3-83

②

DOE/LC/10097-1
(DE83002245)

A STUDY OF AEROBIC OXIDATION AND ALLIED TREATMENTS FOR UPGRADING *IN SITU* RETORT WATERS

Final Report

By
R. Edwin Hicks
Irvine W. Wei

December 1980

Work Performed Under Contract No. AC20-79LC10097

Water Purification Associates
Cambridge, Massachusetts

TECHNICAL INFORMATION CENTER
UNITED STATES DEPARTMENT OF ENERGY

DOE/LC/10097-1
(DE83002245)
Distribution Category UC-91

A STUDY OF AEROBIC OXIDATION AND ALLIED TREATMENTS FOR UPGRADING IN-SITU RETORT WATERS

FINAL REPORT

Prepared by
R. Edwin Hicks
Irvine W. Wei

Water Purification Associates
238 Main Street
Cambridge, Massachusetts 02142

DECEMBER, 1980

Prepared for
U.S. DEPARTMENT OF ENERGY
Laramie Energy Technology Center (LETC)
Laramie, Wyoming 82071

Under Contract
Contract No. DE-AC20-79LC10097

Project Officer: J. Lotwala

ACKNOWLEDGEMENTS

The experimental sections of this study were carried out at Northeastern University by John P. Patinskas, Mikhail Schiller, and Jack C.Y. Chen under the supervision of Professor Irvine W. Wei. The assistance of Professors Frederic Blanc and James O. Shaughnessy is also appreciated. The non-biological treatments were designed by Yaghoub Alliance and the project officer, Dr. R.E. Hicks.

ABSTRACT

This study concerns the treatment of retort water from a modified in-situ shale retort. The water contains organic and inorganic contamination. An oil water separator was designed but tests were not made and are recommended. A steam stripper for ammonia was designed. A thorough experimental investigation of biological oxidation was made. Experiments were made on air and oxygen activated sludge with and without the addition of powdered activated carbon, on a rotating biological contactor and on sequenced equipment. The BOD (initially 4,000 mg/l) could be 90% removed from undiluted wastewater preferably using oxygen activated sludge. COD (initially 10,000 mg/l) was not removed in excess of BOD unless carbon was used. The sequence RBC-PAC-AS removed 85% of the BOD and 66% of the COD but is expensive. Solvent extraction and resin adsorption proved unsatisfactory as follow-on treatments to biological treatment. Activated carbon is satisfactory but expensive. Reverse osmosis proved an excellent alternative to biological oxidation and a separate study, not reported here, was made. Tests on the alternative of raising dirty steam from untreated retort matter were strongly recommended.

Blank Page

TABLE OF CONTENTS

ACKNOWLEDGEMENTS ii

ABSTRACT iii

LIST OF FIGURES ix

LIST OF TABLES xiii

EXECUTIVE SUMMARY xvi

1. INTRODUCTION 1

2. CONCLUSIONS AND RECOMMENDATIONS 3
   - 2.1 Conclusions 3
   - 2.2 Recommendations 3

3. BACKGROUND TO THE WASTEWATER AND ITS BIOLOGICAL TREATMENT 4
   - 3.1 Wastewaters and their Treatment in In-Situ Oil Shale Retorting 4
     - 3.1.1 Wastewater Quality and Quantity 4
     - 3.1.2 Mine Drainage Water and its Treatment for Discharge 5
     - 3.1.3 Gas Condensate, Stripping and Treatment for Reuse 10
     - 3.1.4 Retort Water 19
     - 3.1.5 Summary of Some Overall Wastewater Management Schemes 23
   - 3.2 Review of Previous Studies on Biotreatment of Retort Waters 23
     - 3.2.1 Anaerobic Treatment 27
     - 3.2.2 Aerobic Treatment 29

4. EXPERIMENTAL INVESTIGATION OF BIOLOGICAL TREATMENT 31
   - 4.1 The Retort Water 31
   - 4.2 Pretreatment of Retort Water 33
     - 4.2.1 Ammonia Stripping 33
     - 4.2.2 pH Neutralization 38

TABLE OF CONTENTS (continued)

4.3 Rotating Biological Contactor (RBC) 39
  4.3.1 Introduction 39
  4.3.2 Experimental Apparatus 39
  4.3.3 Experimental Procedures 43
  4.3.4 Results of Batch Operation 46
  4.3.5 Results of Continuous Operation 47
  4.3.6 Hydraulic Loading Rate 59
  4.3.7 Organic Loading Rate 59
  4.3.8 Effects of Staging 61
  4.3.9 Dissolved Oxygen 67
  4.3.10 pH 70
  4.3.11 Extended Aeration of RBC Effluent 70
  4.3.12 Solids Production 70
  4.3.13 The Effect of 20:1 Dilution 70
  4.3.14 Color 73
  4.3.15 Conclusions 73
4.4 Air Activated Sludge (AS) and Oxygen Activated Sludge (OS) 74
  4.4.1 Introduction 74
  4.4.2 Experimental Apparatus and Procedure 74
  4.4.3 Equations 76
  4.4.4 Analytical Procedures 79
  4.4.5 Experimental Results 79
  4.4.6 Model Coefficients 99
  4.4.7 Conclusions 107
4.5 Activated Sludge with Powdered Activated Carbon (PAC-AS) 108
  4.5.1 Introduction 108
  4.5.2 The Wastewater and the Carbon 108
  4.5.3 Equipment and Procedure 109
  4.5.4 Continuous Flow RBC-PAC-AS Procedure 116
  4.5.5 Analytical Methods 118
  4.5.6 System Performance 118
  4.5.7 Sludge Dewatering 136
  4.5.8 Summary and Conclusions 136

4.6 Summary of the Results of Experiments on Biological Treatment ... 138

5. DESIGN OF BIOLOGICAL TREATMENT SYSTEMS ... 140
5.1 Conclusions ... 140
5.2 Rotating Biological Contactor ... 140
5.3 Design of an Oxygen Activated Sludge ... 143
5.3.1 Design Equations ... 143
5.3.2 Summary of Design Equations ... 148
5.3.3 Calculations to Relate Effluent Concentration to Aeration Basin Volume ... 149
5.3.4 Other Design Factors ... 153
5.3.5 Summary and Cost for Oxygen Activated Sludge ... 154
5.4 Activated Sludge with Powdered Activated Carbon Addition ... 156
5.4.1 Design Basis and Equations ... 156
5.4.2 Summary of Design Calculations ... 157
5.4.3 Costs ... 160
5.5 Rotating Biological Contactor followed by Air Activated Sludge with Powdered Activated Carbon Addition ... 162
5.5.1 RBC Design ... 162
5.5.2 PAC-AAS Design ... 162
5.5.3 Costs ... 163

6. PRE- POST- AND ALTERNATIVE TREATMENTS ... 165
6.1 Oil Water Separation ... 166
6.1.1 Design Procedure ... 166
6.1.2 Example of Oil Water Separator Design ... 172
6.1.3 Cost ... 174
6.1.4 Emulsions ... 174
6.2 Ammonia and Acid Gas Stripping ... 178
6.2.1 Free Ammonia Stripping ... 178
6.2.2 The Effect of Fixed Ammonia ... 180
6.3 Solvent Extraction ... 196
6.4 Resin Adsorption ... 197
6.5 Carbon Adsorption ... 199

6.6 Reverse Osmosis 200
6.7 Oxidation 202
6.8 Production of Dirty Steam 205

APPENDICES

Appendix 1 Tabulated COD Measurements from Experiments on the Rotating Biological Contactor 208
Appendix 2 Tabulated BOD Measurement from Experiments on the Rotating Biological Contactor 212
Appendix 3 Tabulated Solids Measurement from Experiments on the Rotating Biological Contactor 216
Appendix 4 Nomenclature Used in Section 4 219
Appendix 5 Determination of MLCSS and MLBSS in PAC-AS System 222

REFERENCES 223

LIST OF FIGURES

Figure Page

3-1 Ammonia and Organics (COD) Stripping from Oxy Gas Condensate 18

3-2 Major Water Steams for Oxy Shale Oil Plant Producing 100,000 BPSD Crude Shale Oil 25

3-3 Production of Dirty Steam from Retort Water in 100,000 BPSD Oxy Shale Oil Plant 26

4-1 Complete Titration Curve of Representative R-17 Retort Water 35

4-2 Alkalinity Test for R-17 Filtered Retort Water Before Stripping 37

4-3 Plan of Laboratory Unit A 40

4-4 Layout of RBC Units 41

4-5 Flow Chart of RBC Treatment and Pretreatment 44

4-6 Changes in BOD with Time for Unit A, Undiluted Retort Water 57

4-7 Changes in COD with Time for Unit A, Undiluted Retort Water 58

4-8 BOD Removed as a Function of BOD Applied 60

4-9 % BOD Removed as a Function of BOD Applied 60

4-10 BOD by Stage, (24-35 Hour Residence Time) 62

4-11 BOD by Stage, (6-12 Hour Residence Time) 63

4-12 COD by Stage, (24-35 Hour Residence Time) 64

4-13 COD by Stage, (6-12 Hour Residence Time) 65

4-14 BOD Removed as a Function of BOD Applied for Various Stages 66

4-15 Dissolved Oxygen as a Function of Overall Organic Loading Rate .. 69

4-16 Experimental Activated Sludge Apparatus 75

4-17 BOD_5 and COD Correlation for Shale Oil Retort Water 82

4-18 Long Term Aeration Results using a 4:1 Dilution of Influent Retort Water 83

4-19 BOD Concentration as a Function of Time for Activated Sludge Study Using Air 85

4-20 Percent BOD Removal as a Function of Food to Microorganism Ratio 86

4-21 Specific Substrate Utilization as a Function of Food to Microorganism Ratio 86

4-22 Sludge Growth Rate as a Function of Food to Microroganism Ratio 90

LIST OF FIGURES (continued)

Figure Page

4-23 BOD$_5$ of Influent and Effluent for Reactors 1, 2, and 3 - Oxygen Activated Sludge 90

4-24 Nominal BOD$_5$ Removal from Equation (4-12) - Oxygen Activated Sludge 91

4-25 Overall BOD$_5$ Removal from Equation (4-13) - Oxygen Activated Sludge 91

4-26 BOD$_5$ Removal as a Function of Food to Microorganism Ratio - Oxygen Activated Sludge 93

4-27 Specific Substrate Utilization Rate as a Function of Food to Microoganism Ratio - Oxygen Activated Sludge 93

4-28 Sludge Growth Rate as a Function of Food to Microorganism Ratio - Oxygen Activated Sludge 94

4-29 Variation of pH in Reactor using Air for Aeration 94

4-30 . Variation of pH using Pure Oxygen for Aeration 95

4-31 Hydraulic Residence Time and Hydraulic Loading for Reactors 1, 2 and 3 during Air Aeration 95

4-32 Hydraulic Residence Time and Hydraulic Loading for Reactors 1, 2 and 3 during Pure Oxygen Aeration 97

4-33 Net Specific Growth Rate as a Function of Specific Substrate Utilization for Air Aeration Activated Sludge Units 97

4-34 Plot of Experimental Data to Determine K_s and k for Air Activated Sludge Units 102

4-35 Net Specific Growth Rate as a Function of Specific Substrate Utilization for Pure Oxygen Activated Sludge Units 104

4-36 Plot of Experimental Data to Determine K_s and k for Pure Oxygen Activated Sludge Units 104

4-37A Freundlich Isotherms for Four Types of PAC 112

4-37B Freundlich Isotherm for Amoco PAC Type PX-21 113

4-38 Treatment Scheme 114

4-39 Schematic Diagram of PAC-AS System 115

4-40 Eckenfelder-type Reactor 119

LIST OF FIGURES (continued)

Figure Page

4-41 Effect of Sludge Age on Removal Efficiency in the AS System 127

4-42 Effect of Sludge Age on Removal Efficiency in the PAC-AS System 128

4-43 Effect of Sludge Age on Removal Efficiency in the RBC-PAC-AS System 129

4-44 Variability of Influent and Effluent BOD_5 133

4-45 Variability of Influent and Effluent COD 134

4-46 Variability of Influent and Effluent TOC 135

5-1 Activated Sludge Material Balance 146

5-2 The Effect of Increasing Aeration Basin Volume on Effluent BOD 151

6-1 Specific Gravity of Clear Water 168

6-2 Absolute Viscosity of Clear Water 168

6-3 Recommended Values of F for Various V_H/V_t 170

6-4 Order of Magnitude Capital Cost Estimate for API Gravity Oil-Water Separators 175

6-5 Stripping and Ammonia Recovery by U.E.C. Phosam-W Process 179

6-6 Dependence of Stripping Column Height on Steam Rate, Ammonia Removal Efficiency and Ammonia Concentration in the Feed 181

6-7 Capital and Operating Costs for Ammonia Stripping 182

6-8 Dissociation of Dissolved Gases in Water as a Function of pH and Temperature 186

6-9 Effect of the Presence of Excess Anions on Cations on the pH of Ammonia Solutions and hence the Concentration of Unionized Ammonia 188

6-10 Effect of the Presence of Excess Anions or Cations on the pH of 1 Molar Ammonia Solutions Containing Dissolved Hydrogen Sulfide 189

6-11 Volatility of NH_3, CO_2, H_2S as a Function of pH 193

6-12 Dependence of Stripping Column Height on Steam Rate for 95% Ammonia Removal Efficiency 194

LIST OF FIGURES (continued)

Figure Page

6-13 Installed Tower and Steam and Chemical Costs for Ammonia Stripping 195

6-14 Simple Arrangement for Wet Oxidation 203

6-15 Schematic of Patented Thermosludge Process 206

LIST OF TABLES

Table Page

3.1 Water Quality Data for Oil Shale Aquifer in Piceance Creek Basin 7
3.2 Suggested Discharge Quality Parameters for Excess Mine Drainage Water 8
3.3 Cost[(a)] (in $/1,000 gal) of Mine Water Treatment by Membrane Processes 10
3.4 Processes for Treating Mine Drainage Waters to Discharge Quality 11
3.5 Ammonia and Acid Gases in MIS Retort Gas 15
3.6 Composition of Gas Condensate 16
3.7 Analysis of Filtered and Stripped Oxy Gas Condensate Sample 19
3.8 Water Balance Around MIS Retort 21
3.9 Retort Water Composition 22
3.10 Major Water Streams Requiring Treatment at a Commercial Scale MIS Retorting Operation 24
3.11 Characteristics of Aerobic and Anaerobic Processes 27
3.12 Treatment Performance of Activated Sludge Process on the Utah Retort Water 30
4.1 Chemical Analyses of Filtered R-17 Retort Water Received for Testing 32
4.2 Chemical Characteristics of Filtered R-17 Retort Water 34
4.3 Effects of Ammonia Stripping on Suspended Solids 38
4.4 Dimensions of RBC Units 42
4.5 Schedule of Experiments 45
4.6 Rotating Biological Contactor Results 48
4.7 Rotating Biological Contactor Results 49
4.8 Rotating Biological Contactor Results 50
4.9 Rotating Biological Contactor Results 51
4.10 Rotating Biological Contactor Results 52
4.11 Rotating Biological Contactor Results 53
4.12 Rotating Biological Contactor Results 54
4.13 Rotating Biological Contactor Results 55
4.14 Rotating Biological Contactor Results 56

