thickening the solutions brought back to the lab. This thickening was important since the level in the pilot plant dipped to 800 mg/l. The final solids concentration in the aerated mixtures was approximately 1/3 lower than the figure given since 1/3 of the volume was sewage. Various solids levels were attempted ranging from 865 to 3120 mg/l.

The strength of the two types of sewage was adjusted so that at times the total COD of the lime sewage was 1) less than (Run 2), 2) equal to (Runs 1, 5, 6) or 3) greater than that of the settled sewage (Runs 3, 4, 7). This allowed a more complete picture to be attained. For all runs where the lime sewage COD was equal to or greater than the settled sewage, its soluble COD was significantly greater.

TABLE 5 presents the soluble COD's of the aerating mixtures (identified by sewage added) at intervals of time after start-up. The soluble COD of the ML (activated sludge mixture) was run to see how successful the washing procedure was and to determine the contribution of the solids.

The lime dosage refers to the treatment level of the lime sewage prepared. The pH given is the pH of the lime sewage before addition to the unit for aeration.

TABLE 5. Summary of Part I

Run	MLSS <sup>1</sup> Conc. mg/l	Lime Dosage (mg/l)	COD's of Initial Solutions (mg/l)					Soluble COD's of Aerated Units at Time Increments					
			ML Soluble	Lime Sewage		Settled Sewage		2 hours		4-6 hours		Next morning	
				Soluble	Total	Soluble	Total	Lime	SS	Lime	SS	Lime	SS
1	----	---	12	76	137	44	133	45	28	32	49	28	41
2	2440	150	--	81	113	105	190	16	16	24	41	24	41
3	----	200	40	80	136	52	84	20	32	20	24	37	41
4	1500	200	15	35	160	26	104	34	39	22	39	26	32
5	865	150	44	86	162	46	158	25	32	8	8	0	0
6	1565	175	74	--	131	--	133	28	30	21	29	10	25
7	3120	200	20	123	157	97	131	34	97	0	4	2	2

<sup>1</sup> Before addition of sewage to units

## PART II

The results for this part are given in the 9 runs as outlined in the procedure. These runs encompass 1) lime-treated sewage and solids receiving lime-treated sewage at 3 pH levels and 3 solids concentrations and 2) the control mixtures using settled sewage and solids grown on this sewage. The solids levels referred to in the result and discussion sections of this paper indicate the activated sludge solids concentrations used in the testing. These solids serve as the microbial seed in an attempt to reproduce the activated sludge process. Not counting the contribution of the sewage, the mixtures in the flasks after the addition of 4 ml of sewage contain 1/5 of the TSS of the initial activated sludge solids added.

The results are presented in three groups of three runs--each group corresponding to the testing of sewage treated with lime to a given pH. Runs for each group were made with 1 ml of activated sludge at concentrations of TSS at 1000, 2000, and 3000 mg/l and four ml of the test sewage. This should help determine the effect of the food/microorganism ratio. The groupings are as follows:

## Group 1--lime dosage to end pH of 9.8

## Run

- 1a--1 ml of activated sludge at a concentration of 1000 mg/l
- 1b--1 ml of activated sludge at a concentration of 2000 mg/l
- 1c--1 ml of activated sludge at a concentration of 3000 mg/l

## Group 2--lime dosage to end pH of 10.5

## Run

- 2a--1 ml of activated sludge at a concentration of 1000 mg/l
- 2b--1 ml of activated sludge at a concentration of 2000 mg/l
- 2c--1 ml of activated sludge at a concentration of 3000 mg/l

### Group 3--lime dosage to end pH of 11.5

#### Run

3a--1 ml of activated sludge at a concentration of 1000 mg/l

3b--1 ml of activated sludge at a concentration of 2000 mg/l

3c--1 ml of activated sludge at a concentration of 3000 mg/l

The data for each run is summarized using a graph of the computed oxygen uptake curves and tables showing COD and solids levels for 1) the four sewage and solids mixtures put into the flasks, 2) the computed values for the combinations using the previous data and the volumes used and 3) the final conditions in the flasks as determined by testing done on the solutions at the end of the run. Figures 4-12 and Tables 6-14, corresponding to the runs, are given in the order mentioned above.

Two things should be pointed out at this point. First, a given pH means that the activated sludge unit receiving daily doses of lime-treated sewage has been allowed time to come to equilibrium at this particular feed level. When testing at a new pH, the lime solids unit was reseeded with activated sludge from the pilot plant aeration tank. No manometric tests described herein involved crosses between activated sludge receiving lime-treated sewage at one pH and lime-treated sewage at another. Second, the use of terms should be explained. For convenience, the activated sludge solids fed lime-treated sewage are called lime solids, and the activated sludge solids fed settled sewage are called settled sewage solids. Lime-treated sewage and settled sewage are occasionally referred to as lime and settled sewage feed. The abbreviation TSS refers to total suspended solids and includes those filtered out by a membrane filter as explained in analytic procedures. The letters FSS stand for fixed suspended solids. These are the portion of the TSS that are not volatilized at 600° C.

In addition to this data, reaction-rate constants ( $k_1$ ) were determined using the method outlined by Thomas (35). This method approximates the first stage uptake of the BOD reaction by a line using a third degree equation. Graphically, this means plotting on arithmetic paper  $(\text{time/BOD})^{1/3}$  as the ordinate and time as the abscissa. The  $k_1$  values are found by multiplying the ratio of the slope to the ordinate intercept by 6 and then dividing by 2.3 to convert to base 10 from base e. Two examples of these plots are given in Figures 13-14 and will be discussed later. These  $k_1$  values are estimates of the rate of stabilization of the decomposable organic matter. The  $k_1$  values are given in TABLE 15. The titles, corrected and uncorrected, refer respectively to 1) BOD values corrected for possible endogenous respiration by subtracting the oxygen demand of the proper activated sludge blank and 2) those not so corrected. Both values were computed to determine any significant trends. The type of activated sludge is listed directly under these titles. The terms listed below the type of sludge refer to the kind of sewage involved in the flask combination.

#### Group 1 Runs

The data for this group is given in Runs 1a-1c, corresponding to Figures 4-6 and TABLES 6-8. The data indicates that for lime solids the average ratio of total COD/TSS is 1.04, and for settled sewage solids is 1.14. The lime solids for Runs 1a and 1c differ significantly from those in 1b for a particular reason. The first two mentioned experiments were done much later in the testing. Before these tests were run the lime unit was reseeded with pilot plant activated sludge. At that time ferric sulfate was being added to aid in solids settling in the final settling tank. This addition results in dark brown activated sludge that is more compact; visually they differ little from the settled

sewage solids. This property continued to linger weeks after the addition. The solids used in Run 1b, on the other hand, were the bulkier, light brown solids as described by Schmid (3). Given the same TSS concentration as the settled sewage solids and ten minutes settling time, these bulkier lime solids occupied roughly three times the volume of either the settled sewage solids or the lime solids complexed with ferric sulfate. The soluble COD's of the prepared activated sludge solutions range from 20-65 mg/l with little difference between the two types. These low values result from the long daily aeration period for the activated sludge units and the centrifugation employed in preparing the solids solutions. The TSS for lime sewage varies from 21 to 56 mg/l, while that for the settled sewage varies from 28 to 128 mg/l, illustrating the particulate removal during lime coagulation.

The total COD for settled sewage ranges from 255 mg/l to 320 mg/l, and that for lime sewage from 151 to 160 mg/l. The lime sewage total COD may show less variation than the settled sewage but the soluble COD of the lime sewage shows more variation, 88-151 mg/l, than the settled sewage at 145-151 mg/l. Thus the lime treatment at this level removes some soluble COD material but not in an easily predictable manner.

The inaccuracy of the data on the final conditions is quickly apparent. The activated sludge process involves the oxidative assimilation of soluble organic material into cell mass, involving an increase in TSS and a decrease in total and soluble COD. Taking the results for all the runs, just the opposite apparently occurred. This is due chiefly to the small amount of fluid (5 ml) available for testing and the resulting high dilution necessary. To calculate solids levels only 5 ml of the mixture is available, and this has been diluted to 1/2 its original strength in the process of cleaning the

material out of the flasks. Given an experiment when the activated solids mixture is at a strength of 3000 mg/l, the final TSS in the flask is 600 mg/l. The final solution for testing is at a level of 300 mg/l. Given 5 ml of the mixture, there is only about 1.5 mg filtered out. This small amount results in large variations. The same general line of reasoning applies to the other tests.

The data of special interest are the reaction-rate constants,  $k_1$ , that indicate treatability. Taking the data for this group the lime sewage, for the same type of solids (seed), shows a higher reactivity rate for all tests and all conditions. To determine how much greater it might be worthwhile to point out that the ratio of the reaction rate ( $k_1$ ) for lime sewage to that of settled sewage for a similar solids is 1.45 overall, and the averages:

- 1.) corrected for endogenous respiration are 1.6 for settled sewage solids, and 1.4 for lime solids
- 2.) for uncorrected data are 1.6 for settled sewage solids and 1.2 for lime solids.

Also, it is important to note that for Run 1b the bulky lime solids are more efficient in stabilizing a given type of sewage. For lime sewage this is 1.01 versus .86, and for settled sewage .69 compared to .64.