LIST OF TABLES (continued)

Table Page

4.15 Dissolved Oxygen Data 68
4.16 pH by Stage for 24 Hour Hydraulic Residence Time 71
4.17 RBC Effluent 71
4.18 Solids Production 71
4.19 BOD and COD Concentrations for Shale Oil Retort Water Using Activated Sludge Treatment 80
4.20 Ultimate BOD Concentrations and Selected Treatment Parameters for Shale Oil Retort Waters Using Air Activated Sludge Treatment 87
4.21 Summary of Treatment Parameters for Air Activated Sludge 89
4.22 Oxygen Consumption in Air Activated Sludge System 96
4.23 Oxygen Consumption in Oxygen Activated Sludge System 98
4.24 Specific Resistance of Activated Sludge 99
4.25 Summary of Treatment Parameters for Air Activated Sludge 100
4.26 Summary of Treatment Parameters for Oxygen Activated Sludge 103
4.27A Model Coefficients 105
4.27B Biokinetic Constants 106
4.28 PAC Specification 110
4.29 PAC Isotherm Test Results 111
4.30 Four-Stage RBC Operation Conditions and Effluent Characteristics. 117
4.31 Operating Conditions and Performance of the AS System 120
4.32 Operating Conditions and Performance of the PAC-AS System (First Period) 121
4.33 Operating Conditions and Performance of the PAC-AS System (Second Period) 122
4.34 Operating Conditions and Performance of the RBC-PAC-AS System 123
4.35 Average Performance 125
4.36 Summary of Operating Conditions 126
4.37 Summary of Sludge Age and Efficiency in the AS System 130
4.38 Summary of Sludge Age and Efficiency in the PAC-AS System 131
4.39 Summary of Sludge Age and Efficiency in the RBC-PAC-AS System 132
4.40 Average Specific Resistance of the Sludges 136
4.41 Removal Percentages Achieved 139

LIST OF TABLES (continued)

Table Page

5.1 Cost and Effluent of Biological Treatments 141

5.2 Calculations for an Oxygen Activated Sludge Plant 150

5.3 Second Stage Calculations for an Oxygen Activated Sludge Plant .. 153

5.4 Cost of Oxygen Activated Sludge Plant 155

5.5 Two Operating Conditions of PAC-AS System 157

5.6 Evaluation of Reactor Volume and Oxygen Requirement 158

5.7 Sludge Production 159

5.8 Costs of PAC-AS Plant 161

5.9 Costs of RBC-PAC-AAS Plant 164

6.1 Recommended Values of Turbulence Factors 169

6.2 Henry's Law Constants for Ammonia, Carbon Dioxide and Hydrogen Sulfide 183

6.4 Results of Solvent Extraction Tests 196

6.5 Tests with Resin Adsorption 198

6.6 Summary of Reverse Osmosis Membrane Screening Tests on Stripped LETC 10 Ton Simulated In-Situ Retort Water 201

6.7 Performance of Reverse Osmosis Flow Unit 200

EXECUTIVE SUMMARY

This is the report on a study of treatments for the major wastewater streams in a modified in-situ shale retorting plant. Three major wastewater streams are identified as to quality and quantity: mine drainage water, gas condensate and retort water. Mine drainage water is expected to be a very large flow and treatments such as reverse osmosis or electrodialysis, intended for desalination, are expected to upgrade this water for discharge. The contaminants in gas condensate have been found to be volatile so that stripping will fit this water for in-plant reuse, mostly as cooling water.

Retort water is heavily contaminated. It contains oil, volatile gases-principally ammonia and carbon dioxide, organic matter and salts. The quantity of retort water per unit of oil produced is higher in a MIS retort than in a surface retort. The excess comes from steam and seepage. In a surface retort, the retort wastewater will, after stripping of volatile contaminants, be used for disposal of spent shale. Because there is more water and because less shale is mined; this disposal is not available in a MIS plant. Treatment is necessary. Oil separation was not tested experimentally. A design and costs of a standard type of oil separator are given but tests are recommended. Designs and costs of steam strippers for volatile gases are also given. Methods for removing organics were tested experimentally. Brief experiments with solvent extraction and resin adsorption were unsuccessful and the tests were not continued. Carbon adsorption appears to be a workable treatment following biological oxidation.

Biological oxidation was investigated thoroughly. Laboratory tests were made on air activated sludge with and without powdered activated carbon, oxygen activated sludge and a rotating biological contactor. There is a large bio-refractory fraction in the COD. About 50% could not be oxidized at all. In procedures not using carbon the weight of COD removed was close to the weight of BOD removed, not higher. Since the raw water averaged 4,000 mg/l BOD and 10,000 mg/l COD, an oxygen activated sludge system, which gave the highest BOD removal of 90% gave an effluent of about 400 mg/l BOD and 6,400 mg/l COD. This is too much COD for any reuse. The system of a rotating biological contactor followed by an air activated sludge with powdered activated carbon gave better results: 85% removal of BOD and 66% removal of COD and an effluent containing 600 mg/l BOD and 3,400 mg/l COD. The powdered activated carbon will, however,

be very expensive and the possibility of reducing the quantity of recovery needs to be investigated.

It was then found that reverse osmosis gave such good removals of all contaminants that a separate study was made of this treatment. The reverse osmosis study is separately reported (DOE contract DE AC20-79LC10089 Laramie), Reverse osmosis is the preferred treatment.

As an alternative to reverse osmosis a test is strongly recommended on the raising of dirty steam from untreated retort water for use in the in-stiu retort.

1. INTRODUCTION

The objectives of this project were (1) to investigate the quantity and quality of wastewater streams in in-situ shale retorting and to summarize possible treatments, (2) to study biochemical oxidation of retort water and (3) to study experimentally and to design additional and alternative treatments for retort water.

At the time the investigation was formulated the control of organics in oil shale wastewaters appeared to be the most critical problem in water management schemes. Based on its success in treating coal conversion wastewaters, it seemed that biological oxidation should prove to be a feasible method for organics reduction. Foregoing experimental investigations of the biological treatment of oil shale wastewaters had not been conclusive due to questions on adequate pretreatment, toxicity removal, and test water selection. In addition, parameters required for the design of biological reactors had not been determined quantitatively. An experimental program to determine the required biokinetic constants as well as to investigate toxicity effects on actual adequately pretreated wastewaters in an activated sludge system was therefore proposed. The experimental investigation was to be backed by the design and costing of complete wastewater treatment trains for commercial scale oil shale plant.

During the first year of the program it was recognized that biological oxidation alone would not prove an adequate organic removal process for some oil shale wastewaters. Consequently additional experimental investigations of pre- and post-treatment process to complement the biological system were proposed. The treatments included solvent extraction, resin adsorption, carbon adsorption, reverse osmosis, powdered activated carbon in the activated sludge and the use of a rotating disk biological system as a low energy means of reducing the organic loading to the activated sludge system.

At this stage it was recognized that two very different types of wastewaters could arise in retorting operations - retort water and gas condensates. Retort waters contain significant quantities of both organic and inorganic contaminants. Inorganic salts can be separated in membrane processes and it appeared possible that if reverse osmosis were used, then the organics might be removed simultaneously. As this simultaneous removal would be of considerable advantage, a separate program investigating the application of reverse osmosis to oil shale wastewater treatment was initiated. At the time of writing the reverse osmosis study had demonstrated that a special organics removal step will not be required for some gas condensates, and that up to 80% of the organics can be removed from some retort waters by reverse osmosis. The reverse osmosis study is the subject of a separate report (Contract DE AC20-79LC10089, DOE, Laramie).

Details on the wastewater streams and some background water management schemes are given in section 3. Also in section 3 is a discussion on previous biological treatment experiments. The results of our biological treatment experiments, which constitute the major part of this report, will be found in section 4. In the final sections 5 and 6 the treatment designs and costs are given along with the results of brief experiments on non-biological treatments.

2. CONCLUSIONS AND RECOMMENDATIONS

2.1 Conclusions

BOD (initially 4,000 mg/l) can be 90% removed from the undiluted retort water which was tested. The preferred technique is oxygen activated sludge.

Fifty percent of the COD (initially 10,000 mg/l) is biorefractory. COD was not removed in excess of BOD by the activated sludge tests.

Powdered activated carbon added to an air activated sludge system does cause added removal of COD. The cheapest satisfactory sequence was to precede the PAC-AS system by a rotating biological contactor (RBC). However, the carbon is expensive.

Solvent extraction and resin adsorption were not useful as follow-on treatments to biological treatment. Activated carbon is useful but the COD load is high and carbon will be expensive.

Reverse osmosis is the preferred alternative treatment and a separate study is being made.

2.2 Recommendations

If biological treatment is to be considered, powdered activated carbon should be used and an investigation on the economics and practicality of reducing the carbon requirement or of recovery is needed.

Reverse osmosis should be field tested; this has been started.

The economics and practicality of raising dirty steam from untreated retort water should be examined.

As another alternative the economics of a low pressure oxidation by oxygen may be considered. If the economics are favorable a test will be needed.

3. BACKGROUND TO THE WASTEWATER AND ITS BIOLOGICAL TREATMENT

3.1 Wastewaters and Their Treatment in In-Situ Oil Shale Retorting

3.1.1 Wastewater Quality and Quantity

Determination of the quantity of wastewater to be treated does not pose undue difficulties for the present study. Firstly, a good approximation of the flow rates of the various wastewater streams can be determined by material balance, and this has been done for the several retorting processes[17]. Secondly, the quantity of water does not significantly affect the performance of treatment processes. While the quantity does affect the cost of treatment, the cost-flow rate dependence is known and is normally readily presentable either analytically or graphically.

Establishing a basis for wastewater quality poses more difficulty, and is of considerable importance when predicting process performance. In fact it is probably fair to state that many of the conflicting experimental findings that have been reported for treatment processes may be attributed to differences in the quality of the waters used for testing. Differences in quality occur, as can be expected, in wastewaters generated from different retorting processes. However, significant quality changes occur within a given process due to changes in raw shale grade, changes in operating conditions, and in non-steady state processes (in-situ retorting) changes in quality occur with time. Characterization problems are compounded by several factors. Firstly, most oil shale processes are in a state of development so that water samples obtained from any given process are not representative of that process as it might be operated commercially. Secondly, until recently, sampling procedures had been haphazard with very different wastewaters being mixed to form composite samples. These composites have little value as the different wastewaters arising in a process should, in a commercial scale operation, be treated separately. Finally, analysis of the very large number of compounds present in oil shale waters is not straightforward. "Standard methods" procedures may give erroneous results due to interfering substances, and results reported by different laboratories for identical waters frequently show discrepancies[36].

For these reasons water quality will be discussed here in general terms of concentration ranges for classes of pollutants rather than attempting to present absolute concentrations for specific compounds. This approach is adequate for the selection and design of wastewater treatment processes. In cases where specific compounds do have an important effect, these will be discussed. The categories into which the pollutants are grouped were selected - essentially on the basis of the classes of wastewater treatment processes - as follows:

(a) grease and oil
(b) suspended solids
(c) ammonia and the acid gases (CO_2, H_2S)
(d) inorganics (excluding NH_3 and carbonate species)
(e) organics, and
(f) trace metals

The three major "waste"-water streams requiring treatment at an oil shale plant are excess mine drainage water, retort water, and gas condensate.

3.1.2 Mine Drainage Water and Its Treatment for Discharge

Mine drainage water is the ground water that has to be pumped down to facilitate shale mining or in-situ retorting. The quantity of mine drainage water to be handled is extremely site-dependent and cannot be estimated by material balance. For instance in the Piceance Creek Basin significant groundwater can be expected to be produced near the center of the basin, while developments on the South and near the rim can expect little or no groundwater.

Both sites C-a and C-b, situated near the center of the Piceance Creek Basin, are being developed for modified-in-situ (MIS) retorting. Values for anticipated ground water flows obtained from the developers range from 4,000 to 11,250 gpm for a 57,000 bbls/day production of crude shale oil. While this range will be adopted here for the treatment designs representative of in-situ retorting in the Piceance Creek Basin it is emphasized that the reported values are estimated and that very different flows may be experienced in practice. Further, the flow rates will most certainly vary during the lifetime of the plant.

The mine drainage water, even at the lowest flow rate of 2.4 bbl water/bbl oil, represents the largest water stream in the plant. While some of this water will be used as source water makeup to the plant, there will normally be excess mine drainage water requiring disposal. A method of utilizing this excess water currently being advocated by one of the developers is to slurry spent shale from surface retorting operations, and use the slurry for backfilling the in-situ retorts. This procedure will, if successful, not only seal the in-situ retort and so prevent long-term groundwater contamination, but also serve as a disposal method for spent shale and provide a means for on-site consumption of excess mine drainage water. In fact, it has been estimated that slurry backfill operations will require more than 3 bbl water/bbl in-situ oil produced. It is not clear that sufficient water will be available over the lifetime of the plant.

For the purposes of this report it will be assumed that slurry backfill will not be used. Even if sufficient water is available, it seems that the excess mine drainage water is too valuable a resource in the water short Midwest for it to be cemented up in the retorts. For the same reason, reinjection is not advocated as a disposal means. Excess mine drainage water will therefore be treated to relevant permit levels for river discharge.

It has generally been assumed that the quality of the mine drainage water will closely resemble the water in the aquifer that is drawn down (Ref. 19 (Vol. 3) and Ref. 20). This can be expected to be true so long as the groundwater does not contact or is not stored in contact with freshly rubblized raw shale. If the water does contact freshly exposed shale, contaminants, particularly organic acid salts, may be leached out. The extent of the leaching may be dependent on the water volume, contact time with the raw shale, suspended shale solids in the water and other factors. Because sufficient data is not available at this time, we have to assume that the mine drainage water is characterized by the aquifer water. Information on this important point is needed.

Water quality data for the aquifers in the Piceance Creek Basin have been published by the U.S.G.S.[21], and further data is available[22]. A summary taken from Reference 17 is shown here in Table 3.1. The main constituent is sodium bicarbonate which is the major component of the total dissolved solids (TDS). Some reduction in TDS will be required prior to river discharge, and this can be readily achieved by, for example, ion exchange. As can be seen from Table 3.2, however, it is the ammonia, boron, fluoride and phenol that are of most concern, and these components are not as easily removed to the low values specified in permits.

Specific ion exchange/adsorption resins are available for each of the above substances and would be feasible for treatment of the mine drainage water. However this approach is expensive and a less specific treatment

TABLE 3.1

WATER QUALITY DATA FOR OIL SHALE AQUIFER IN PICEANCE CREEK BASIN

CONSTITUENT	*Concentration (mg/l unless noted)*			
	UPPER MINE AQUIFER		*LOWER MINE AQUIFER* (a)	*VALUES ADOPTED FOR STUDY*
	Range (a)	*Mean*(b)		
BICARBONATE	350-2100	482	265-4300	750
BORON	<0.16-11	0.3	.05-12	2-4
CALCIUM	5.4-52	35	4-28	50
CARBONATE	0-53	0.9	0-360	50
CHLORIDE	4.1-151	12	1-700	20
FLUORIDE	3.1-19	0.4	6.5-45	15
MAGNESIUM	4.2-54	52	1.9-29	60
SILICA	10-19	26	2-19	15
SODIUM	200-780	212	143-2320	300
SULFATE	<5-370	325	<4-350	350
TDS	750-1800	905	356-5747	1350
pH (units)	8.3-8.9	6.8	8.3-9.3	~8.5
PHENOL, μg/l	<1-174	2.5		2.5
AMMONIA	<1-1.8	1.2	17	1.2

(a) Data from range published in Ref. 21, unless otherwise noted.
(b) Data from mean values published in Ref. 22, unless otherwise noted.

TABLE 3.2

SUGGESTED DISCHARGE QUALITY PARAMETERS FOR EXCESS MINE DRAINAGE WATER

MORE RESTRICTIVE PARAMETERS	LEVEL	REASON
Total suspended solids (mg/l)	30	Current permits.
Total Dissolved Solids		
(ton/day)	1	Exception to Colorado River Salinity Standards.
(mg/l)	500	Colorado River Salinity Standard at Hoover Dam.
Total Fluoride (mg/l)	2	Drinking water.
Total Boron (mg/l)	.75	Agricultural use.
pH	6-9	Current permits.
Ammonia-N	.2 mg/l or .2 g/m^3 of river flow	Cold Water Fishery Standards.
Phenolic Compounds	.001 mg/l or 1 mg/m^3 of river flow	Cold Water Fishery Standards.

procedure is desirable. Reverse osmosis or electrodialysis are candidate processes which have been demonstrated to be commercially viable on waters as saline or more saline than the mine drainage waters. Electrodialysis will only separate those molecules which are in ionic form in solution. Boron, for example, requires that the solution pH be about 8.5 to 9 to become ionic. In general electrodialysis also does not have a capability for separating soluble organic molecules. Reverse osmosis, on the other hand, has a moderate capability for separating soluble organic molecules, but a very poor capability for separating boron from acidic waters. It is only at a quite high pH (∿9.5-10) that a 75% rejection of boron is attained. Phenol rejection is significant only at high pH as well. Fluoride rejection is typically about 90%. Both of the processes require a moderate to good level of prefiltration to remove suspended solids which will be contained in the mine water. The mine water is alkaline and electrodialysis would require pretreatment with sulfuric acid to prevent scaling on the membranes. Acid addition or chelating agents may also be required for the reverse osmosis system to prevent precipitation of salts. We emphasize that both of the systems would provide a product with a lower total dissolved solids than required for discharge. As a rule, reverse osmosis would give the lowest TDS product with a typical value for the mine water considered of from 100-200 mg/l, while the electrodialysis product might range from 200-400 mg/l.

We have made study cost estimates for both membrane processes without disposal of the concentrated solutions and without boron and phenol removal[25]. The estimates, based on a 15% annual amortization of capital are shown in Table 3.3. The costs for the two processes are similar although electrodialysis would become less attractive at the higher end of the TDS range shown in Table 3.1. Reverse osmosis costs are not significantly dependent on influent TDS and have the added advantage that the system can be operated to remove boron, phenol and ammonia.

A cost not so far discussed is that for the concentrate disposal. If we assume an 85% recovery and 90% separation of the dissolved solids, then the wastestream has about 6 times the concentration of the mine water and about one-seventh its volume. The cost of disposal of this stream, ranging from about 0.3 to 2.0 million gallons per day, can be a major part of the treatment cost. Concentrate disposal can be either by evaporation in ponds or preferably in a vapor compression (RCC) evaporator. If a "thermal sludge"

TABLE 3.3

COST(a) (IN $/1,000 gal) OF MINE WATER TREATMENT BY MEMBRANE PROCESSES

Flow Rate (gpm)	Reverse Osmosis	Electrodialysis(b)	
	Initial TDS (mg/l)		
	900 - 3,000	900	1,350
2,000	0.94	0.75	0.88
9,000	0.67	0.66	0.74

(a) Appropriate costing for comparative purposes.

(b) D.C. electricity generated on site available at 3¢/kwh.

or similar type unit is used on site for steam raising then it may prove possible to blend the concentrate with the feed to this unit. The concentrate will contain sodium bicarbonate, possibly near its solubility limit. It may prove possible to recover this material for sale, particularly as both CO_2 and excess heat are readily available at an oil shale plant.

A summary of the various processes relevant to the treatment of excess mine drainage water to discharge quality is given in Table 3.4.

3.1.3 Gas Condensate

This wastewater stream arises from the treatment of the gases evolved during the retorting of the oil shale. The retort gas contains hydrogen sulfide and ammonia which must be removed before it can be used as a fuel. Hydrogen sulfide removal will probably be in a Stretford unit which requires that the gas be cooled to $\sim 100^\circ F$. The gas cooling, which can be effected in the scrubber tower for ammonia removal, results in the production of an intermediate quality water stream by condensation.

The quantity of gas condensate produced can be estimated from the retort gas rate. A typical value for the dry (MIS) retort gas rate, estimated from Ref.31, is in the region of seven times the mass of oil produced, or about 29,000 ft^3 dry gas per bbl oil produced. For a plant producing 57,000 bbl oil per day, the dry gas flow rate is about 1.2×10^6 cfm, or 5.6×10^6 lb/hr. The water vapor gas can be estimated assuming the gas to be saturated when it leaves the retort:

The vapor pressure of water in the range $100^\circ F$ - $200^\circ F$ is given by[32]

$$\ln p = a - b/(t^\circ F + c) \qquad (1)$$

TABLE 3.4

PROCESSES FOR TREATING MINE DRAINAGE WATERS TO DISCHARGE QUALITY

Constituent	Treatment	Remarks
TDS (Discharge limit 500 mg/l)	Ion Exchange (IX)	A weak acid cation bed, degasser, strong base anion bed system is efficient and economical. Only part of stream need be treated. Boron, fluoride, phenol and ammonia would not be adequately removed.
	Reverse Osmosis (RO)	High pH is required for phenol and boron removal.
	Electrodialysis (ED)	Not suitable for boron and phenol removal.
Ammonia (Discharge limit 0.2 mg/l)	Clinoptilolite IX[26]	Low concentrations probably achievable. Suitable as polishing step only.
	Stripping[13]	Aeration in a holding/equilization pond prior to river discharge is advisable, but not efficient for achieving low NH3 values.
	Reverse Osmosis	High removal efficiencies possible.
Boron (Discharge limit 0.75 mg/l)	Specific IX	Rohm and Haas Amberlite IRA 943 is reportedly effective. Recommended only as a polishing step if necessary.[28]
	Reverse Osmosis	Acceptable rejections at high pH only.

(Continued)

TABLE 3.4 (continued)

PROCESSES FOR TREATING MINE DRAINAGE WATERS TO DISCHARGE QUALITY

Constituent	Treatment	Remarks
Fluoride (Discharge limit 2.0 mg/l)	Chemical Precipitation (Lime)	Efficient and economical for high concentrations. Reduction below 8 mg/l requires use of phosphoric acid and calcium fluoride.
	Adsorption	Activated alumina and bone char have been used. Cost of regeneration is excessive, both for chemicals and waste disposal. Recommended only as a polishing step.
	Reverse Osmosis	90% fluoride rejection typical in a single pass.
Phenol (Discharge limit 0.001 mg/l)	Resin Adsorption	Rohm and Haas Amberlite XAD-4 Polymeric resin is capable of quantitatively removing low concentrations of phenol.[29]
	Reverse Osmosis	Effective at high pH only. Suitable membranes are available.[30]

where p = vapor pressure of water at $t^{\circ}F$, psia

a = 14.466

b = 6996.6, and

c = 382.33

If P is the gas total pressure, psia, then the volume fraction water vapor in the wet gas x, at $t^{\circ}F$, is

$$x = (p/P) = \exp a - b/(t^{\circ}F + c) /P \tag{2}$$

or on a dry basis

$$X = \frac{x}{1-x} \text{ vol water vapor/vol dry gas} \tag{3}$$

It is convenient to calculate the water rate on a mass basis:

$$X' = (18\ X)\ (MW) \text{ lb water vapor/lb dry gas} \tag{4}$$

where MW = molecular weight of the dry retort gas.

The retort gas will probably leave the retort at about 140°F and, in Colorado, be at a pressure of ∿12.6 psia. If it is cooled to 100°F, the amount of water vapor condensed out can be calculated to be, for a dry gas molecular weight of 31.6

$$\text{gas condensate rate} = X'_{140^{\circ}F} - X'_{100^{\circ}F}$$

$$= 0.172 - 0.047$$

$$= 0.125 \text{ lb } H_2O\text{/lb dry gas}$$

or 0.67×10^6 lb H_2O/hr (1,350 gpm) for an oil production rate of 57,000 bbl/day

In addition to the water condensed, there is a recycle water stream required for washing the gas stream free of ammonia. It is probable that in a commercial operation the gas cooling and ammonia scrubbing will occur in a single unit[18] and so the wash water will be mixed with the gas condensate produced. Using van Krevelen vapor liquid data for the NH_3 - H_2S - CO_2 - H_2O

system[33], we have estimated that a wash water flow rate of 720 gpm is required to achieve an essentially ammonia free gas. The total gas condensate stream requiring treatment is thus about 2,000 - 2,100 gpm of which the net production rate is 1,350 gpm, the remainder being recycled. This net production rate is equivalent to about 0.8 bbl water/bbl oil produced. It is larger than would occur in surface retorting and reflects the relatively large steam feed of a barrel of steam per barrel of oil produced used in the MIS retorting scheme considered here[31].

The composition of the gas condensate has not been well established, as until recently, gas condensate samples from (simulated) MIS operations had not been obtained. The ammonia and acid gas composition can however be estimated from the gas composition using material balance and vapor-liquid calculations. The concentrations of the relevant constituents in a MIS retort gas from a complete composition published in Reference 18, are shown in Table 3.5, and a method of calculating liquid compositions in equilibrium with ammonia/acid gases in the vapor phase is described in detail in reference 34. The calculated gas composition based on a counter current scrubbing tower using the liquid rates given above are given in Table 3.6.

Inorganics are not expected to be significant in the gas condensate although anions such as Cl and SO_4 may be present. Volatile organics, on the other hand, are present in the retort gas, and some will be knocked out in the ammonia scrubber and be removed with the gas condensate.

A small quantity of gas condensate sample was received for a parallel study and a preliminary analysis has been made.[35] The results are included in Table 3.6. While the ratio of CO_2 to ammonia in the estimated and measured columns of the table are essentially equal, the measured quantities are less than half of the estimated values. It is believed that this is because the gas condensate sample received was not recovered in a gas scrubbing operation, i.e., all the ammonia (and equivalent CO_2) was not removed from the gas. It is therefore suggested that the estimated NH_3 and CO_2 values are more representative of a commercial operation. For the same reason the organics in the sample gas condensate may be low, although the discrepancy here should not be as large. Concentrations selected for use in this study are included in Table 3.6; it is understood that actual concentrations may differ significantly from the values shown.

TABLE 3.5

AMMONIA AND ACID GASES IN MIS RETROT GAS*

CONSTITUENT	MASS %	VOLUME %	
	WET	WET	DRY
NH_3	0.37	0.62	0.80
CO_2	38.15	24.70	32.00
H_2S	0.18	0.15	0.20
H_2O	14.41	22.80	—
Molecular Weight	28.5		31.6

---

* Full composition in reference[18]

TABLE 3.6

COMPOSITION OF GAS CONDENSATE (mg/l unless noted)

Constituent	Estimated (a)	Measured (b)	Values adopted for this study
NH_3	21,330	9,600 (c)	20,000
CO_2	41,800	18,900	40,000
H_2S	118	Not determined	100
TDS	Low	300 (d)	Low
Hardness	-	< 2	Low
COD	Moderately high	3,800	2,000
pH (units)	-	8.6	8.6

(a) Calculated from gas composition and vapor-liquid equilibrium data. Values taken from reference[18].

(b) Values from preliminary determinations on gas condensate sample received from LETC[35].

(c) Calculated from measured alkalinity.

(d) Sample dried at 180°C so value should not include significant quantities of NH_4HCO_3, $(NH_4)_2CO_3$, or organics[36].

The degree of treatment of the gas condensate stream will depend on its end use. It will most certainly be used within the plant and will not be discharged. This will be true even if excess mine drainage water is available, as it is more economical to treat the cleaner mine water to discharge quality. It will generally be necessary to remove ammonia and the acid gases as well as the organics. The inorganic (TDS) concentration is low and will not be a problem for most reuse options. Of all the heavy metals and trace elements occurring in oil shale, mercury and cadmium are probably the only two that may be transferred to the gas condensate with any significance during the course of the burn[37]. However the data presented suggest that concentrations of these elements in the gas condensate are not likely to be a problem excepting, possibly, in the condensate collected towards the end of a burn.