Table 6 Summary of Data for Run 1a

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	1090	65	1010	—
SS solids mixture	950	65	825	—
Lime sewage	161	97	56	—
Settled sewage	290	145	68	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
SS solids Lime sew.	319	91	210	322	—	—	109
Lime solids Settled sew	450	129	256	338	—	—	186
Lime solids blank	218	13	202	177	—	—	15
SS solids blank	190	13	165	193	—	—	12
SS solids Settled sew	422	129	219	386	—	—	178
Lime solids Lime sew.	347	91	247	332	—	—	124

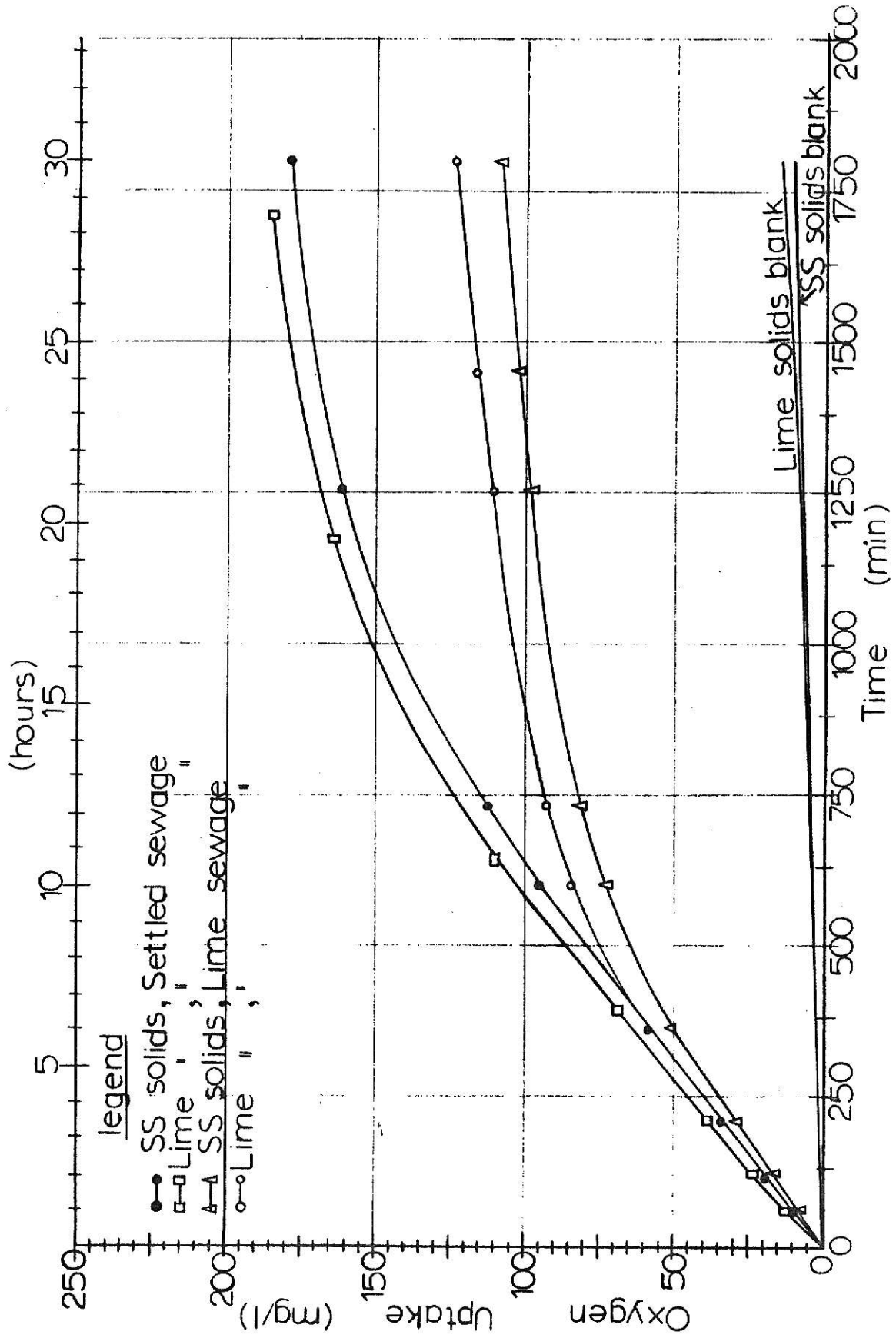


Fig 4 Oxygen uptake curves for Run 1a

Table 7 Summary of Data for Run 1b

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	2110	24	2090	540
SS solids mixture	2330	20	2055	500
Lime sewage	155	151	36	—
Settled sewage	255	151	128	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
SS solids blank	466	4	418	584	—	680	63
Lime solids blank	422	5	411	504	193	280	34
SS solids Settled sew.	670	125	513	628	120	440	255
Lime solids Lime sew.	546	126	447	676	111	320	179
SS solids Lime sew.	590	125	440	568	100	400	202
Lime solids Settled sew.	626	126	520	612	140	440	255

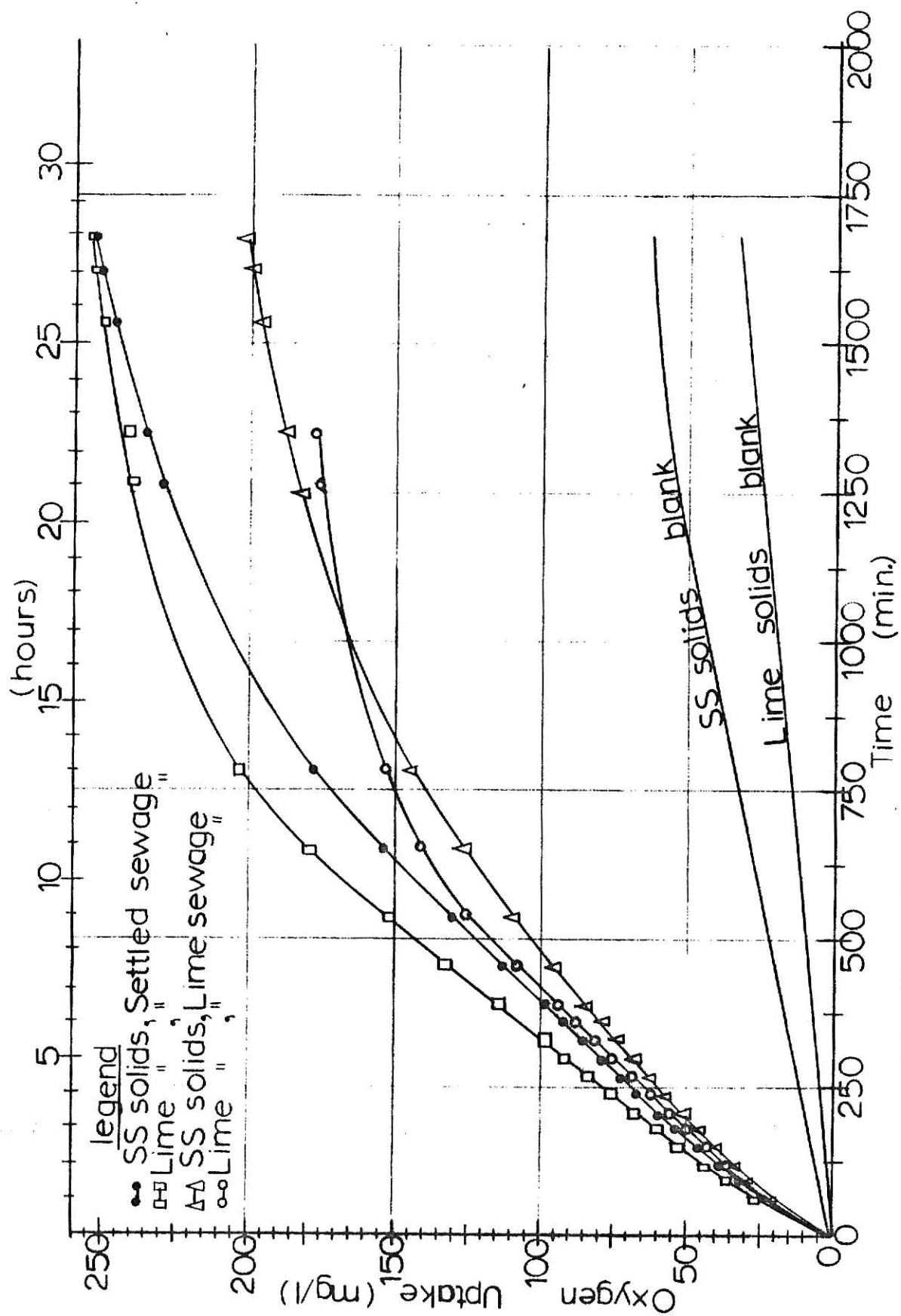


Fig 5 Oxygen Uptake Curves for Run 1b

Table 8 Summary of Data for Run 1c

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	—	32	3085	—
SS solids mixture	—	36	3230	—
Lime sewage	160	88	21	—
Settled sewage	320	148	66	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
SS solids blank	—	7	650	830	162	440	63
Lime solids blank	—	6	617	558	97	360	34
SS solids Lime sew.	—	78	663	639	68	240	149
Lime solids Settled sew.	—	125	670	815	131	440	201
SS solids Settled sew.	—	126	699	800	—	280	226
Lime solids Lime sew.	—	77	635	591	94	440	151