Ammonia and the acid gases can be removed by stripping, with steam stripping being the recommended procedure for industrial scale operations. Ammonia fixation is not likely to be a problem due to the low concentration of inorganic salts (apart from ammonia and carbonate species). Liming and scaling are therefore not likely to be of concern. The stripped ammonia, amounting to some 240 ton/day for the flows and concentrations given above, may be separated from the acid gases and recovered as a marketable anhydrous product. At this production rate, and assuming a steam cost of $\$2.50/10^6$ Btu and a product value of $120 ton/day, the process may even be profitable. Although energy costs are rising, and the ammonia market is currently depressed, ammonia recovery is still recommended as a means of offsetting the treatment costs.

An Oxy gas condensate sample, having the analysis shown on Table 3.7, was stripped in our laboratory. The batch was stripped by boiling at atmospheric pressure for about 90 minutes. Both ammonia and organics (as measured by COD) were removed at approximately equal rates. The organics removal was not expected, but is not surprising in as much as this wastewater is derived from the retort gases and is in the vapor phase at temperatures down to about $150^{\circ}F$, see Figure 3-1. In fact if stripping were carried out at slightly elevated pressure and temperature as would occur in an industrial steam stripper, then it can be expected that close to 100% organics removal will be obtained.

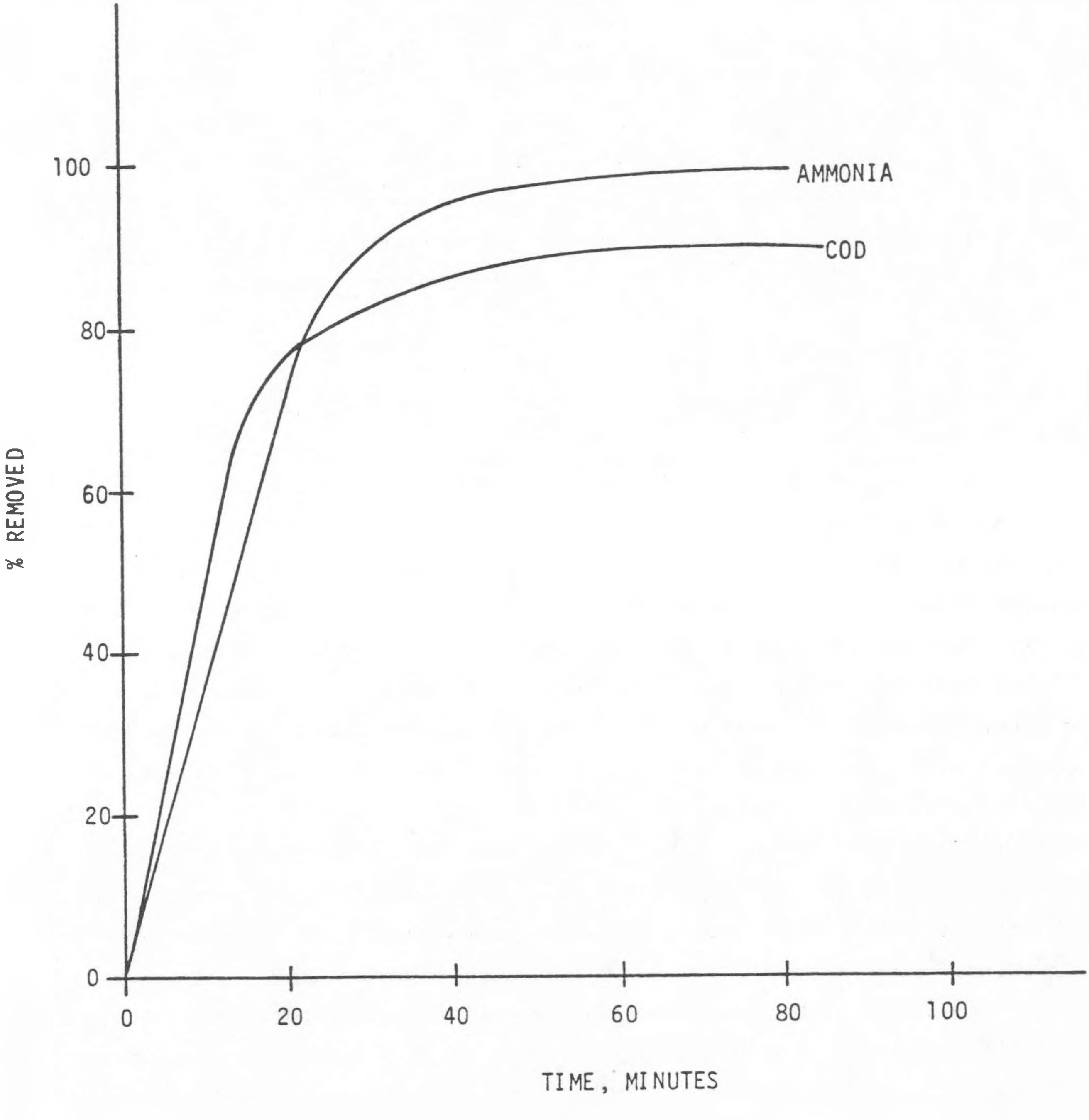


Figure 3-1. Ammonia and organics (COD) stripping from Oxy gas condensate. Batch stripping at 100°C.

TABLE 3.7

ANALYSIS OF FILTERED AND STRIPPED Oxy GAS CONDENSATE SAMPLE

Constituent	Filtered Gas Condensate mg/l	Stripped Gas Condensate mg/l
Ammonia (N)	7,600	70
Alkalinity	24,000	385
Hardness	< 2	
TDS (105°C)	270	400
COD	2,300	450
Feed pH	8.6	8.6
Product pH	8.6	8.8

As seen from Table 3.7, the stripped water is of suitable quality for plant reuse. Further treatment through RO membranes produces a high quality water suitable for river discharge. Organics removal by subsequent RO ranged from 75 to 95%, apparently increasing with increasing feed pH.

If other gas condensates are as easily stripped as this sample control of organics may not present a problem. Alternative treatments, all of which are more expensive, are biological oxidation, biological oxidation with powdered activated carbon, resin adsorption, reverse osmosis and carbon adsorption.

Oil and grease will be present as well, and will have to be separated. Oil water separation is, judging from visual inspection of oil shale wastewaters, not expected to be a problem with the gas condensate stream. Significant separation difficulties are anticipated for the retort waters.

3.1.4 Retort Water

Of the three water streams considered the retort water is the most dirty and can be expected to be the most difficult to treat. Retort waters arise mainly in in-situ retorting where water condensation from the gas phase occurs in the cooler regions of the retort, and mixed with the oil, percolates down through the rubblized unburned shale. In surface operations the retort temperature can be controlled, and will probably be adjusted to prevent formation of a significant retort water stream[18].

The quantity of retort water produced can be estimated from the total hydrogen balance for the retort. The water leaving the retort is derived from moisture on the shale, combined water, hydrogen combustion and water entering the retort as steam and/or in the air. The sources and distribution of the water have been determined from the material balance for a MIS process given in Ref. 18, and are summarized in Table 3.8. The Table shows that about 1.25 bbl wastewater are produced per bbl oil, and of this 0.44 bbl/bbl is as retort water. This amounts to about 750 gpm for the 57,000 bbl per day plant under consideration. This figure assumes negligible ground water infiltration. In practice, some infiltration can be expected; how much will depend on retorting procedures and will also be site and time dependent. We will use an upper limit of retort water production of 1 bbl H_2O/bbl oil on the grounds that water production should, desirably, not overwhelm oil production. The upper limit tolerable in practice will be imposed by production economics, and will depend on the cost of retort water treatment and its reuse possibilities.

Retort water samples from true in situ, modified in situ, and simulated modified in situ have been available for some time, and have been subject to detailed analyses. Reported concentrations show very wide ranges as can be seen from Table 3.9, and reflect the different retorting procedures and degree of ground water dilution. Additional analyses are given on Tables 4.1 and 4.2. Retort waters are obviously very dirty, containing ammonia and acid gases, inorganic salts, and organics. While the ammonia concentration may be lower than in the gas condensate, it will be more difficult to separate due to fixation by the strong anions present. Also ammonia rates are lower, making recovery less economical, although it should prove feasible to combine the stripped gas streams from the gas condensate and retort water strippers for recovery.

Inorganics are considerably higher than in the gas condensate, although there should not be a problem for most reuse options. They may however interfere with other treatment processes (toxicity to biological oxidation, ammonia fixing and scaling in the stripper) and require removal for these reasons.

A comparison of the three water streams, their expected flow rates and

TABLE 3.8

WATER BALANCE AROUND MIS RETORT(a)

WATER IN AND WATER FORMED	bbl H_2O/bbl OIL	% OF TOTAL
Free water on shale (1% of shale)	0.16	10.2
Combined water in shale (1% of shale)	0.16	10.2
Water produced by combustion (by hydrogen balance)(b)	0.19	12.1
Water in combustion air (1% of air, by mass)	0.04	2.6
Steam(c)	1.02	64.9
TOTAL	1.57	100.0

WATER OUT		
In "dry" product oil (1.5% by mass)	0.01	0.6
As gas condensate	0.81	51.6
In treated retort gas (Sat'd at 100°F)	0.31	19.8
As retort water (by difference(d)	0.44	28.0
TOTAL	1.57	100.0

(a) Assuming negligible seepage of ground water.
(b) Balance in reference[18].
(c) According to retorting scheme in reference[31].
(d) Assuming water remaining in retort to be insignificant.

TABLE 3.9

RETORT WATER COMPOSITION (mg/l unless noted)

Constituent	Water Source		
	Omega 9 (a) True In-Situ	S-47 (b) Simulated MIS	ES-79-071(c) Paraho
Ammonia (total)	7,300	6,400	42,000
Chloride	824	7,800	47,000
Sulfate	2,000	1,700	15,400
Sodium	4,300	76	360
Calcium	12	8	830
Alkalinity ($CaCO_3$)	16,200	20,750	30,000
TDS	14,200	7,700	142,000
BOD	(740)	(~50% of COD)	-
COD	8,100	15,000	190,000
pH (units)	8.7	8.7	8.6

(a) Data from reference[36]. This retort water is believed to be considerably diluted by ground water infiltration.

(b) Data from LETC and WPA analyses. No infiltration possible as it results from a simulated in-situ retort.

(c) Data from LETC and WPA analyses. This retort water is extremely dirty and is a composite of several waste streams. Infiltration not possible in this surface operation.

qualities, and possible treatment processes is given in Table 3.10. Retort waters offer the most difficult water treatment problem and it is essential that adequate water management be exercised to reduce and contain this stream. The treatment of retort water is discussed in the rest of this report.

3.1.5 Summary of Some Overall Wastewater Management Schemes

Two overall wastewater management schemes are shown in Figures 3-2 and 3-3. In the scheme of Figure 3-2 mine drainage water is the only water source for the plant. Most of the mine water is treated for discharge and the rest is treated for boiler feed. Gas condensate is stripped and is then assumed to be usable in the cooling tower with the surplus treated for boiler feed. Retort water is stripped and treated to boiler feed water quality using treatments discussed in the rest of this report.

Unlike many of the surface retorts, the MIS retorting procedure proposed specifies a steam feed rate to the underground retort of about 1.4 times the product oil rate on a mass basis. This steam is consumed in the retort in the sense that it is recovered as a dirty process condensate that is not at all suitable for recycle back to the boiler system. It may be possible to raise at least part of this steam directly from the retort water without treatment. The raising of dirty steam from dirty water is discussed in section 6. The management scheme incorporating this steam raising is shown on Figure 3-3.

3.2 Review of Previous Studies on Biotreatment of Retort Waters

Biological treatment is widely used as a cost-effective means of removing biodegradable dissolved organics from municipal and industrial wastewaters. It has been stated that the majority of organics present in retort water are carboxylic acids and neutral compounds and are biodegradable[56,62]. Preliminary studies with actual retort waters have indicated that biological treatment is technically feasible if proper pretreatment is provided to remove toxic substances present. These preliminary studies will be summarized in the following paragraphs.

The two basic types of biological treatment are aerobic and anaerobic processes, and their general characteristics may be compared as shown in Table 3.11. Anaerobic processes have the advantages of requiring no oxygenation equipment, producing usable methane, and smaller quantity of biological sludge for disposal. On the other hand, aerobic processes are faster and

TABLE 3.10

MAJOR WATER STREAMS REQUIRING TREATMENT AT A COMMERCIAL SCALE MIS RETORTING OPERATION

	Mine Drainage Water (Table 3.1)	Gas Condensate (Table 3.6)	Retort Water (Table 3.8)
Flow rate bbl/bbl oil gpm	2.4-6.8 4,000-11,250	0.8 1,350	0.44-1.0 750- 1,660
Ammonia and acid gases	Low, but NH3 in discharge must be less than 0.2 mg/l.	High, but stripping easy and not costly.	Moderately high, Stripping complex due to NH3 fixing.
Inorganic Salts	Moderately high; removal to discharge quality straight forward. B, F, and phenols can be a problem.	Low, not a problem for reuse.	High, removal complicated due to extreme low quality of the water.
Organics	Low.	Moderate. Removal by biox, adsorption or wet air oxidation.	High. Toxicity and interference may complicate removal.
Oil and Grease	Low	Low	Emulsion problems expected.
Trace Elements	Not expected to be a problem, but more information required.		