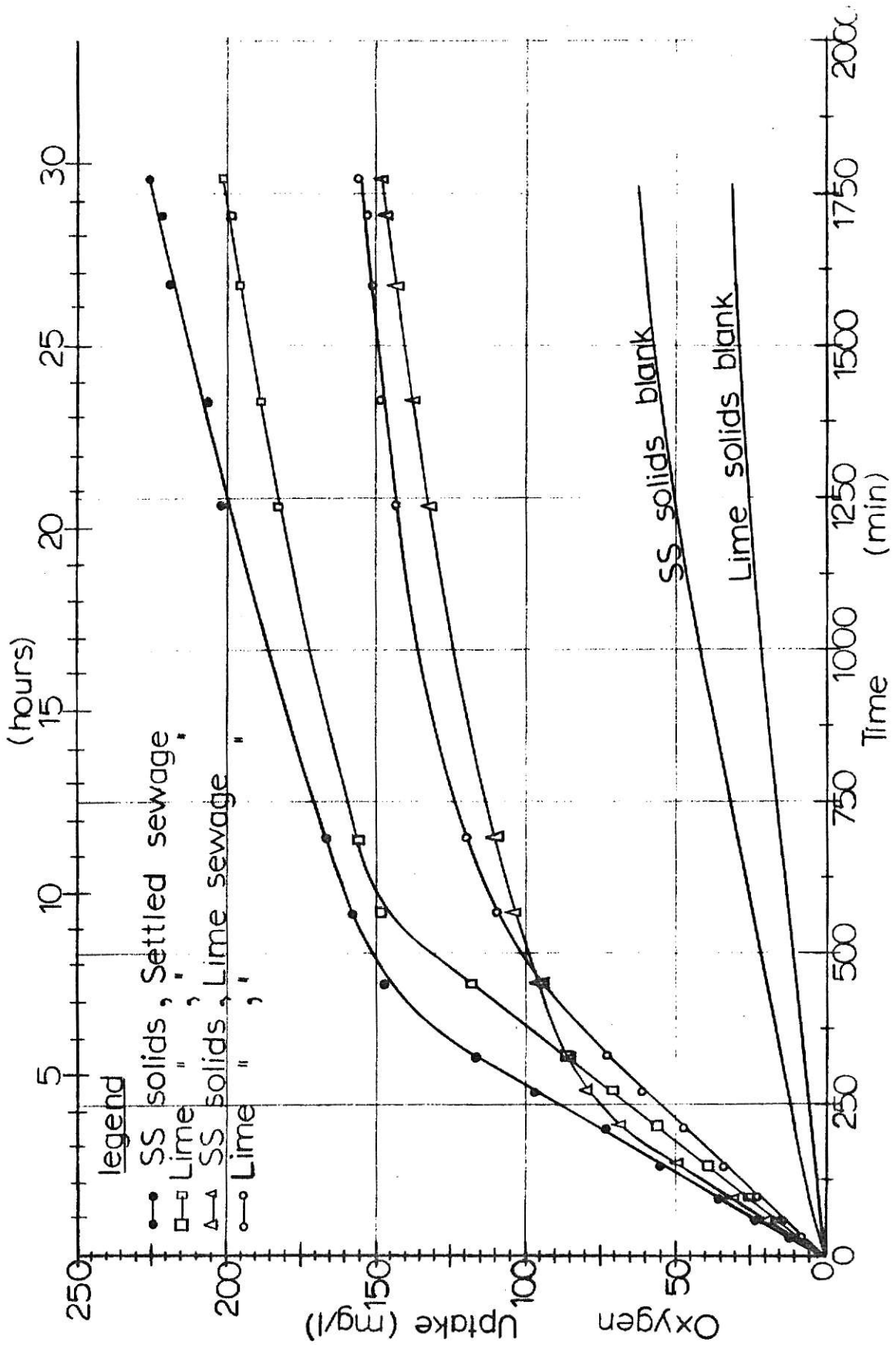


Fig. 6 Oxygen uptake curves for Run 1c

## Group 2 Runs

The data for this group is given in Runs 2a-2c, corresponding to Figures 7-9 and TABLES 9-11. The ratio of total COD/TSS for the activated sludge solids mixtures varies from .91 to 1.19 for lime solids and from 1.25 to 1.52 for the settled sewage solids. The total COD of the settled sewage ranged from 196 to 324 mg/l and for the lime sewage from 88 to 128 mg/l. The soluble COD of the settled sewage ranged from 80 to 116 mg/l and for lime sewage from 72 to 104 mg/l. The level of filterable solids existing in the lime sewage varied from 15 to 38 mg/l and for the settled sewage from 38 to 68 mg/l. This illustrates that the lime floc was removing particulate matter from solution. The amount of particulate matter present in these three tests was less than in the previous three.

The total COD's of the final mixtures in Runs 2b and 2c reflect more accurately the expected change from the initial conditions. However, since at least one of the mixtures in each run showed a gain in COD, the overall accuracy is questionable.

The  $k_1$  values for Group 2 indicate that the lime sewage reaction rates are greater than those for settled sewage, given the same solids. The only exception is Run 2b with lime solids. This exception is discussed later. The ratios of the reaction rates ( $k_1$ ) for lime sewage to that for settled sewage for a similar solids reveal that, on the average:

- 1.) For uncorrected data the ratio is 1.5 for settled sewage solids, and 1.2 for lime solids.
- 2.) Data corrected for endogenous respiration gives average ratios of 1.8 for settled sewage solids and 1.5 for lime solids.

Table 9 Summary of Data for Run 2a

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	864	48	955	300
SS solids mixture	1312	64	980	265
Lime sewage	128	104	31	—
Settled sewage	324	116	38	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
Lime solids blank	173	10	191	192	88	80	12
SS solids blank	262	13	196	288	73	40	26
SS solids Settled sew.	522	106	226	464	70	120	198
Lime solids Settled sew	432	102	221	368	86	40	171
Lime solids Lime sew.	275	93	216	304	68	40	99
SS solids Lime sew.	365	96	221	320	68	—	101

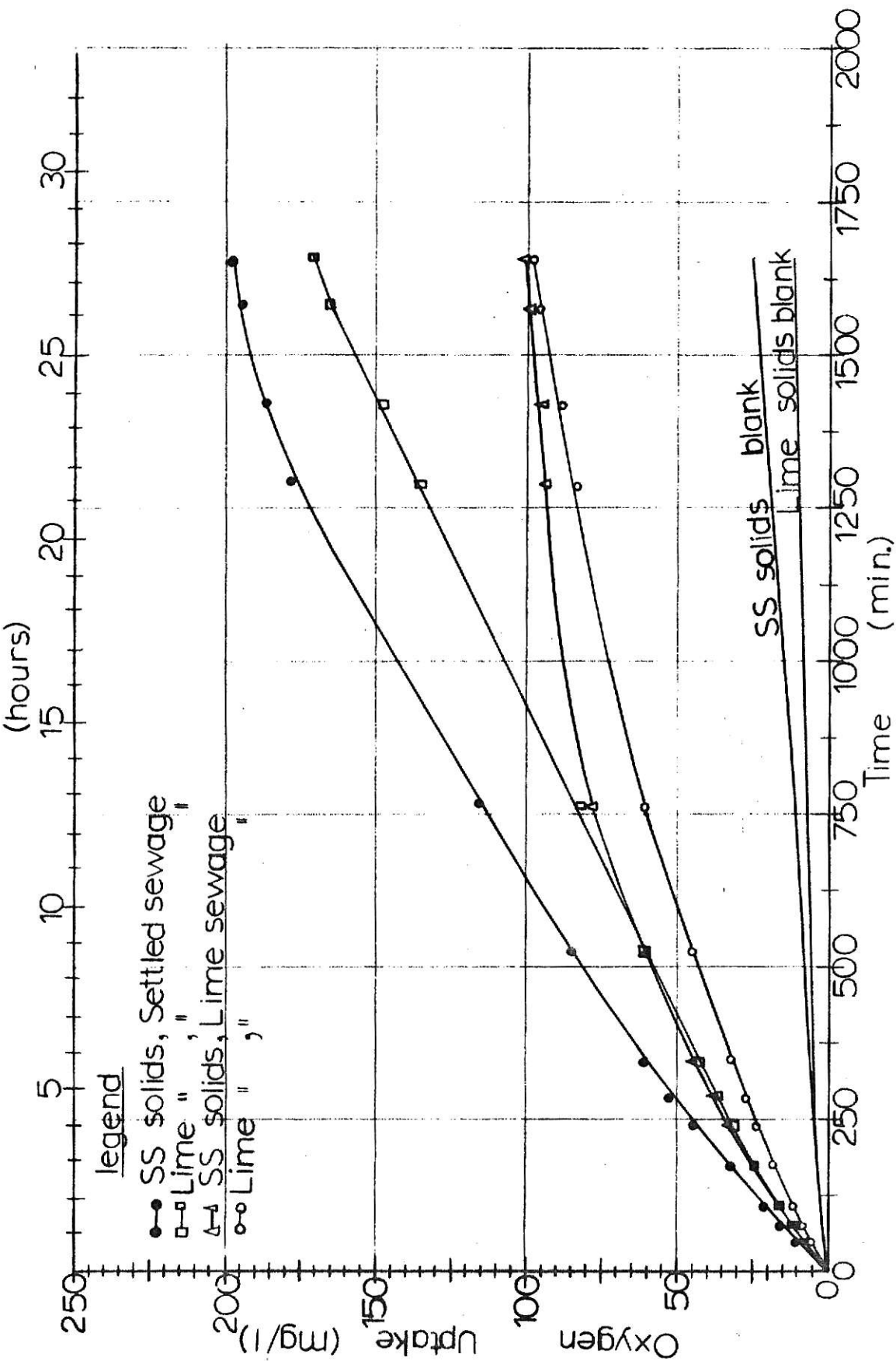


Fig 7 Oxygen uptake curves for Run 2a

Table 10 Summary of Data for Run 2b

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	2350	49	1980	455
SS solids mixture	2525	27	2015	480
Lime sewage	111	75	15	—
Settled sewage	284	89	68	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
Lime solids Settled sew.	697	81	450	600	79	440	220
SS solids Lime sew.	594	65	415	492	108	320	92
SS solids Lime sew.	594	65	415	668	138	520	101
Lime solids Lime sew.	559	70	408	548	122	400	163
Lime solids Lime sew.	559	70	408	580	90	400	154
SS solids Settled sew.	732	76	457	652	97	480	226

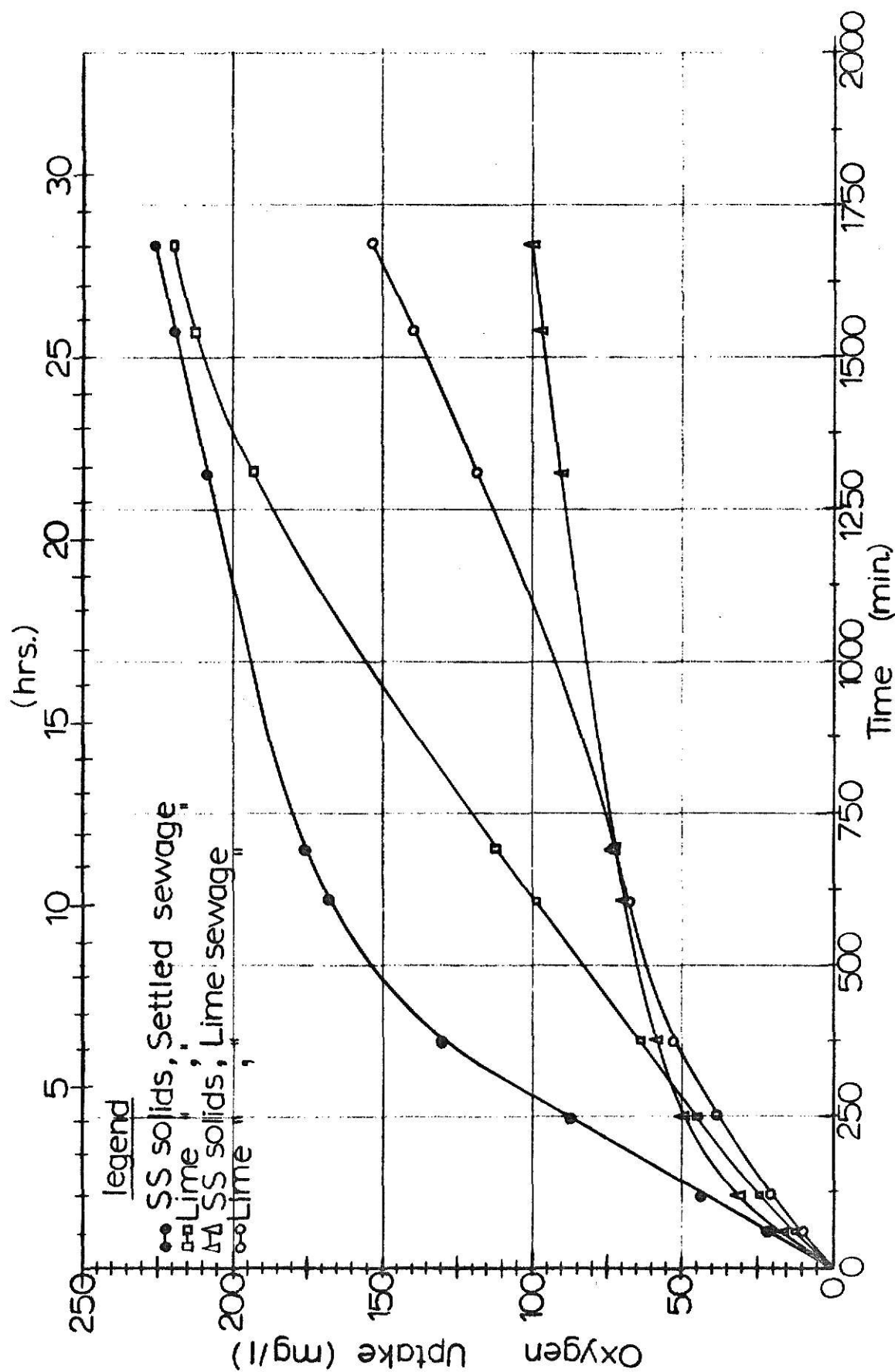


Fig. 8 Oxygen uptake curves for Run 2b

Table 11 Summary of Data for Run 2c

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	3000	28	3055	940
SS mixture	4220	32	2860	740
Lime sewage	88	72	17	—
Settled sewage	196	80	42	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
Lime solids blank	600	7	611	560	76	360	30
SS solids blank	845	8	572	592	87	280	75
Lime solids Settled sew	757	69	644	576	—	560	184
SS solids Lime sew.	914	64	585	880	44	600	155
Lime solids Lime sew.	670	63	624	576	78	520	156
SS solids Settled sew.	1000	70	605	848	84	640	251

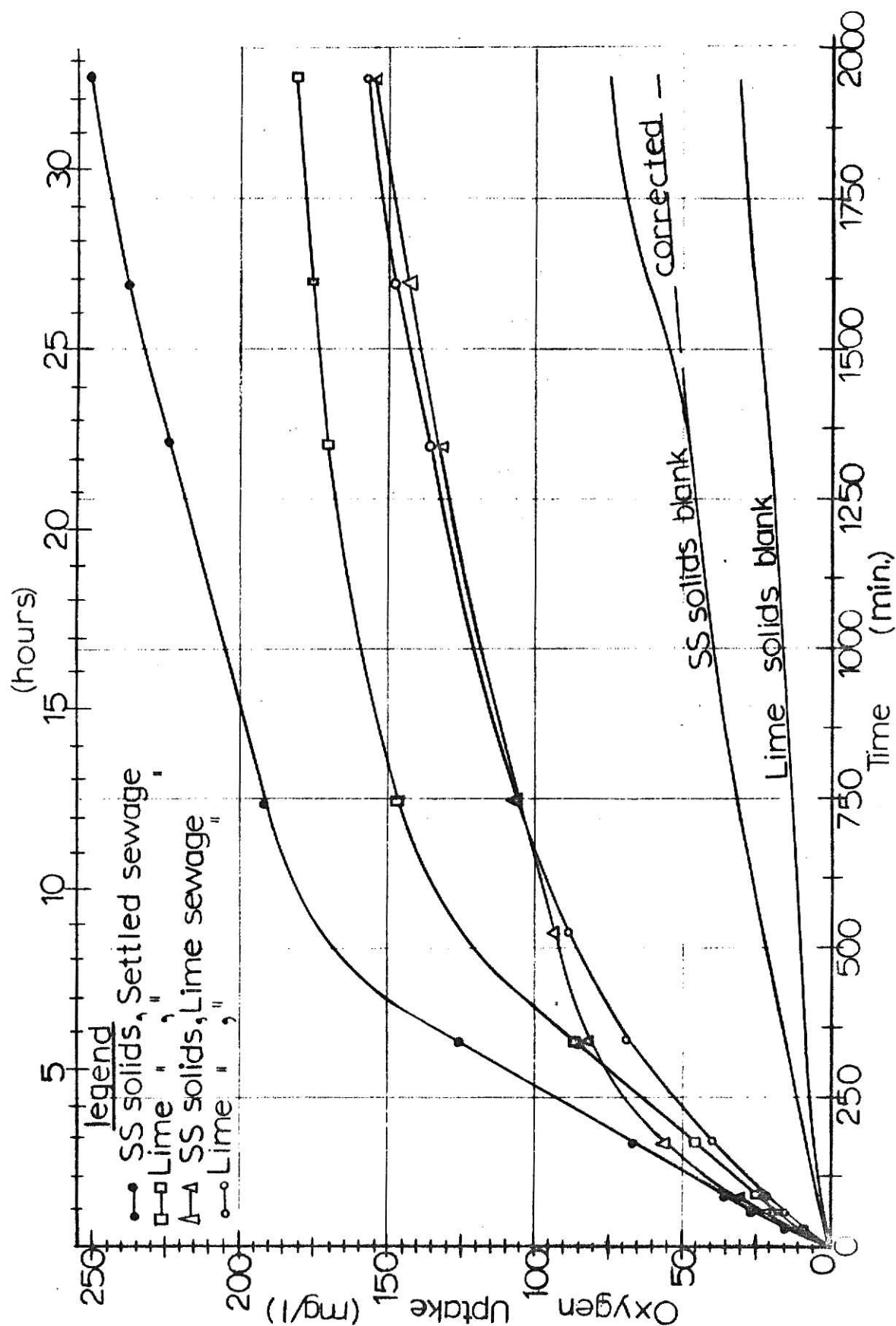


Fig.9 Oxygen uptake curves for Run 2c

### Group 3 Runs

The data for this group is given in Runs 3a-3c, presented in Figures 10-12 and TABLES 12-14. The total COD/TSS ratio for lime solids varies from .495 to 1.31, and that for SS solids from 1.12 to 1.25. The soluble COD for the solids solutions is still reasonably low, varying from 16 to 28 mg/l for SS solids and from 28 to 69 mg/l for lime solids.

The total COD for the settled sewage ranges from 259 to 300 mg/l, while that for the lime sewage ranges from 81 to 125 mg/l. The TSS for lime sewage varies from 8 to 23 mg/l and from 60-76 mg/l for settled sewage. The soluble COD varies from 81 to 125 mg/l for lime sewage and from 105 to 134 mg/l for settled sewage. The close relationship between soluble and total COD reveals the extent of removal of particulate matter by lime treatment, as does the TSS level.

Again little accuracy is apparent in the summation of final conditions. Given equal conditions, the lime sewage has a higher reaction rate than settled sewage except for Run 3a with lime solids. This particular exception is explained later in this paper.

The ratios of the  $k_1$  factors for lime sewage/settled sewage for the same solids are, on the average:

- 1.) For uncorrected data the ratio is 1.4 for settled sewage solids and 1.1 for lime solids.
- 2.) For corrected data the ratio is 1.9 for settled sewage solids and 1.1 for lime solids.

Table 12 Summary of Data for Run 3a

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	1240	28	980	215
SS solids mixture	1190	16	1060	165
Lime sewage	109	93	17	—
Settled sewage	259	105	76	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
Lime solids blank	248	6	196	210	60	320	23
SS solids blank	238	3	212	437	96	440	30
Lime solids Settled sew.	455	89	257	405	118	200	154
SS solids Settled sew.	445	87	273	421	109	200	206
Lime solids Lime sew.	335	80	209	700	102	200	101
SS solids Lime sew.	325	76	246	323	91	160	109

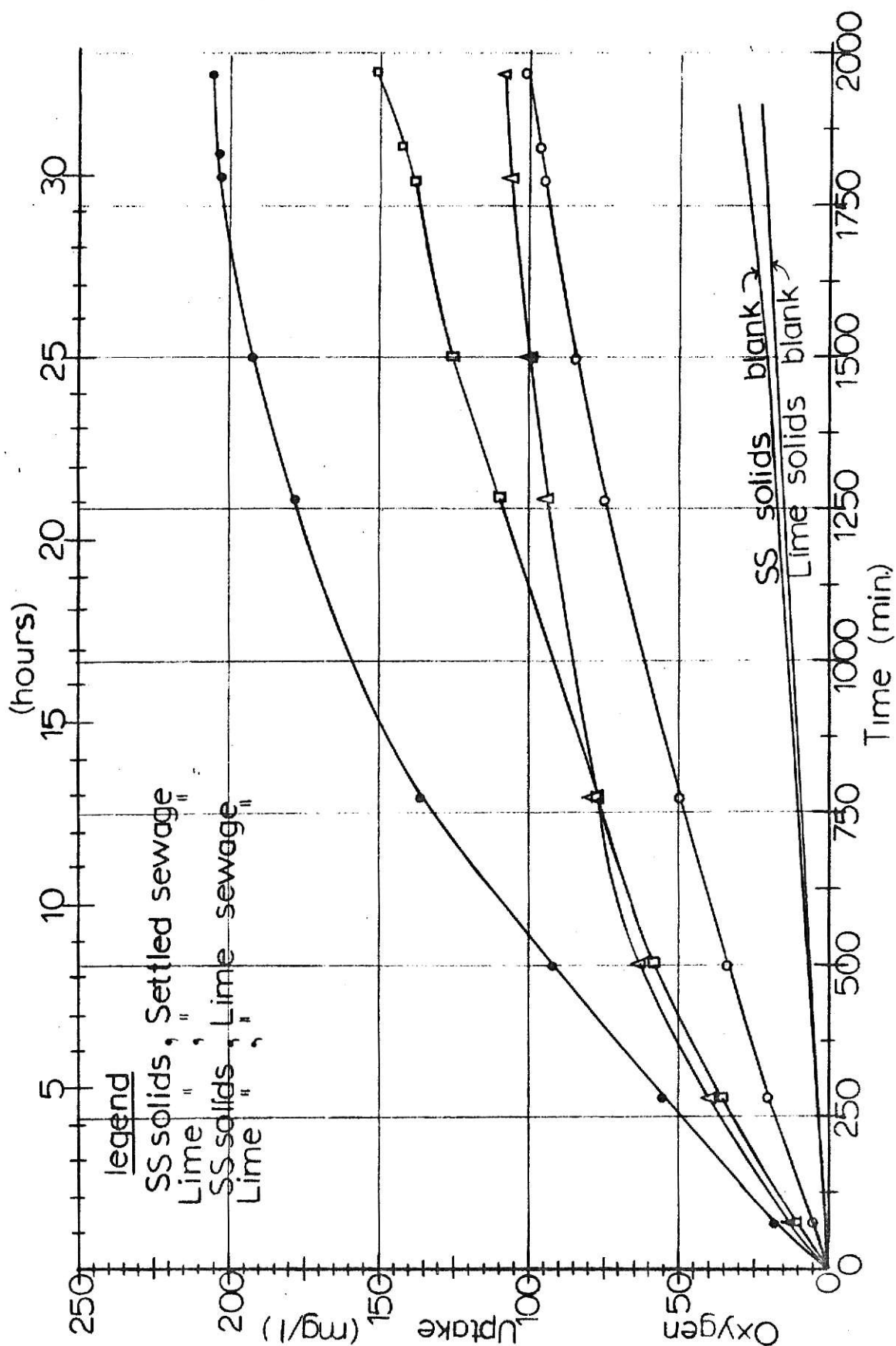


Fig. 10 Oxygen Uptake Curves for Run 3a

Table 13 Summary of Data for Run 3b

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	1095	69	2215	1175
SS solids mixture	2405	28	1920	460
Lime sewage	81	81	23	—
Settled sewage	247	105	60	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
SS solids blank	481	6	384	404	45	160	20
Lime solids blank	219	14	443	404	90	—	3
Lime solids Settled sew.	416	78	491	258	67	280	64
SS solids Settled sew.	678	90	432	535	112	360	189
Lime solids Lime sew.	284	79	461	210	57	360	28
SS solids Lime sew.	546	70	388	486	86	120	103