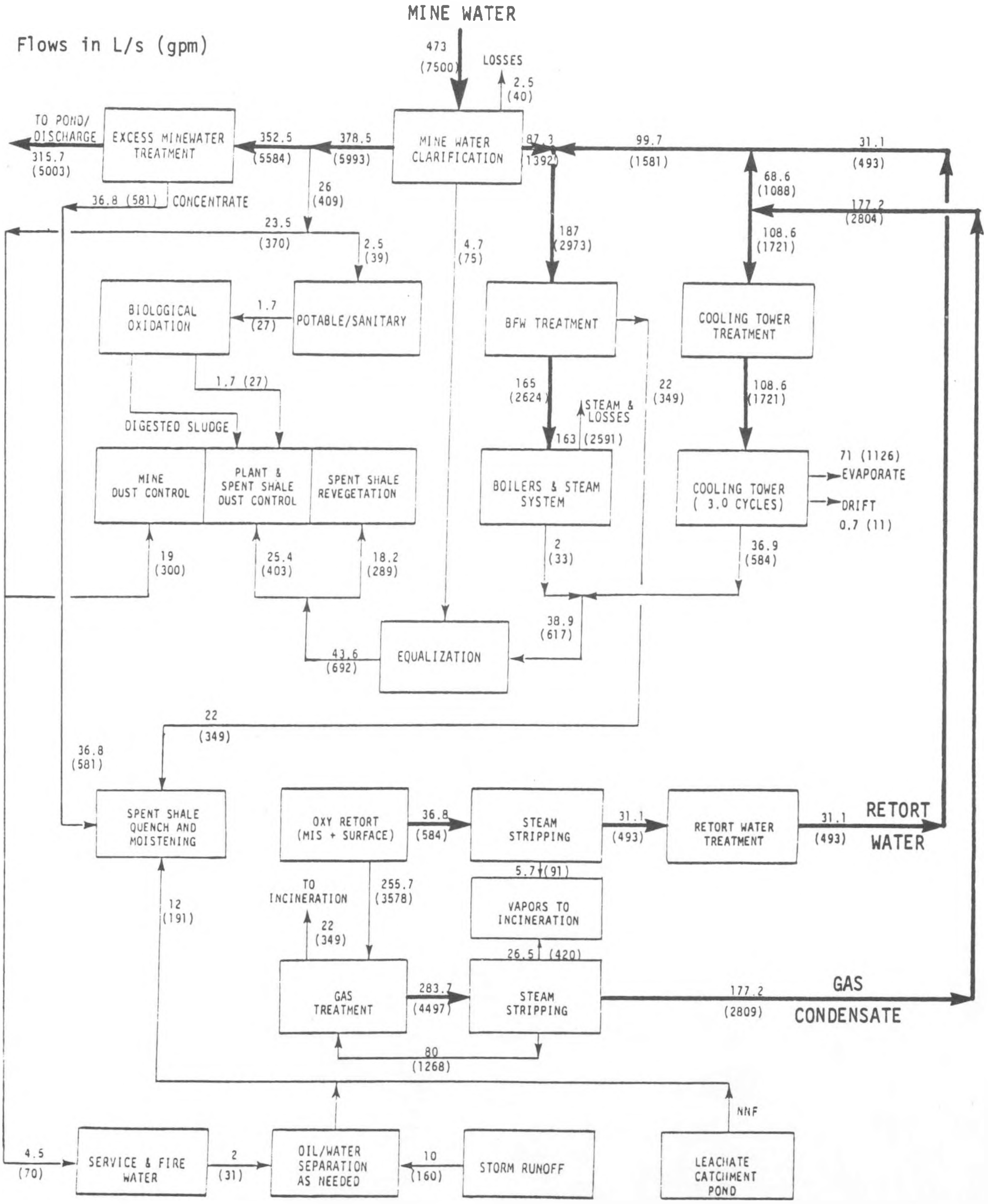


Figure 3-2. Major water streams for Oxy shale oil plant producing 100,000 BPSD crude shale oil. Full retort water treatment.

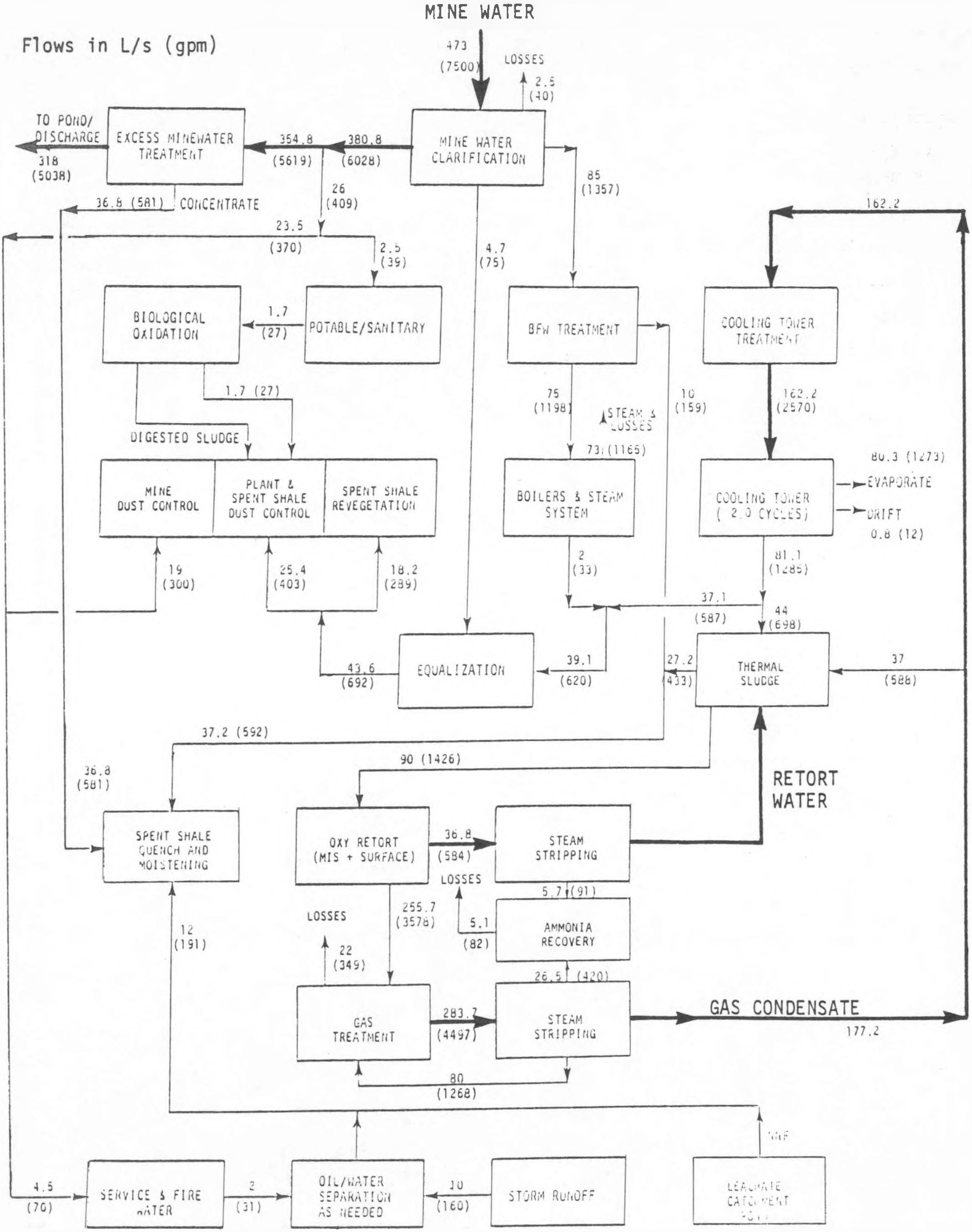


Figure 3-3. Production of dirty steam from retort water in 100,000 BPSD oxy shale oil plant.

TABLE 3.11

CHARACTERISTICS OF AEROBIC AND ANAEROBIC PROCESSES

	Aerobic Process	Anaerobic Process
Dissolved Oxygen	Present	Absent
Transfer of Oxygen to Aqueous Phase	Required	Not Required
Usable End Product	None	Methane
Reaction Rate	Fast	Slow
Biological Sludge Production	High	Low
Diversity of Organisms	High	Low
Susceptibility to Toxic Substances	Low	High

relatively less susceptible to toxicity problems.

3.2.1 Anaerobic Treatment

(a) U C Berkeley Study[58,61]

Anaerobic biological treatment is mostly used for the digestion of municipal sewage sludge and is not used very much on industrial wastes. Recent studies[58,61] on the anaerobic treatment of oil shale retort water was conducted at University of California at Berkeley (U C Berkeley), and their findings are as follows:

1) The retort water studied had to be pretreated to remove toxic constituents (ammonia and sulfide) and to add deficient nutrients (calcium, magnesium and phosphorus) before it could be successfully treated with the anaaerobic fermentation process. Pretreatment included pH adjustment, air stripping and skimming, and nutrients addition.

2) A digested sludge from a conventional municipal sewage treatment plant was successfully acclimated to the retort water studied.

3) A major fraction of the organics in the retort water studied was stablized by conversion to CH_4 and CO_2 using the anaerobic fermentation process. BOD_5 and COD removal efficiences were 89-90% and 65-70%, respectively.

4) The effluent from anerobic fermentation of the retort water studied (BOD_5:530 - 580 mg/l) might be suitable for treatment by conventional aerobic processes.

5) The growth of the methane formers, which stablize the organics, is nutrient limited in the retort water studied.

6) The pretreatment of the retort water studied removed 49% of the BOD_5. This was probably due to the reduction in solubility of high molecular weight fatty acids. At neutral pHs' they precipitate out of the solution and do not exert a BOD.

The long hydraulic residence times required for anaerobic treatment, about 50 days in the study, means excessively large holding tanks and high capital costs. Anaerobic treatment consequently does not appear to be economical. Cell recycle was mentioned as a possible modification to maintain a long cell residence time and allow a reduction in hydraulic residence time. However, the feasibility of such a modification remains to be determined[61].

(b) BPNL Study

Battelle Pacific Northwest Laboratory (BPNL) recently also studied the anaerobic treatment of retort waters from a Utah horizontal modified in situ operation, Lawrence Livermore Laboratory's six ton simulated in situ retort, and from Paraho's surface retort facility[59]. Bench-scale units were operated as conventional, completely mixed, mesophilic (30-37°C) digesters with solids residence times ranging from 15 to 50 days. The major findings of this BPNL study are as follows:

1) The pretreatment methods studied were steam stripping to remove ammonia, precipitation with $FeCl_3$ to remove arsenic and other heavy metals, and the addition of powdered activated carbon to adsorb toxic organics.

2) In general only limited success was achieved for the anaerobic treatment of these three retort waters.

3) The anaerobic treatment of the Utah in situ retort water was successful when the retort water was blended at a 1:4 ratio with primary sewage sludge, and dosed with 1500 mg/l powdered carbon. Continuous operation at a 1:4 feed ratio without carbon was not successful, nor was digestion with or without carbon at higher feed rates.

4) Satisfactory anaerobic treatment of undiluted Utah in situ retort water was not achieved even with pretreatment for ammonia and arsenic removal. An attempt to digest pretreated Paraho retort water was likewise unsuccessful.

5) Steady state anaerobic treatment of a steam-stripped Livermore retort water was accomplished when it was dosed with 2,000 mg/l carbon.

6) During the anaerobic process it appears that a majority of the gas production emanates from the degradation of volatile acids present in the retort water feed. The conversion of other organics does not appear significant.

7) Substances that may have been responsible for the poor performance of anaerobic treatment include sulfate, thiosulfate and sodium. Sulfate and thiosulfate accounted for about 2,500 mg/l sulfur in the retort water feed.

8) The pretreatment methods mentioned in 1) are probably not effective in substantially removing sulfate and thiosulfate. Significant fractions of these S-containing substances were likely converted to sulfides in the anaerobic reactors, leading to a potential sulfide toxicity problem.

9) The sodium concentration was about 5,000 mg/l, which is generally considered toxic in sewage sludge digesters.

3.2.2 Aerobic Treatment

(a) BPNL Study

BPNL also studied the aerobic treatment of retort water[45,60]. A simulated retort wastewater, composed of aliphatic acids (acetic and octanoic acids), acetamide, phenol, cresol, and ammonia in a slightly saline solution, was first used on a trickling filter and an activated sludge unit. These units operated quite effectively together in removing 95% TOC from the simulated retort water. However, TOC removal was consistently better across the activated sludge unit than across the trickling filter. The trickling filter performance generally varied between 10% and 50%.

Two actual retort waters were subsequently treated by activated sludge. One of the retort waters came from the 7 ton simulated in situ retort at the

Lawrence Livermore Laboratory and the other from an in situ test site near Vernal, Utah. The results of this bench-scale treatability study showed that although good biological growth and TOC removal occurred in diluted solutions during the initial acclimination period, an apparent toxicity problem developed as the percent of actual retort water was increased. Thiocyanate and arsenic were first suspected as the toxicants. Thiocyanate was ruled out since its concentrations were below the threshold value of 500 mg/l for activated sludge. Arsenic could be a toxicant since it exceeded the threshold value of 0.1 mg/l for activated sludge. The arsenic concentrations were 1.3 and 4.5 mg/l in the Livermore and Utah retort water.

The Utah retort water was then treated with iron and manganese hydroxide to remove arsenic down to 0.3 mg/l. However, acclimation of activated sludge with or without powdered activated carbon (PAC) addition, at a dosage of 100 mg/l, was not successful.

Successful activated sludge treatment of the Utah retort water was later achieved with proper pretreatments: steam stripping to remove ammonia from 2650 to < 15 mg/l, precipitation with iron and manganese hydroxide to remove arsenic down to < 0.1 mg/l, acclimation over a one month period, and controlling the pH in the neutral range. Two bench-scale activated sludge units were operated, one with PAC and the other without, and their treatment performance is summarized in Table 3.12.

TABLE 3.12

TREATMENT PERFORMANCE OF ACTIVATED SLUDGE PROCESS ON THE UTAH RETORT WATER

Parameter	PAC Sorption Only	With PAC Addition	Without PAC Addition
COD Removal (%)		72	63
TOC Removal (%)	6	58	45
Thiocyanate Removal (%)	0	>99	68
Sludge Growth (% per day)		10	7

The success of this run was attributed to the combined effects of arsenic removal, type of feed, long acclimation, and controlled pH.

Further studies indicated that PAC addition at 300 mg/l accomplished about the same removal of COD and TOC as 2,000 mg/l PAC. Results with a different batch of retort water from the same site in Utah indicated lower COD and TOC removal of about 64% and 50%, respectively, using 300 mg/l PAC addition. Additional studies also indicated that arsenic removal might not be necessary to effect good COD reductions.

4. EXPERIMENTAL INVESTIGATION OF BIOLOGICAL TREATMENT

The objectives of this experimental investigation were to:

(1) Determine the feasibility of treating retort water by biological processes including rotating biological contactors (RBC), air activated sludge (AAS), oxygen activated sludge (OAS), and activated sludge with powdered activated carbon (PAC-AS);

(2) Determine any pretreatment necessary to make biological treatment feasible;

(3) Determine key parameters which may be used for the preliminary design of biological treatment processes.