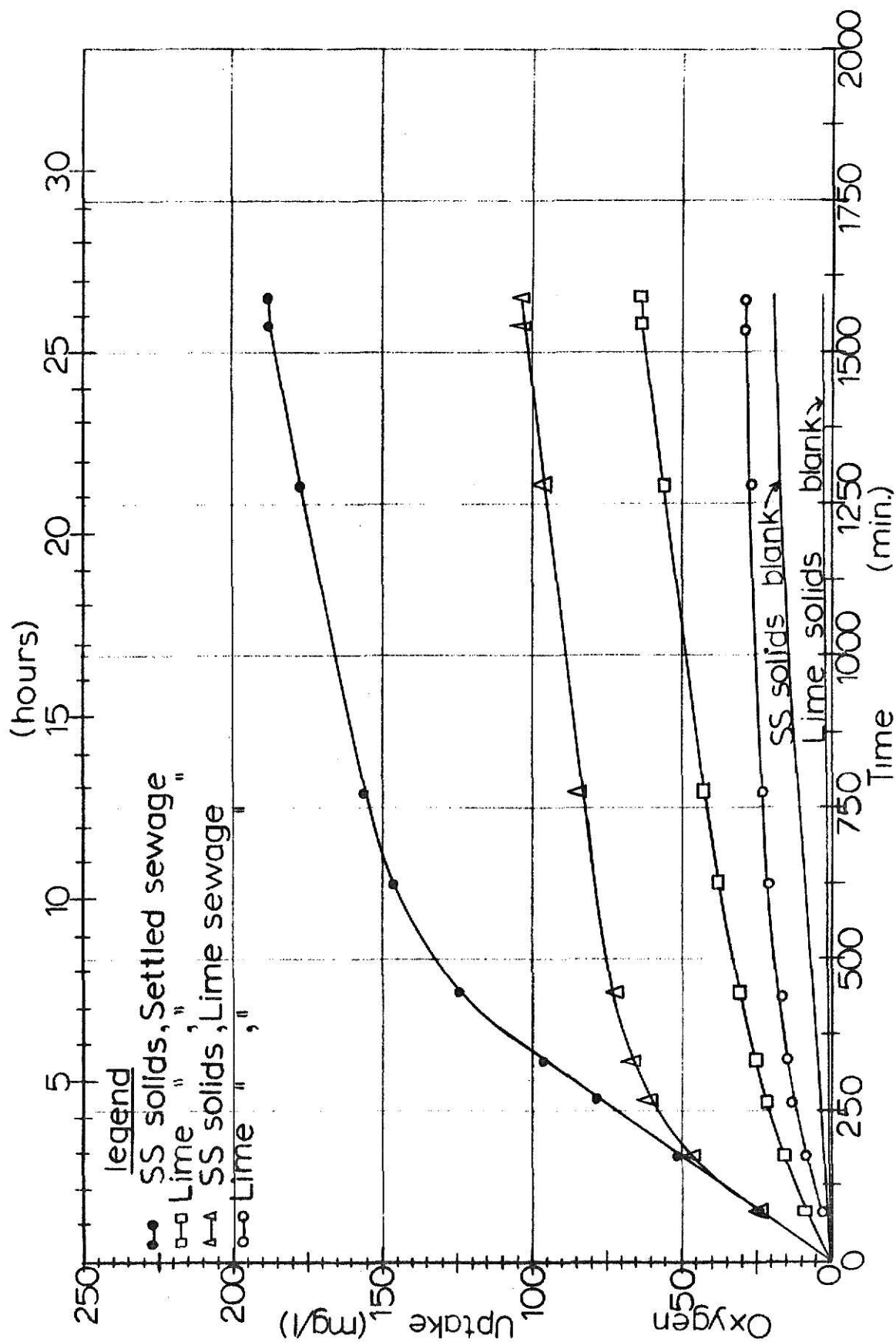


Fig 11 Oxygen uptake curves for Run 3b

Table 14 Summary of Data for Run 3c

Mixture	Total COD	Soluble COD	TSS	FSS
Lime solids mixture	3425	41	2620	410
SS solids mixture	3505	16	2955	690
Lime sewage	125	125	8	—
Settled sewage	300	134	70	—

Flask Combination	Initial Conditions			Final Conditions			
	Total COD	Soluble COD	TSS	Total COD	Soluble COD	TSS	Oxygen Uptake
Lime solids Lime sew.	785	108	530	816	188	720	76
SS solids Lime sew.	801	103	597	704	140	560	122
SS solids Settled sew.	941	110	647	1184	210	1040	235
Lime solids Lime sew.	785	108	530	768	194	480	76
Lime solids Settled sew.	925	115	580	880	211	760	134
SS solids Lime sew.	801	103	597	816	240	560	118

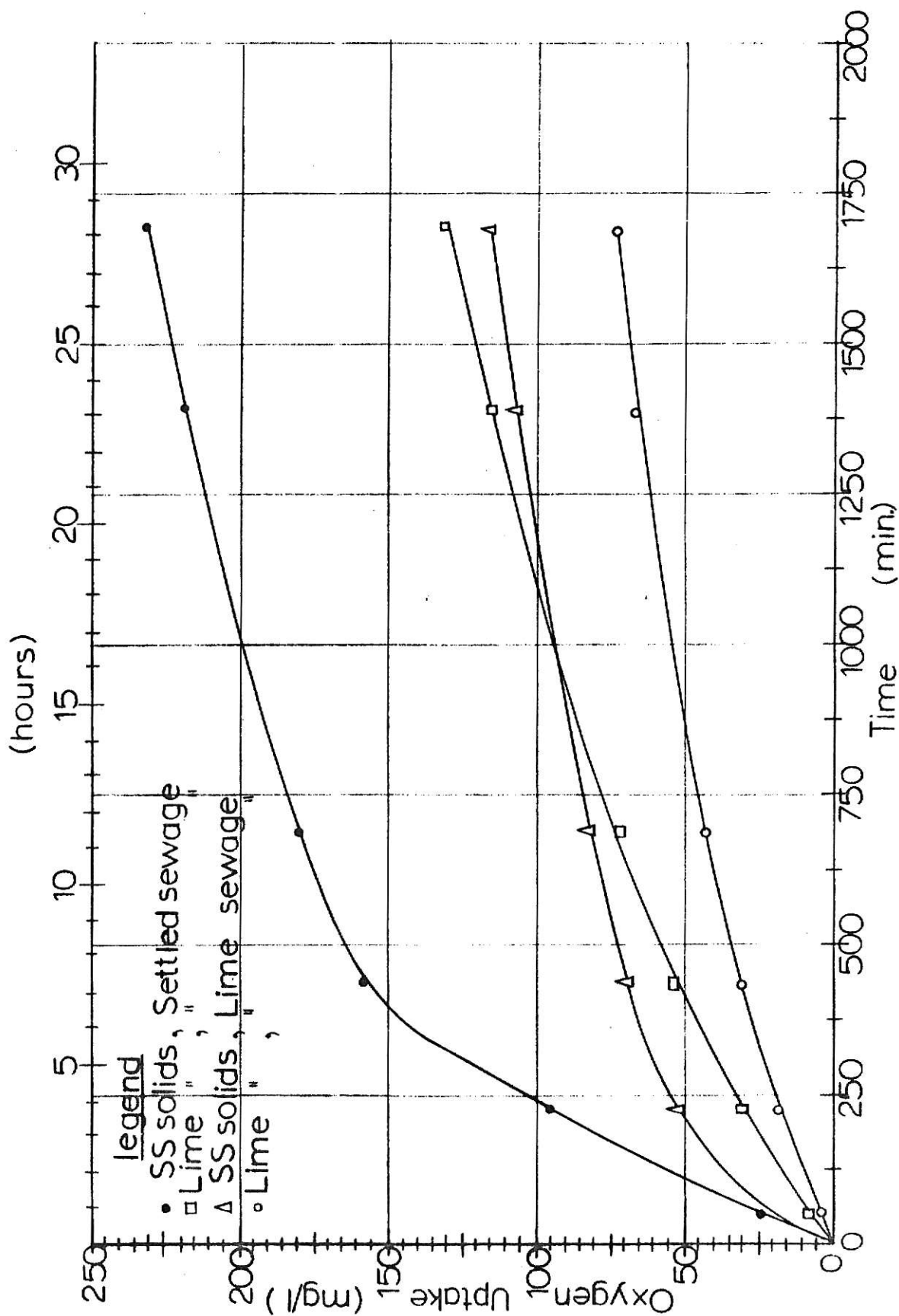


Fig. 12 Oxygen uptake curves for Run 3c

TABLE 15. The  $k_1$  Reaction-Rate Constants

Runs	Lime Treated Sewage pH	MLSS <sup>2</sup> Conc. mg/l	Final Suspended Solids Conc. in Mixture mg/l	Combinations							
				Uncorrected				Corrected			
				SS Solids		Lime Solids		SS Solids		Lime Solids	
				SS	Lime	SS	Lime	SS	Lime	SS	Lime
1a	9.8	1000	200	.36	.75	.49	.67	.43	.86	.63	.85
1b	9.7	2000	400	.64	.69	.86	1.01	.72	.96	1.93	1.15
1c	9.8	3000	600	.98	1.37	.88	1.04	1.29	1.86	.89	1.15
2a	10.5	1000	200	.41	.87	.23	.47	.49	1.12	.22	.42
2b	10.5	2000	400	1.06	1.29	.42	.28	----	----	----	----
2c	10.5	3000	600	1.07	1.15	.93	1.00	.97	1.38	.97	1.04
3a	11.5	1000	200	.54	.90	.48	.22	.63	1.23	.48	.29
3b	11.5	2000	400	1.00	1.31	.73	1.08	1.00	1.89	.77	1.25
3c	11.5	3000	600	1.28	1.47	.61	.69	----	----	----	----

<sup>1</sup> Before neutralization<sup>2</sup> Conc. of 1 ml activated sludge solution added to flask