To achieve these objectives the following tasks were undertaken and will be discussed in details in the subsequent sections.

(1) Chemical characterization of the retort water;

(2) Selection and establishment of necessary pretreatment procedures;

(3) Treatability study on RBC;

(4) Treatability study on AAS and OAS;

(5) Treatability study on PAC-AS;

(6) Performance study on RBC followed with PAC-AS (RBC-PAC-AS).

4.1 The Retort Water

Forty-six 30-gallon barrels of a retort water were trucked to Northeastern University from Laramie Energy Technology Center (LETC) in October 1979. This water was from run 17 of the 150 ton simulated in situ retort and was designated as R-17 retort water. This R-17 retort water had reportedly been stored and filtered through 0.4 micron membrane filter at LETC. It was supposedly well mixed before it was placed in the barrels for delivery.

As we started characterizing the R-17 retort water, a significant barrel to barrel variation in chemical composition was found. This variation was quantified by taking samples from every barrel of filtered R-17 retort water for the determination of pH, NH_3-N, and TOC. The results are shown in Table 4.1. Although pH is essentially constant at 8.6, both NH_3-N and TOC vary significantly from barrel to barrel. Since NH_3-N would be adjusted by stripping prior to biotreatment, only the variation in TOC presented a potential problem for future experiments. The problem of organic variation

TABLE 4.1

CHEMICAL ANALYSES OF FILTERED R-17 RETORT WATER RECEIVED FOR TESTING[a]

Barrel	TOC mg/l	pH	NH_3-N mg/l
1	2600	8.6	3150
2	3400[b]	↓	3900
3	2350	↓	3800
4	2300	↓	3300
5	2100	↓	4950
6	2500	↓	3275
7	2700	↓	-
8	2350	↓	3450
9	2400	↓	3100
10	3000[b]	↓	3700
11	2300	↓	3600
12	2600	↓	3150
13	2500	↓	3200
14	2350	↓	3500
15	2450	↓	3000
16	3000[b]	↓	3050
17	2450	↓	3000
18	2200	↓	3400
19	2500[b]	↓	2900
20	2500[b]	↓	3400
21	2300	↓	3150
22	2200	↓	3250
23	2250	↓	2850
24	2500	↓	3050
25	2600	↓	3950
26	2750	↓	3500
27	3300[b]	↓	4000
28	3750	↓	3300
29	2600	8.6	3600
30	2400	↓	3150
31	1900[b]	↓	3000
32	2600	↓	3300
33	2800[b]	↓	3800
34	2850	↓	3450
35	2700[b]	↓	3000
36	3200[b]	↓	4450
37	2300	↓	2975
38	2450	↓	3300
39	3050	↓	3700
40	2400	↓	3475
41	2500	↓	3200
42	2550	↓	3300
43	3750	↓	3400
44	2450	↓	3350
45	2650	8.65	3100
46	3100[b]	8.6	3550
Range	1900 to 3750	8.6	2850 to 4950
Average	2670	8.6	3400
Median	2500		3300

---

a. This water was received in October 1979, and analyzed in November and December, 1979.

b. TOC determined with 100 fold/dilution. All other TOC with 50 fold/dilution.

later turned out to be a serious one as it was found extremely difficult to reach a steady state in the reactors of the activated sludge study. This will be further discussed in the sections on activated sludge.

However, on the basis of the comparison in Table 4.1 barrel number 6 was chosen as a "representative" barrel for more complete chemical characterization. The results are shown in Table 4.2. A complete titration curve is shown in Figure 4-1.

The R-17 retort water had a strong and distinct oily odor and dark brown color. Although this water was passed through a 0.4 micron filter at LETC before being dispatched for the purpose of reducing biological activity during transit and storage, when received, the water contained some suspended matter indicating either biological or chemical activity.

4.2 Pretreatment of Retort Water

Based on the chemical characteristics of the R-17 retort water, it was deemed necessary to provide certain pretreatment processes prior to the biobiological treatment. The necessary pretreatment included ammonia stripping and pH neutralization.

4.2.1 Ammonia Stripping

Stripping can be used to remove dissolved gases from a liquid and is probably the most economical means of ammonia removal. The most common method of ammonia stripping is to run the liquid down through a column counter current to a gas or vapor. The pH must be raised to 10 or higher in order to shift the NH_4^+-NH_3, equilibrium in favor of NH_3 which is easily stripped. Since the solubility is lowered with increased temperature the physical size of the stripping tower is smaller when higher temperatures are used.

The average concentration of ammonia in the R-17 retort water is 3,400 mg/l, well above the toxic threshold of 800-1,000 mg/l. In a small scale batch test the ammonia stripping process was found to be adequate in reducing the ammonia nitrogen concentration. This small scale testing using laboratory equipment led to the design and construction of a batch stripping apparatus capable of stripping 1 barrel of retort water (about 30 gallons) per run. The apparatus consisted of a 30 gallon stainless steel tank fitted with 2 Chromalox 240V, 5kW immersion heaters and air spargers. Air was supplied by a compressor. The entire apparatus was placed under a chemical

TABLE 4.2

CHEMICAL CHARACTERISTICS OF FILTERED R-17 RETORT WATER

(Barrel #6)

pH = 8.6

Alkalinity = 6,500 mg/l CaCo

Ammonia Nitrogen = 3,275 mg/l

TOC = 2,500 mg/l

COD = 10,840 mg/l

BOD_5 = 3,300 mg/l

BOD Rate Coefficient K (base e) = 0.207

K (base 10) = 0.09

BOD_L = 4,870 mg/l

Total Solids = 6,271 mg/l

Total Suspended Solids = 74 mg/l

Total Dissolved Solids = 6,197 mg/l

Total Fixed Solids = 1,106 mg/l

Fixed Suspended Solids = 16 mg/l

Total Volatile Solids = 5,165 mg/l

Volatile Suspended Solids = 59 mg/l

Oil & Grease = 50 to 270 mg/l

Arsenic = 0.875 mg/l

Cyanide = 20.8 mg/l

Sulfate = 1,715 mg/l

Sulfide = 222 mg/l

Volatile Acid = 500 mg/l as HAc

Metals:

Cadmium < 0.1 mg/l

Calcium = 6.2 mg/l

Chromium = 0.1 mg/l

Copper = 0.5 mg/l

Iron = 2.6 mg/l

Lead = 0.1 mg/l

Magnesium = 10.0 mg/l

Mercury = $1.8x10^{-3}$ mg/l

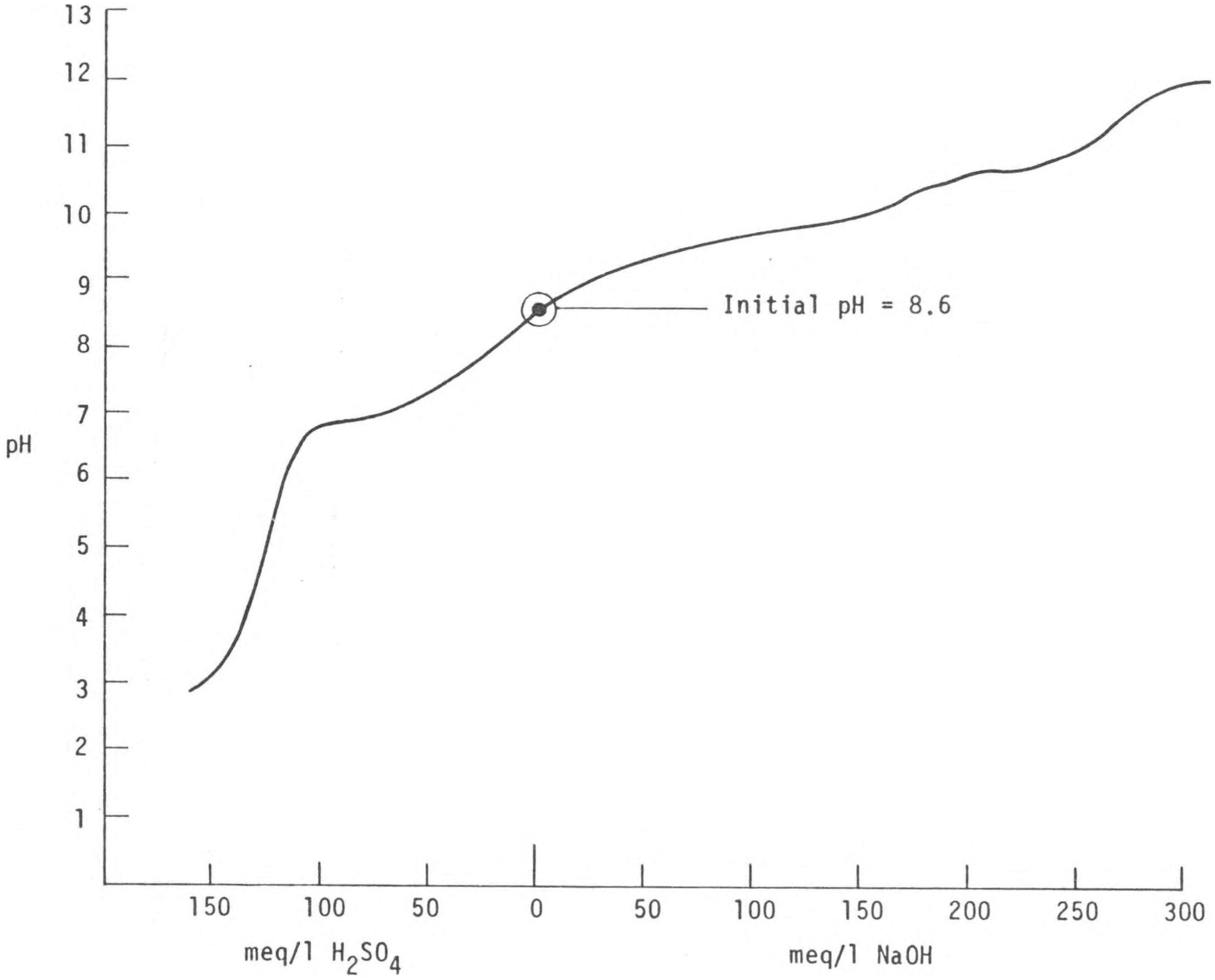


Figure 4-1. Complete titration curve of representative R-17 retort water.

a hood and vented to the roof of the building. An estimated 300 mg/l of ammonia nitrogen are required to provide sufficient nutrient nitrogen for every 5000 mg/l of BOD present. To insure that enough nitrogen was present, the stripping operation was stopped when the ammonia concentration went below 400 mg/l.

The ammonia stripping procedures used was:

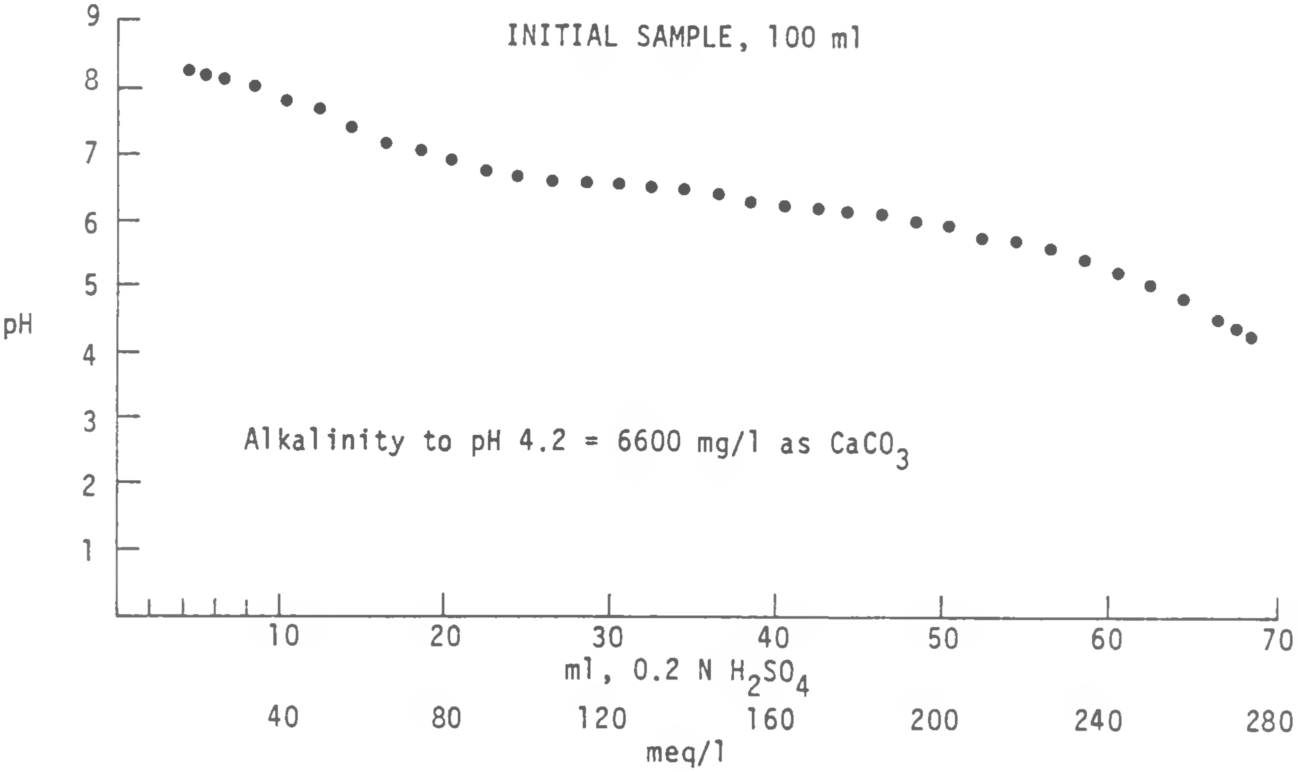
1. Fill tank with contents of 1 barrel;
2. Take sample and check pH and NH_3 concentration;
3. Preheat retort water to 90^oC;
4. After temperature is reached start aeration (air flow rate of 15 to 25 l/min for 30 gallons of retort water);
5. After 1 hour of aeration add KOH
   - use enough KOH to raise the pH to a value between 11 and 12;
6. Record change in NH_3-N with time until a concentration of less than 400 mg/l is reached;
7. Bring up to the original volume with tap water.