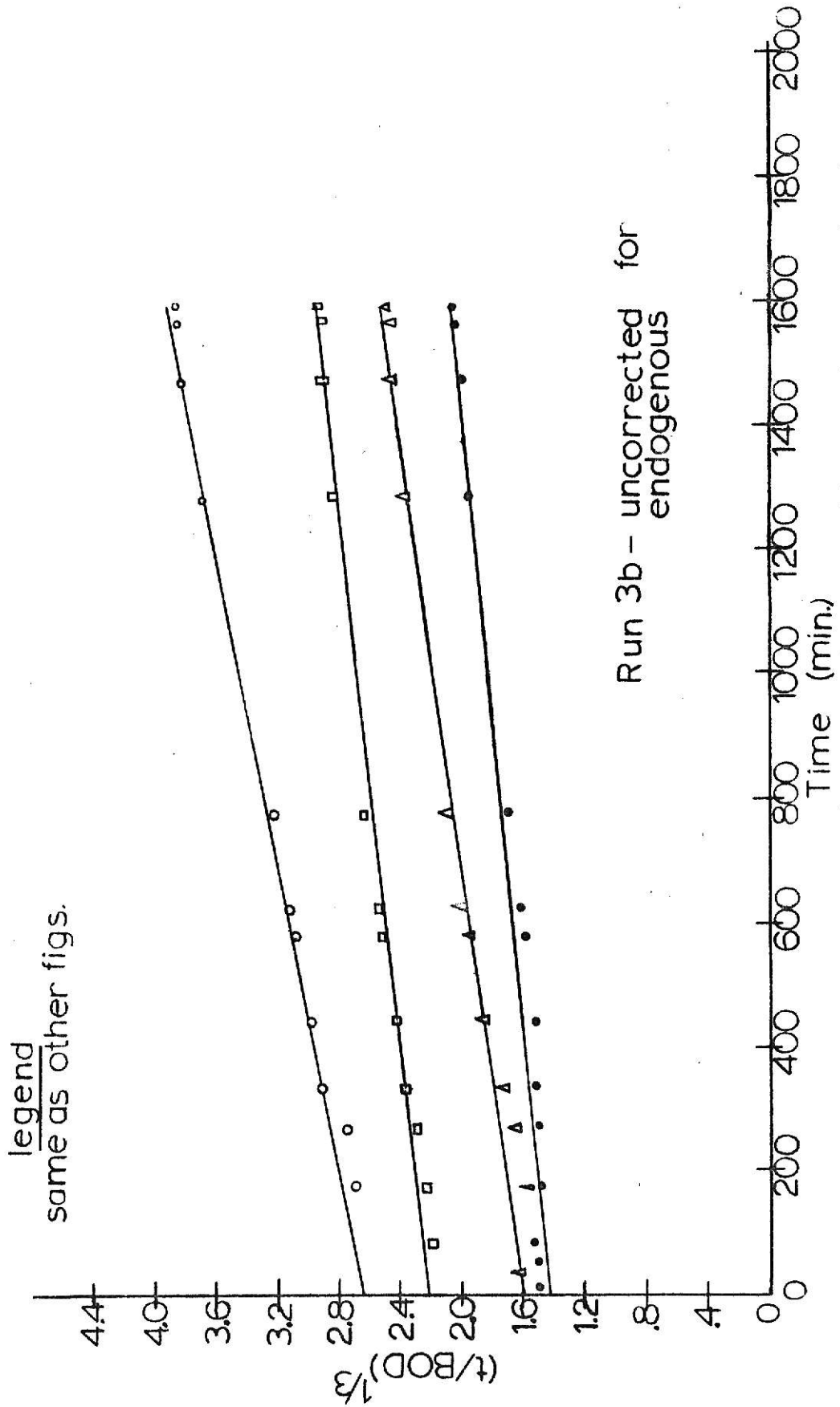


Fig.13 Calculation of  $k_1$  reaction rate constants

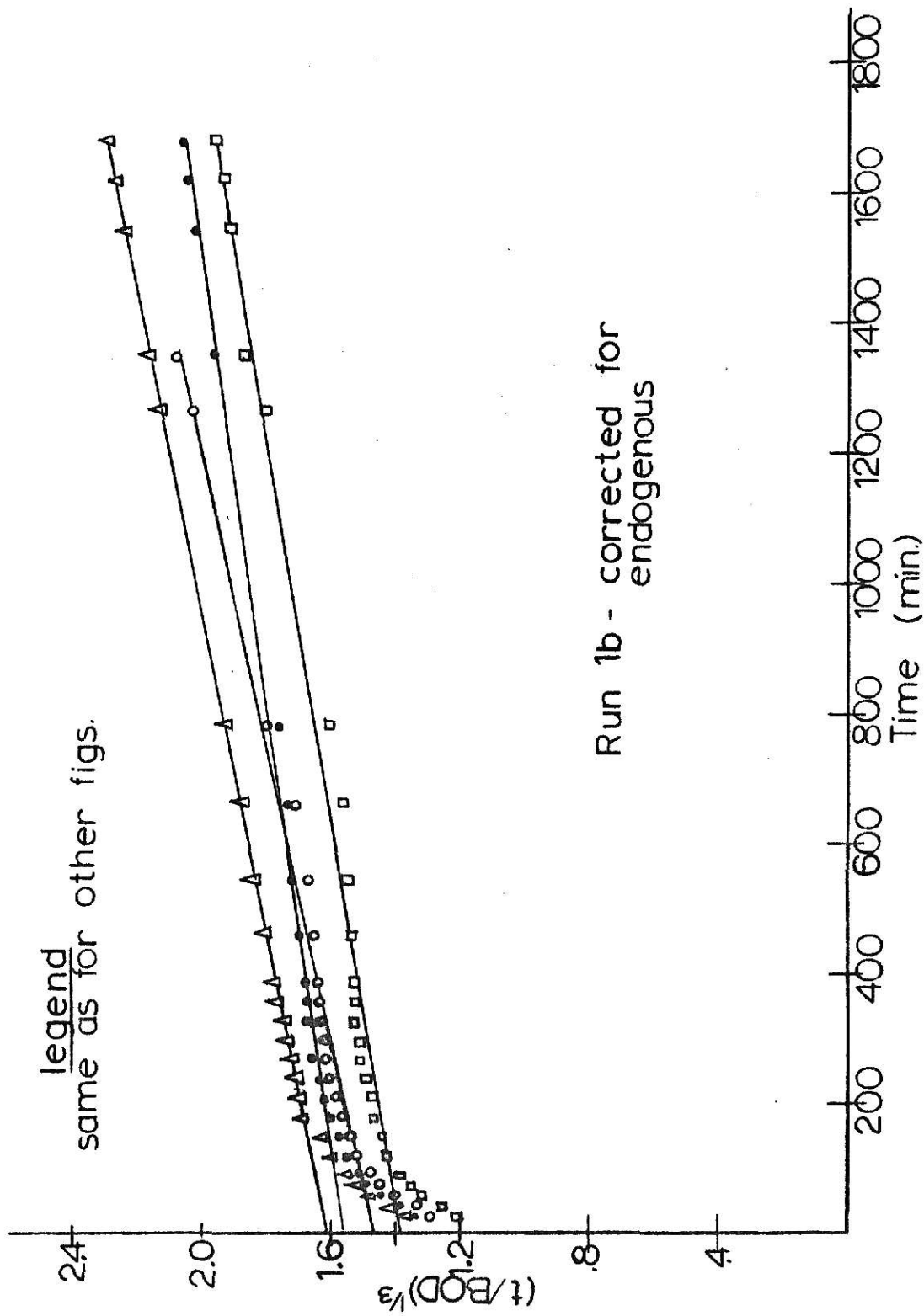


Fig. 14 Calculation of  $k_1$  reaction rate constants

## ACCURACY DATA

Part of the Warburg manometric accuracy data is presented in TABLE 17. This involves some duplication, but primarily triplication, at a pH level of 9.8 for the lime solids and the lime sewage. These calculations are representative of the patterns encountered. The average per cent variation represents the per cent error involved at a given level of oxygen uptake. The overall error for the data presented in TABLE 17 was 3.4 per cent, ranging from 2.2 to 5.2 per cent. The data for lime solids and sewage at a pH of 11.5 indicated an error of 2.1 per cent, and at a pH of 10.5, an error of 3.3 per cent.

The accuracy of the COD tests is presented below:

TABLE 16.--COD Accuracy Data

Theoretical Oxygen Demand mg/l	Range of Recovered COD (%)	Average Recovered COD (%)
2000	98-102	98
500	97-101	93
427	95- 98	97
250	90- 95	95
125	98-100	98

All the tests were run using prepared solutions of dextrose in distilled water. All tests were run according to the standard method for 10 ml samples as given in Standard Methods (34). The tests of the mixtures containing a concentration of 2000 mg/l were run by dilution to a factor of five (sample of 2.0 ml and 8.0 ml of distilled water). This was to determine if any discernible accuracy was lost when testing the activated sludge solids solutions normally diluted in this manner.

TABLE 17. Uptake Accuracy Data<sup>1</sup>

Time (minutes)	Lime Solids Settled Sewage			SS Solids Settled Sewage		
	1	2	3	1	2	3
75	15	17	19	24	23	26
155	33	36	37	49	48	51
255	56	61	61	76	80	85
375	80	86	87	106	112	118
615	120	129	135	127	136	142
1220	148	158	171	155	164	170
1445	155	167	179	170	174	178
1885	168	180	193	187	188	192
	Overall = 5.2 Average			Overall = 3.3 Average		
	Lime Solids <sup>2</sup> Lime Sewage			SS Solids <sup>2</sup> Lime Sewage		
	1	2	-	1	2	3
60	16	16		20	20	23
180	42	43		56	57	57
300	65	65		84	88	90
480	90	87		98	101	102
720	104	98		104	107	110
1253	117	113		117	121	125
1420	122	116		120	125	129
1720	141	121		127	137	136
	Overall = 2.2 Average			Overall = 2.9 Average		

<sup>1</sup>All uptake values in mg/l of oxygen<sup>2</sup>All lime-treated sewage treated to pH 9.8<sup>3</sup>The average percent variation equals the average difference from the mean divided by the mean

The COD accuracy tests do not, of course, reflect the variation that exists in a given sewage or solids solution. This data only reflects the accuracy lost through faulty procedure.

## DISCUSSION

### PART I

The discussion of this part is concerned primarily with soluble COD's at intervals of time. The MLSS (activated sludge concentration) varies enough to cover most concentrations existing in a large-scale plant. Except for the first run, the soluble COD of the solution containing lime sewage is less than or equal to that containing settled sewage after two hours. After four hours and the next morning, this was true of all runs.

Run 5 is one of the most interesting ones. The total COD for both types of sewage is roughly equal, but the soluble COD of the lime sewage is appreciably higher. Yet after two hours the unit containing lime sewage has a lower soluble COD. This indicates that even though the total demand is comparable, the rate of stabilization for lime sewage is greater, given comparable conditions. Since the soluble COD represents most of the decomposable material, it could be argued that the seemingly increased rate is due to the more favorable conditions existing for the lime sewage. However, in Run 7 the initial lime sewage soluble COD is 24% higher than that of the settled sewage, but after two hours the solution containing lime sewage has decreased in soluble COD by 58 percent, while the one containing settled sewage has decreased by only 12 percent.

In the end, though, the point could be made that the solids used, obtained from a process involving lime treatment, are more easily adapted to lime-treated sewage. The only evidence against this concerns the soluble COD's run the morning after a test was initiated. These show the solution

containing lime sewage to have a lower soluble COD, except for those two runs where the residual was too low to distinguish much difference. This indicates more complete removal, if not more efficient removal. The acclimation of the settled sewage to the lime solids had ample time (about 18 hours) to occur, with complete stabilization of the soluble organic matter.

The data gathered in this section is not completely conclusive, but indicates that the aerobic oxidation of lime sewage differs from that of settled sewage and that it is worth further research. The next section describes the work undertaken to investigate this further.

## PART II

These results will be explained and theorized in general, and particular points of interest will be discussed separately for each group.

The overall results indicate that for a given solids seed, the lime sewage is stabilized more rapidly than the settled sewage. This is based on  $k_1$  values, which indicate the rate of stabilization of the soluble organic matter. The following table presents data that indicates how much more efficiently the lime sewage is stabilized. Only the uncorrected values are used since the corrected values show nothing significantly different.

Basically, there are two things that must be expanded on. First, an explanation must be offered for the slightly greater efficiency of settled sewage solids over lime solids in stabilizing lime sewage, as indicated by the averages in the left column versus those in the right hand column. The one exception is discussed in Group 1. This general trend can be attributed to two things. The settled sewage solids possibly support 1) a higher concentration of microorganisms and 2) a more versatile distribution of organisms. This stems from the toxic effect of the pH levels of the lime-treated sewage.

TABLE 18. Factors of Relative Stabilization

Ratios of Lime Sewage $k_1$ Values to Settled Sewage		
Run	SS Solids	Lime Solids
1a	2.1	1.4
1b	1.1	1.2
1c	1.4	1.2
	Average = 1.5	Average = 1.3
2a	2.1	2.0
2b	1.2	.7
2c	1.4	1.1
	Average = 1.6	Average = 1.3
3a	1.7	.5
3b	1.3	1.5
3c	1.1	1.1
	Average = 1.4	Average = 1.1

This limits the range of organisms that can exist, even when the sewage was neutralized to a pH of 8, as was done at lime treatment levels of pH 10.5 and 11.5. It was impossible to neutralize the latter one further, since in coming to equilibrium the lime-activated sludge unit tended to turn slightly acidic (pH 6) by the next day. Since the most favorable pH for bacteria is considered to be close to neutral, these variable conditions are not conducive for a stable microbial population. This is essentially indicative of just what occurred. When testing at pH = 11.5, it was almost impossible to stabilize the lime solids unit. When settling out the solids for the purpose of the daily sewage addition, the supernatant was cloudy even though as much as an hour and one-half was allowed for settling. The continued loss of solids was accompanied by the lack of stability in the protozoan population. Most of the time few protozoa could be found, and these were usually rotifers. To combat this, the lime unit was fed two liters of lime-treated sewage that was neutralized

twice a day. This did not help. It was almost impossible to maintain any stability during the month of testing at this pH. Frequent reseeded with solids from the pilot plant was done to assist. Tests were never done very close to this reseeded to prevent faulty results.

The second item that requires explanation concerns the major data of importance--the  $k_1$  values. Since the data strongly indicates that the lime sewage is more biodegradable, the question arises as to why this is so. The first main theory concerns the hydrolysis of large molecular weight compounds into smaller fragments. Zuckerman and Molof (12) (13) claimed that at a pH of 11.5 the effect of lime treatment was to give a molecular weight distribution substantially different from that of raw sewage. They claimed that the main peak after treatment was at a molecular weight of 400, while before treatment two peaks existed--one  $< 400$  and one  $> 1200$ --the one at 1200 being the most inclusive. They unfortunately did not test at other pH values so the extent at other levels of treatment is not clear. However, this is still a strong possibility at all three pH's tested. The reason for this concerns the data in Part I and the pilot plant data gathered here at Kansas State University. This data indicates that more complete removal, as well as more efficient removals, can be expected. The only way this increase could occur is to make the organic matter more susceptible to biological oxidation. Breaking organic molecules into smaller fragments makes the transfer of substrate from the liquid medium into the organism a more efficient process (33). Since hydrolytic enzymes are limited and the cell hydrolytic process requires time (33), this is a particularly important factor. It would account for both the increased efficiency and the more complete removal.

The second theory concerns the adsorption of material by the complex

crystalline precipitate that results from lime treatment. This precipitate is considered (3) to be an apatite with base formula  $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ . The variable composition may result from substitution of hydrogen ions.

This floc which results from the complexing of the  $\text{Ca}(\text{OH})_2$  with the phosphates can present charged portions of the floc to the medium.

Zuckerman and Molof (12) (13) suggested adsorption as a possible factor in their research. The adsorption of long, complex organic molecules with localized charges would remove some material that is refractory. These materials would be small in concentration (10) (11) but would be difficult to degrade. As pointed out by Mills and Stack (27) and Ludzack and Ettinger (28), branching reduces the degradability of a substance. Also, materials that have localized charges are repelled by the charges that exist in the cells transport mechanism (35).

This theory is not substantiated but is one of the two main possibilities. The lower soluble COD's for lime-treated sewage indicate that some soluble organic matter is being removed by flocculation-precipitation. The extent of this removal is not easily described since it varies greatly. A further question arises as to how much of the adsorbed material is refractory.

The examples of the plots, Figures 13 and 14, used to determine  $k_1$  values show two things. First, in Figure 13 is shown a reasonably good example of many of the plots. This plot shows a good approximation to a line--very reasonable accuracy can be expected. Most of the plots were this good. The second plot, Figure 14, shows the initial period of high oxygen uptake. Taking this into account would give misleading results since it lasts for such a short period of time.

## Group I

In this group it is important to note the total oxygen uptakes listed in the tables. This reveals that no matter which solids seed was used, the final oxygen uptakes depend on the kind of sewage used. The rate at which this goal was reached differs significantly among the different combinations. This indicates that the proportions of sewage (4 ml) and activated sludge solids (1 ml) chosen were favorable in this group. This was an objective, to make the final demand dependent upon the type of sewage used, but to allow various factors involving both the solids and the sewage to come into play. This was particularly true of this group, but applies to most of the runs. The effect of lime treatment on the treatability of the sewage was suspected (12) (13), but the part played by the solids was not clear.

As mentioned in the results, the solids for Runs 1a and 1c differed somewhat from those of Run 1b. Those in Run 1b are characteristic of a process using lime-treated sewage at a pH of 9.8. They are bulky, filamentous (3), and light brown-gold in color. As detailed earlier, they occupy approximately 3 times the volume of the conventional SS solids or of the lime solids in Run 1a and 1c. It should be made clear though, that no discernable difference existed between the protozoa population in the two types of lime solids of this group. Both types exhibited the predominance of stalked ciliates that Schmid described (3). There was a difference between the protozoan populations of the lime solids and the settled sewage solids. The settled sewage solids contained a more prominent population of free swimming ciliates and rotifers. Thus, the only major difference between the two lime solids that could be discerned was the more filamentous (dispersed) character that was indicated by bulkiness. The lighter color is due to this, partially, but cannot be explained as

readily. It is the results of many factors, not all of which are completely understood.

It is important to be aware of this distinction. The second run involved the bulkier solids, and as pointed out, it is more efficient at stabilizing the lime sewage (1.01 to .86) and settled sewage (.69 to .64) than the settled sewage solids. This is attributed to the bulkiness which permits a more efficient surface area for microbial action. While additional runs are not available to substantiate this data, it is strongly considered to be an important factor. The runs in this group are particularly interesting because there was no neutralization of the daily solution prepared for addition to the lime solids unit. This was closer to the actual conditions existing in a large scale process based on lime-biological treatment. Testing the pH of the activated sludge after addition of the daily lime-treated sewage dosage, approximately 1 hour was required to bring the pH of the unit down to 7.4. This was true even when adding 2 liters of sewage to a unit with a final volume of 3 liters. To accomplish this requires the production of substantial amounts of  $\text{CO}_2$ . The ability to stabilize this quickly indicates a stable microbial population that can endure substantial shock loading. This is particularly interesting when it is noted that this addition occurs 23 hours after the previous one. The bacteria are undoubtedly in the endogenous phase with substantially reduced populations.

## Group 2

The main points that must be considered in this group are the character of the lime-activated sludge at  $\text{pH} = 10.5$ , and the exception to the general pattern existing in Run 2b.

The character of the lime-activated solids at this  $\text{pH}$  is characterized by a small but reasonably diversified protozoan population. It was possible, but difficult, to maintain a stable activated sludge at this  $\text{pH}$ . Unless neutralized before the daily addition, foaming of the lime solids unit occurred. However, neutralization of the sewage prevented no serious problems. The  $\text{pH}$  did not turn acidic to any appreciable extent by the next day.

The data for this group indicates, as does most of the data, that the lime sewage is more biodegradable. Overall, the uncorrected data indicates that it is 1.35 times as degradable. This is even considering Run 2b, where for lime solids the settled sewage is more degradable. However, the oxygen uptake plot of the lime solids and lime sewage combination in Figure 8 shows that nitrification has occurred. This result is substantiated by a duplication of this particular combination in this run. It indicates almost exactly the same thing. Projecting the curve to eliminate the nitrification effect, the  $k_1$  factor becomes .62 instead of .28, making the factor for lime sewage greater than that for settled sewage (.42).

### Group 3

The difficulty of maintaining the activated sludge at this pH of 11.5 has been explained. It is one of the major difficulties encountered in the entire testing program. It is not entirely unexpected that the only real contradictory result is obtained within this set of data. The encouraging fact is the consistency that exists.

## ACCURACY DATA

The Warburg manometric data replicates indicate that consistent results can be expected. As pointed out in the literature review, Caldwell and Langelier (22) reported average deviations (like those given here) of 2.3 percent for settled sewage with no activated sludge added. The addition of sludge should increase the variability of the results because of its undefined character. A maximum average deviation of 5.2 as reported here is excellent.

The COD accuracy tests are encouraging. They indicate that the lack of accuracy in the final conditions for each run was due to the lack of available quantities for testing and not in the procedure. The precision<sup>2</sup> of the COD test is reported as 92 percent of the theoretical oxygen demand.

---

<sup>2</sup>The precision of a test refers to its ability to measure the conditions as they exist.