In step 4 the heated retort water was aerated for one hour without any alkali addition. This step would remove some free ammonia and substantial amount of alkalinity. As shown in Figure 4-2, the alkalinity was reduced from 6600 mg/l to 2750 mg/l, thus reducing the buffering capacity of the water and consequently the amount of KOH needed to raise the pH. In this way the resultant concentration of total dissolved solids would also be minimized.

The amount of KOH necessary to raise the pH of the R-17 retort water to between 11 and 12 was determined by titration. It was found that approximately 10 grams of KOH are needed per liter of retort water. It therefore takes about 1200 grams to adjust the pH in each 30 gallon barrel. KOH rather than NaOH was used to raise the pH because it would not further increase the high Na content of the retort water, which might become inhibitory to biological growth.

The suspended solids concentration was found to be increased by the stripping process. Table 4.3 shows the suspended solids concentration before and after stripping.

The greatest increase in solids was in the form of fixed suspended solids. This may have been caused by inorganic matter precipitated by increasing the pH during stripping.



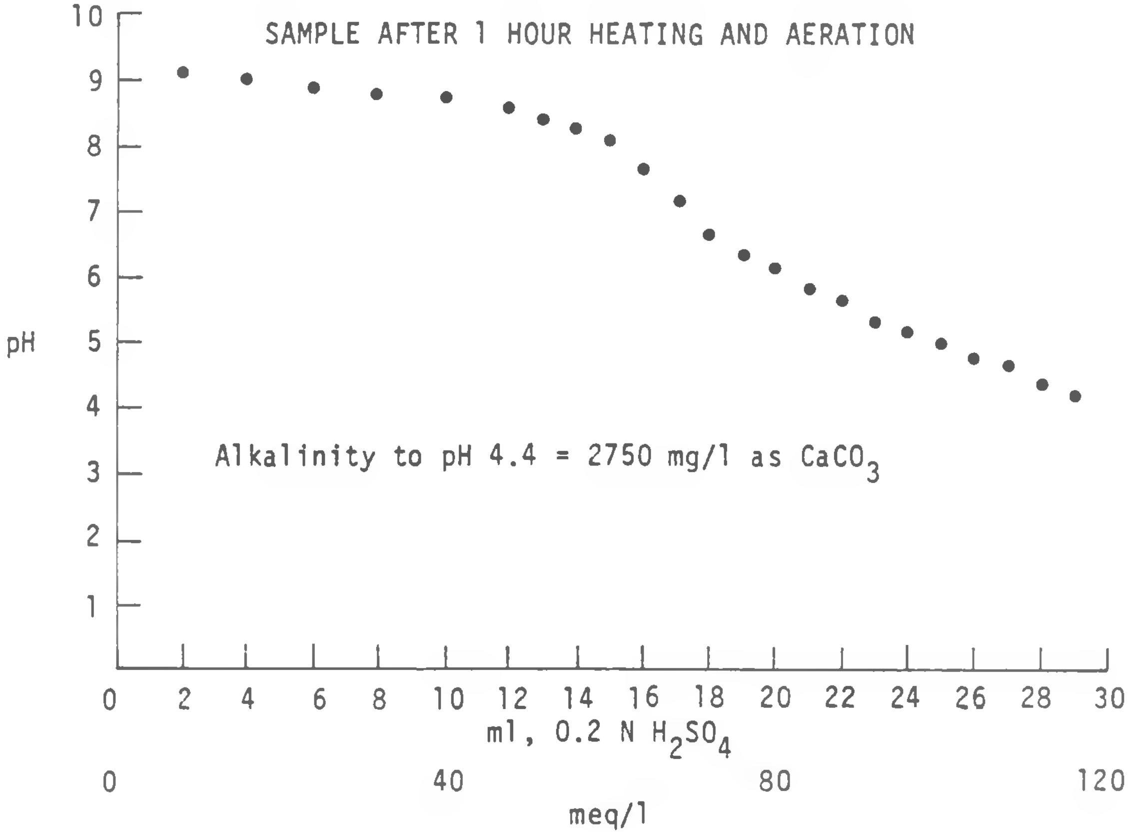


Figure 4-2. Alkalinity test for R-17 filtered retort water before stripping.

TABLE 4.3

EFFECTS OF AMMONIA STRIPPING ON SUSPENDED SOLIDS

	BEFORE STRIPPING	AFTER STRIPPING	CHANGE	% CHANGE
Total SS (mg/l)	74	195	+121	+164
Volatile SS (mg/l)	59	79	+20	+34
Fixed SS (mg/l)	16	116	+100	+625

4.2.2 pH Neutralization

Phosphoric acid was chosen to neutralize the pH of the stripped retort water because it also provides nutrient phosphorous. We found that it took about 5 mls of phosphoric acid to adjust each liter of R-17 retort water to 7.0. An estimated 40 mg of phosphorous are necessary for each 4000 mg of BOD to be removed. By adding 5 ml of phosphoric acid to each liter of retort water we added over 1500 mg of phosphorous which greatly exceeds the phosphorous nutrient requirement. So the availability of phosphorous would not be a limiting factor in the subsequent biological treatment.

After neutralization the suspended solids content of the water was usually found to be several hundred mg/l. In order to minimize the interference with subsequent mass balance due to these suspended solids in the bioreactor influent, the neutralized water was filtered through sub micron filters to reduce the suspended solids concentration to about 100 mg/l or less.

4.3 Rotating Biological Contactor (RBC)

4.3.1 Introduction

The rotating biological contactor (RBC) consists of a rotating shaft on which are mounted plastic discs which serve as a medium for attached biological growth. The discs rotate through the wastewater with 40% of the discs being submerged and 60% being exposed to the air. Using alternate contact with the substrate in the wastewater and oxygen in the air, carbonaceous and nitrogenous biodegradable material is stabilized.

When the biomass reaches a certain thickness it is sheared off by the shearing force exerted when the medium rotates through the wastewater. Rotation of the medium keeps the stripped solids in suspension until they pass through the unit and settle in a clarifier.

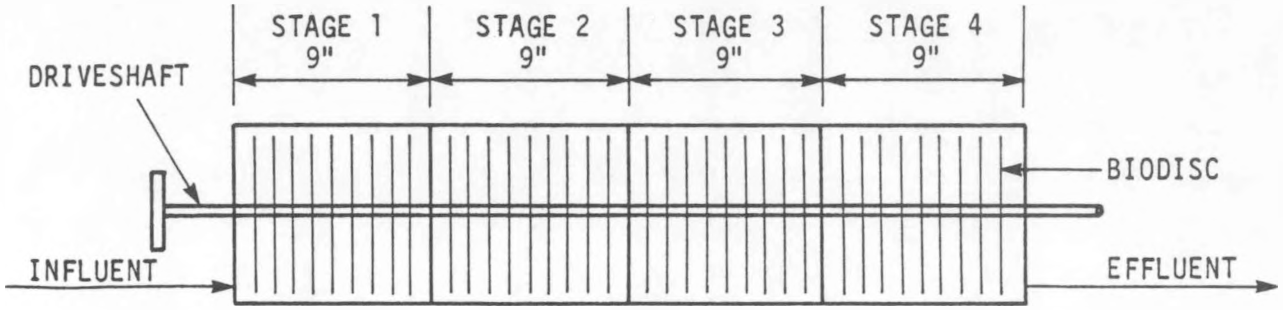
The purpose of this investigation was to determine the effectiveness of the RBC process in treating R-17 retort water. The effects of detention time, organic loading and staging were evaluated to determine their effects on BOD, COD and TOC removal.

The RBC was evaluated as a possible secondary treatment and as a pretreatment to an activated sludge unit with PAC added. The RBC was also used to treat retort water diluted 20-1 to identify possible toxic effects.

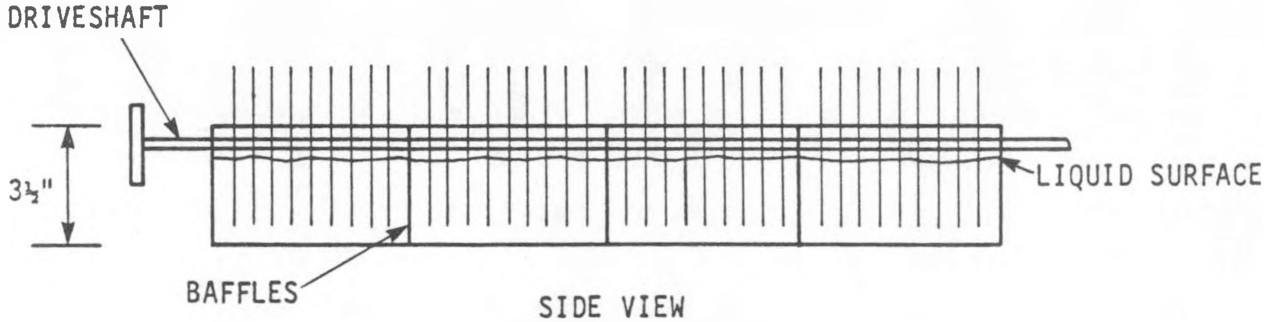
4.3.2 Experimental Apparatus

The experimental apparatus consisted of 4 bench scale RBC units run in parallel. Figure 4-3 is a plan of one of the units (Unit A). Plexiglass baffles are used to divide the units into stages. The baffles have 1 inch diameter submerged ports to allow a flow. The discs are 7½ inches in diameter and are constructed of polyethylene. The surface of the discs are irregularly shaped in order to cause mixing which keeps the solids in suspension.

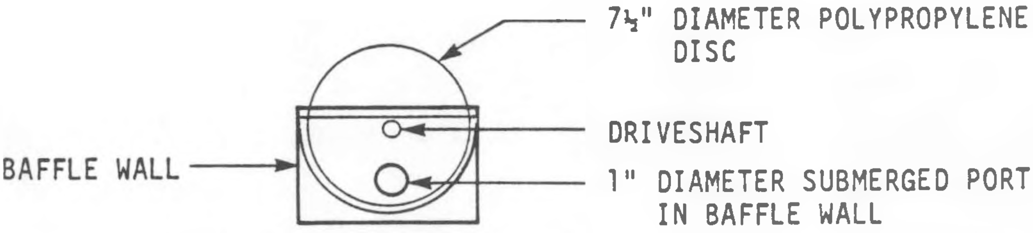
Figure 4-4 shows a layout of the 4 units. The units are identified by letters A, B, C, and D. Units A and B were 4-stage units while units C and D had 3 stages. Units A, C and D had 9 discs per stage and a volume to surface area ratio of .09 gallons per square foot. Unit B had 6 discs per stage with a volume to surface area ratio of .12. Other physical parameters are shown in Table 4.4.



TOP VIEW



SIDE VIEW



END VIEW

Figure 4-3. Plan of laboratory unit A

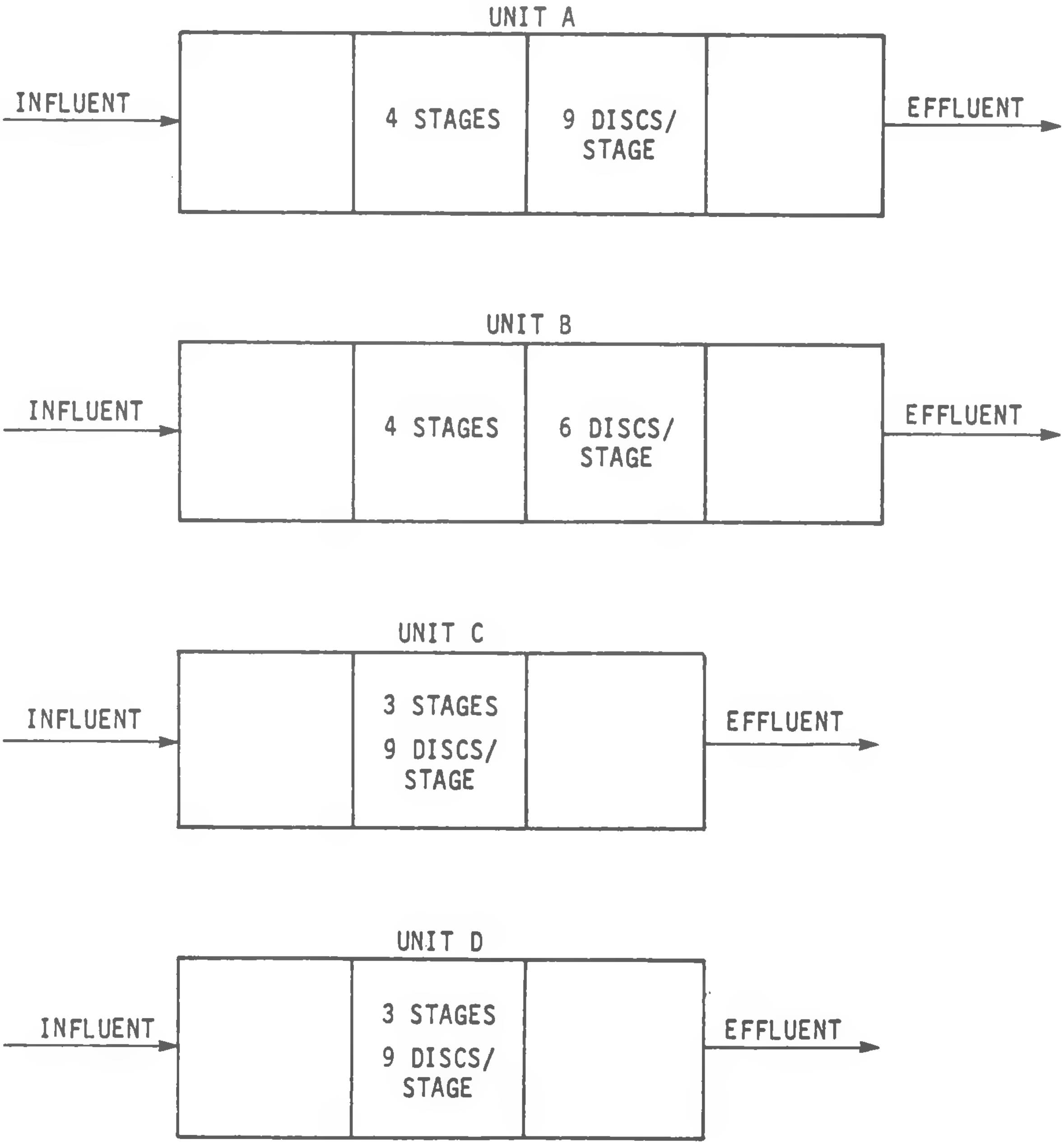


Figure 4-4. Layout of RBC units.