## CONCLUSIONS

1. Raw sewage that is chemically treated with lime solution before settling is more biologically degradable than sewage that is settled only. This comparison is based on the rate of stabilization of both kinds by activated sludge.
2. The bulky filamentous activated sludge that results from feeding lime-treated sewage at pH 9.8 is more efficient than conventional activated sludge-fed sewage. The reason for this is not clear but is possibly related to the bulkiness of the activated sludge. The addition of ferric sulfate to the aeration tank of a lime-biological process may eliminate the settling problems of the activated sludge in the final settling tank, but seems to reduce the efficiency of the sludge at stabilizing waste at the same time.
3. It is possible to test accurately the biodegradability of a particular sewage using small volume (15 ml) Warburg flasks. This requires, however, a substantial investment in time and effort. Trial and error runs must be undertaken to determine the conditions most suitable for the particular research in mind.
4. Hydrolysis and adsorption are the main agents at work affecting the biodegradability of lime-treated sewage. Hydrolysis appears to be the most important factor of the two, according to present information (12) (13). The pH appears to be the major factor in hydrolysis, and the lime floc the major factor in adsorption.
5. It is possible for activated sludge acclimated to lime-treated sewage

(pH 9.8) to endure heavy shock loadings and still reach pH equilibrium quickly.

6. In general, these conclusions mean that a lime-biological treatment system as described by Schmid (3)(4)(5) can stabilize the raw sewage more efficiently and more completely (in terms of effluent COD and BOD versus that of raw sewage) than a conventional treatment process. This means, in terms of design parameters, that shorter aeration periods can produce final effluents low in COD.

## RECOMMENDATIONS FOR FURTHER RESEARCH

1. Further testing is required using large volume flasks (150 ml) on larger volumes of sewage and activated sludge. This allows greater accuracy, which might permit the extent of the influence of activated sludge and lime treatment to be determined.
2. It was pointed out in the literature review (20) that the biodegradability of a wastewater depends on the relative contribution of industrial waste. Manhattan, Kansas, has very little industry. It would be very valuable to test sewage with a higher proportion of industrial waste (and a lower biodegradability) to determine the effect of lime treatment.

## BIBLIOGRAPHY

1. Hunter, J. V. and Heukelekian, H. "Determination of Biodegradability Using Warburg Respirometric Techniques." Proceedings of the 19th Purdue Industrial Waste Conference, 1964.
2. Montgomery, H. A. C. "The Determination of Biochemical Oxygen Demand by Respirometric Methods." Water Research, Vol. 1, No. 10, October, 1967.
3. Schmid, L. A. "Optimization of Phosphorus Removal with Lime Treatment." Ph.D. Dissertation, University of Kansas, 1968.
4. \_\_\_\_\_. "Pilot Plant Demonstration of a Lime-Biological Treatment Phosphorus Removal Method." Annual Report submitted to the FWPCA covering June 1, 1969-May 31, 1970.
5. \_\_\_\_\_. "Phosphate Removal Demonstration Project." Progress Report to the FWPCA concerning project 17050DC, covering June 1, 1970-November 1, 1970.
6. Humenick, M. J., and Kaufman, W. J. "An Integrated Biological-Chemical Process for Municipal Wastewater Treatment." Paper presented at the 5th International Water Pollution Research Conference, San Francisco, 1970.
7. Hunter, J. V., and Heukelekian, H. "The Composition of Domestic Sewage Fractions." Journal of the Water Pollution Control Federation, Vol. 37, No. 8, August, 1965.
8. Heukelekian, H., and Balmat, J. "Chemical Composition of the Particulate Fraction of Domestic Sewage." Sewage and Industrial Wastes, Vol. 31, No. 4, April, 1956.
9. Painter, H. A., and Viney, M. "Composition of a Domestic Sewage." Journal of Biochem. and Microbiology Tech. and Eng., Vol. 1, No. 143, 1959.
10. Bunch, R. L., Barth, E. F., and Ettinger, M. B. "Organic Materials in Secondary Effluents." Journal of the Water Pollution Control Federation, Vol. 33, No. 2, 1961.
11. Helfgott, T., Hunter, J. V., and Rickert, D. "Analytic and Process Classification of Effluents." Journal of the Sanitary Engineering Division, Proceedings of the ASCE, Vol. 96, SA 3, 1970.

12. Zuckerman, M. M., and Molof, A. H. "High-Quality Reuse Water by Chemical-Physical Wastewater Treatment." Journal of the Water Pollution Control Federation, Vol. 42, No. 3, Part 1, March, 1970.
13. Molof, A. H., and Zuckerman, M. M. "High-Quality Reuse Water from a Newly Developed Chemical-Physical Treatment Process." Paper presented at the 5th International Water Pollution Research Conf., San Francisco, 1970.
14. Umbreit, W. W., Burris, R. H., and Stauffer, J. F. Manometric Techniques and Related Methods for the Study of Tissue Metabolism. Burgess Publishing Company, Minneapolis, Minnesota, 1948.
15. Burkhead, Carl. "Energy Relationships in Aerobic Microbial Metabolism." Ph.D. Dissertation, University of Kansas, 1966.
16. Corbet, A. S., and Wooldridge, W. R. "An Investigation of the Accuracy of the Barcroft Differential Manometer in Respiration Studies." Biochem. Journal, Vol. 30, No. 1, 1936.
17. Wooldridge, W. R., and Standfast, A. F. B. "The Use of the Barcroft Differential Manometer in the Estimation of the Oxygen Adsorption of Sewage." Biochem. Journal, Vol. 30, No. 1, 1936.
18. \_\_\_\_\_. "Some Experiments on the Oxidation of Sludge and Sludge-Sewage Systems." Biochem. Journal, Vol. 30, No. 1, 1936.
19. \_\_\_\_\_. "Certain Factors that Influence the Rate of Activated Sludge and Sewage Oxidations." Biochem. Journal, Vol. 30, No. 1, 1936.
20. Schulze, K. L., and Hoogerhyde, T. C. "Bio-degradability as Measured by Differential Manometer." Developments in Industrial Microbiology, Vol. 8, 1967.
21. Vath, C. A. "A Sanitary Engineer's Approach to Biodegradation of Nonionics." Soap and Chemical Specialities, Part I-Feb., Part II-March, 1964.
22. Caldwell, D. H., and Langelier, W. F. "Manometric Measurement of the Biochemical Oxygen Demand of Sewage." Sewage Works Journal, Vol. 20, No. 2, March, 1948.
23. Lee, E. W., and Oswald, W. J. "Comparative Studies of the Dilution and Warburg Methods for Determining B.O.D." Sewage and Industrial Wastes, Vol. 26, No. 9, September, 1954.
24. Dawson, P. S. S., and Jenkins, S. H. "The Oxygen Requirements of Activated Sludge Determined by Manometric Methods." Sewage Works Journal, Vol. 21, No. 4, July, 1949.

25. Montgomery, H. A. C., and Gardiner, D. K. "Experience With a Bacterial Inoculum for Use in Respirometric Tests for Oxygen Demand." Water Research, Vol. 5, 1971.
26. Balmat, J. "Biochemical Oxidations of Various Particulate Fractions of Sewage." Sewage and Industrial Waste, Vol. 29, No. 7, July, 1957.
27. Mills, E. J., Jr., and Stack, V. T., Jr. "Biological Oxidation of Synthetic Organic Chemicals." Proceedings of the 8th Purdue Industrial Waste Conference, 1953.
28. Ludzack, F. J., and Ettinger, M. B. "Chemical Structures Resistant to Aerobic Biochemical Stabilization." Journal of the Water Pollution Control Federation, Vol. 32, No. 11, Nov., 1960.
29. McKinney, R. E., Tomlinson, H. D., and Wilcox, R. L. "Metabolism of Aromatic Compounds by Activated Sludge." Sewage and Industrial Wastes, Vol. 28, No. 4, April, 1956.
30. Leigh, G. M. "Degradation of Selected Chlorinated Hydro-carbon Insecticides." Journal of the Water Pollution Control Federation, Vol. 41, No. 11, Part II, November, 1969.
31. Lamb, C. B., and Jenkins, G. F. "B.O.D. of Synthetic Organic Chemicals." Proceedings of the 7th Purdue Industrial Waste Conference, 1952.
32. Young, R. H. F., Ryckman, D. W., and Buzzell, J. C. "An Improved Tool for Measuring Biodegradability." Journal of the Water Pollution Control Federation, Vol. 40, No. 12, August, 1968. (Research Supplement)
33. Irvine, R. L., and Busch, A. W. "Factors Responsible for Non-Biodegradability of Industrial Wastes." Journal of the Water Pollution Control Federation, Vol. 41, No. 11, November, 1968. (Research Supplement)
34. American Public Health Assoc., Inc. Standard Methods for the Examination of Water and Wastewater. 12th ed., New York, N. Y., 1965.
35. McKinney, R. E. Microbiology for Sanitary Engineers. New York: McGraw-Hill Book Co., 1962.
36. Thomas, H. A. "Graphical Determination of BOD Curve Constants." Water and Sewage Works, 97, 123, (1950).
37. Brock, Thomas D. Biology of Microorganisms. Englewood Cliffs, New Jersey: Prentice-Hall, Inc., 1970.

**THE EFFECT OF LIME TREATMENT OF SEWAGE ON  
OXYGEN UPTAKE BY ACTIVATED SOLIDS**

**by**

**RALPH L. FLOURNOY**

**B. S., Kansas State University, 1970**

---

**AN ABSTRACT OF A MASTER'S THESIS**

**submitted in partial fulfillment of the**

**requirements for the degree**

**MASTER OF SCIENCE**

**Department of Civil Engineering**

**KANSAS STATE UNIVERSITY  
Manhattan, Kansas**

**1971**

This research tested the effect of lime treatment of raw sewage on the biodegradability of the wastewater. This was accomplished using activated sludge as the microbial seed. Units were set up in the lab to grow activated sludge on lime-treated sewage and settled sewage. Various combinations of lime and settled sewage plus activated sludge-fed lime sewage or settled sewage showed that lime sewage is more biologically degradable than settled sewage. It also revealed that activated sludge fed lime sewage at a treatment level of pH 9.8 is slightly more efficient at stabilizing a waste. This activated sludge is also capable of enduring heavy shock loadings and returning to equilibrium quickly.

The major mechanisms at work affecting the biodegradability of lime-treated sewage are hydrolysis and adsorption. Hydrolysis breaks large molecular weight compounds into smaller fragments that are assimilated more readily by microorganisms. Adsorption removes some of the soluble organic matter, but it is not certain if refractory material is preferentially removed to any significant extent.

This data suggests that whether on a large scale or not the lime-biological process effects a more complete removal of COD and BOD material than conventional treatment in less time.