TABLE 4.4

DIMENSIONS OF RBC UNITS

UNIT	LENGTH (inches)	NUMBER OF STAGES	NUMBER OF DISCS	DISCS PER STAGE	DISC DIAMETER (inches)	AREA PER DISC (ft^2)	DISC AREA PER UNIT	VOLUME/UNIT		VOLUME: SURFACE AREA RATIO
								GAL.	LITER	
A	36	4	36	9	7.5	.83	30	2.6	9.8	.09
B	36	4	24	6	7.5	.83	20	2.6	9.8	.12
C	27	3	27	9	7.5	.83	22.5	2.1	8.0	.09
D	27	3	27	9	7.5	.83	22.5	2.1	8.0	.09

4.3.3 Experimental Procedures

Daily Operation

Data on the daily operation of the RBC units is presented in Table 4.5. From 11/19/79, when the units were started, until 1/10/80 the units were run as a batch. Every 3 days the units were emptied and refilled with stripped retort water with the pH adjusted to 7.0.

The units were seeded with effluent from a bench scale activated sludge unit also being used to treat retort water. This unit was started well before the RBCs and was reportedly working well at the time of the seeding.

On 1/10/80 a flow of retort water was started in units A and B. In order to determine whether organics could be further removed by dilution, effluent was diluted 20:1 with tap water and fed into unit D. A flow into unit C was set up using straight retort water diluted 20-1. A flow chart of the treatment processes used is shown in Figure 4-5.

Flow rates were controlled with variable speed Masterflex pumps. All of the data on treating undiluted retort water was obtained using unit A. On this unit the flow was adjusted over a range of 4.7 to 27.2 ml/min. This corresponds to a hydraulic loading rate of 0.06 to 0.17 gpd/ft^2. The flow through unit B was held constant at 4.7 ml/min, setting the hydraulic loading rate at .09 gpd/ft^2. Unit B was operated as a stand-by unit in case of a breakdown of unit A. Since the flows into units C and D were 20:1 dilutions of retort water or effluent from unit A the flow rates were set much higher to achieve comparable organic loadings. The flow rate into unit C was 38 and 52 ml/min for a hydraulic loading of 0.65 and 0.89 gpd/ft^2. Unit D was run at a flow rate of 121 ml/min, setting the hydraulic loading rate at 2.10 gpd/ft^2.

Sampling and Analytical Procedures

After changing the flow rate 3 days were allowed for the unit to reach equilibrium before sampling. Samples were then taken every 2 or 3 days until sufficient data was obtained for that particular flow rate.

Samples were taken from each stage, the influent and the effluent. A 100 ml beaker was used to withdraw the sample from each location. The samples were then filtered through a Watman GF/C filter and analyzed for suspended solids and volatile suspended solids. The filtrate was then

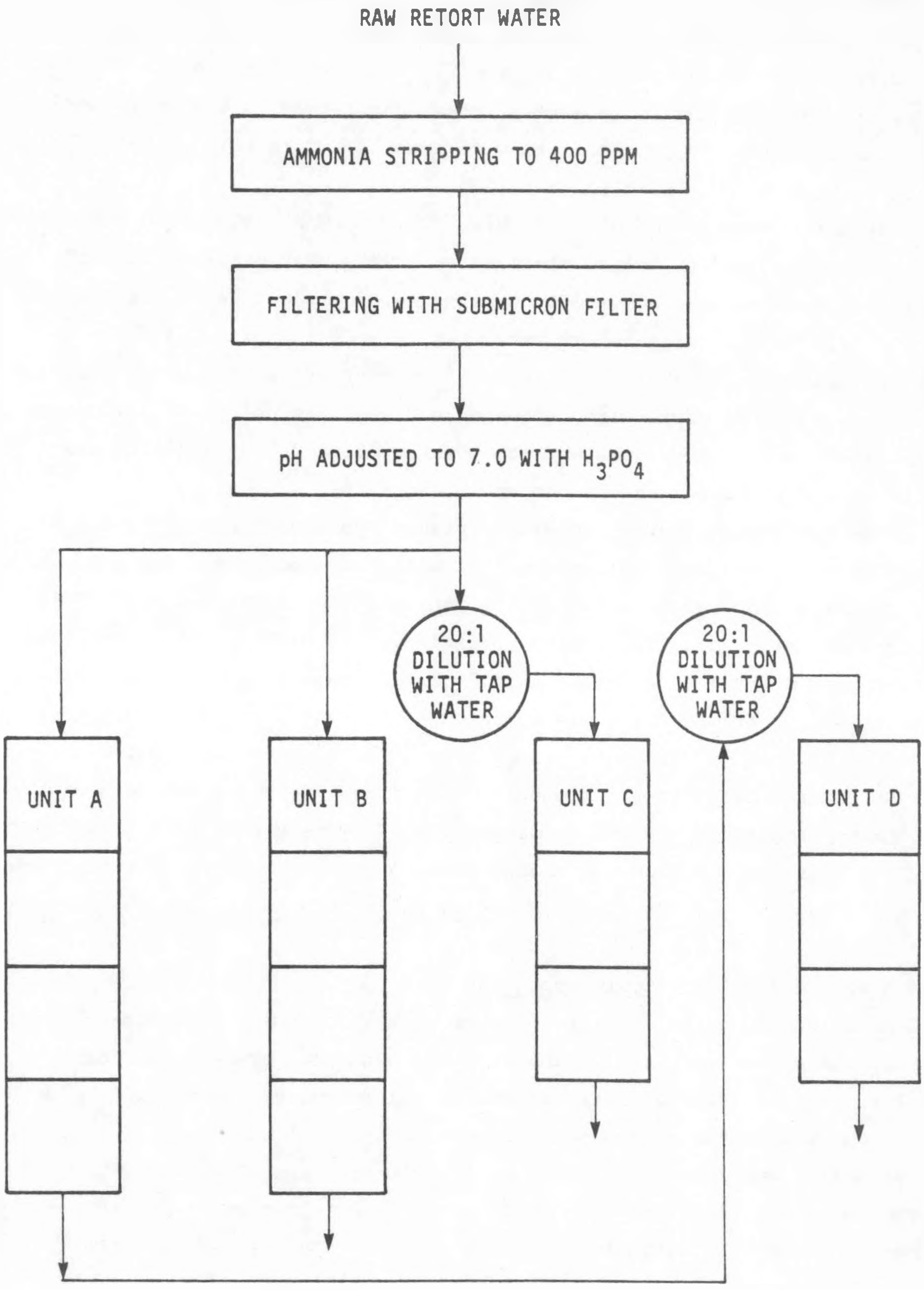


Figure 4-5. Flow chart of RBC treatment and pretreatment.

TABLE 4.5

SCHEDULE OF EXPERIMENTS

UNIT	DATES OPERATED	FLOW (ml/min)	RESIDENCE Time (Hrs)	HYDRAULIC LOADING Rate (gpd/ft^2)	ORGANIC LOADING Rate (lb BOD/(1000 ft.^{2})(day)
A	11/19/79 - 1/10/80	-	72	-	.96
B	11/19/79 - 1/10/80	-	72	-	1.4
C	11/19/79 - 4/10/80	-	72	-	1.0
D	11/19/79 - 2/26/80	-	72	-	1.0
A	1/10/80 - 2/24/80	4.7	35	.06	1.8
B	1/10/80 - 8/15/80	4.7	35	.09	2.7
D	2/26/80 - 4/30/80	121	1.1	2.10	1.5
A	2/24/80 - 3/36/80	6.0	27	.08	2.6
A	3/26/80 - 4/21/80	6.8	24	.09	2.8
C	4/10/80 - 5/ 5/80	38	3.5	.65	.97
A	4/21/80 - 5/10/80	13.6	12	.17	5.6
C	5/ 5/80 - 6/24/80	52	2.6	.89	1.4
A	5/10/80 - 5/16/80	27.2	6.0	.35	11.4
A	5/16/80 - 6/ 8/80	13.6	12	.17	5.6
A	6/ 8/80 - 6/13/80	18.1	9.0	.23	7.6
A	6/13/80 - 8/15/80	13.6	12	.17	5.6

analyzed for BOD and COD to determine the soluable organic content. BOD, COD, suspended and volatile suspended solids tests were performed according to procedures in the 14th edition of Standard Methods.[7] Soluble TOC was also measured in some samples using an Envirotech Organics Analyzer.

Solids Removal

One problem associated with bench scale RBC units is a build-up of solids on the bottom of the units. Solids accumulated due to the low turbulence in these units. Full-scale RBC units have sufficient turbulence to keep solids in suspension.

To remove accumulated solids the units were periodically shut down and the retort water drained into a bucket. After 15 minutes of settling the supernatant was drawn off and put back into the RBC unit. The remaining sludge was analyzed for solids concentration and then wasted. The total solids wasted was then calculated and used in a mass balance in which solids production per pound of BOD removed was calculated.

4.3.4 Results of Batch Operation

Batch Operation

During the two month start-up period from November, 1979 to January, 1980 the units were run on a batch basis and only limited data, consisting of COD, pH and temperature, were obtained. Poor bacterial growth was observed on the discs and a maximum of 25% COD removal was found for a 72 hour detention time.

Operational problems during the start-up period included a low water temperature, a high evaporation rate and splashing due to excessive foaming. During January, 1980 heaters were attached to the undersides of the RBC units. Wooden-framed covers were also constructed and fitted to the top of each unit. These modifications increased the temperature from an average of 12°C to about 20°C. The covers were designed to prevent loss of water by splashing. Water losses through evaporation and splashing were reduced from about 2 liters/day to about 1 liter/day. The heaters and covers were used for the duration of the study and the reactor temperatures were controlled at $22^\circ C \pm 3^\circ C$.

Rotational Speed

The optimum disc rotational speed has been reported to be 1 ft/second at the periphery.[2] For the 7.5 inch diamter disc used in this study 1 ft/sec. is equivalent to 30 rpm. This speed was used during the start-up period with poor results. It was then though that the shear force may have been too great. On January 12, 1980 the rotational speed was reduced to 15 rpm. (0.5 ft/sec peripheral velocity). Around this time bacterial growth increased and the speed was not changed for the remainder of the study.

4.3.5 Results of Continuous Operation

All raw data on the measurement of BOD_5, COD, and solids are listed in Appendices 1, 2, and 3. A summary of average values of the laboratory data is presented in Tables 4.6 through 4.14. Tables 4.6 through 4.11 present data on undiluted retort water using unit A while Tables 4.12 through 4.14 present data taken on 20:1 dilutions.

Each table summarizes the average values of the measured RBC performance parameter for a given hydraulic residence time. Data includes average values of soluble BOD and COD. TOC data is shown for residence times of 12 and 9 hours.

Tables 4.6 through 4.14 indicate low removal efficiency at all residence times, with best removal occuring at the longest detention. Sixty-three percent of the BOD and 26% of the COD were removed at the longest residence time of 35 hours. At a 12 hour residence time the BOD removal dropped off slightly, down to 57%. Removal efficiency dropped off drastically for residence times shorter than 12 hours. At a 9 hour residence time 19.5% of the COD and 45% of the BOD were removed while 16% of the COD and 36% of the BOD were removed at a residence time of 6 hours.

A plot of influent and effluent BOD vs time is shown in Figure 4-6. Influent BOD values varied from 3400 to 4400 ms/l with 75% of the values falling between 3800 and 4200 ms/l. Effluent BOD were somewhat erratic for the first 30 days of the study, after which they were fairly consistent until day 104. After this time the effluent BOD increased sharply due to a decrease in the residence time.

Figure 4-7 is a plot of influent and effluent COD vs. time. Influent values of COD varied from a low of 9500 to a high of 11,900 ms/l. Eighty percent of the influent COD values were between 9500 and 10,400 ms/l. During the first 15 days the effluent COD was relatively high, probably because the units had not yet reached equilibrium. From day 23 through day 98 the effluent COD remained fairly constant and then decreased substantially during days 101 and 104. After day 104 the effluent COD increased sharply due to a decrease in the hydraulic residence time to 6 hours and a corresponding

TABLE 4.6

ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 2-6 to 2-12-80, Unit A, undiluted retort water

Hydraulic Residence Time - 35 hours
BOD Loading Rate - 1.8 lb/(1000 ft.^{2})(day)
Initial pH - 7.0

(a) COD

Sample	Soluble COD (mg/l)	Cumulative COD Removal (mg/l)	Cumulative Removal %
Influent	9,983	0	-
Stage 1	8,208	1,775	18
Stage 2	7,925	2,058	21
Stage 3	7,690	2,293	23
Stage 4/ Effluent	7,371	2,612	26

(b) BOD

Sample	Soluble BOD (mg/l)	Cumulative BOD Removal (mg/l)	Cumulative Removal %
Influent	3,900	0	0
Stage 1	1,629	2,271	56
Stage 2	1,524	2,376	58
Stage 3	1,449	2,451	60
Stage 4/ Effluent	1,337	2,563	63

TABLE 4.7

ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 2-24 to 2-29-80, Unit A, undiluated retort water

Hydraulic Residence Time - 27 hours
BOD Loading Rate - 2.6 lb/(1000 ft.^{2})(day)
Initial pH - 7.0

(a) COD

	mg/l		
Sample	Soluble COD	Cumulative COD Removal	Cumulative Removal %
Influent	10,296	-	-
Stage 1	8,309	1,987	19
Stage 2	8,160	2,136	21
Stage 3	7,911	2,385	23
Stage 4/ Effluent	7,639	2,657	26

(b) BOD

	mg/l		
Sample	Soluble BOD	Cumulative BOD Removal	Cumulative Removal %
Influent	4,175	-	-
Stage 1	1,951	2,224	53
Stage 2	1,901	2,274	54
Stage 3	1,797	2,378	57
Stage 4/ Effluent	1,733	2,442	58

TABLE 4.8

ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 3-28 to 4-4-80, Unit A, undiluted retort water

Hydraulic Residence Time - 24 hours

BOD Loading Rate - 2.9 lb/(1000 $ft.^2$)(day)

Initial pH - 7.0

(a) COD

Sample	Soluble COD (mg/l)	Cumulative COD Removal (mg/l)	Cumulative Removal %
Influent	9,947	-	-
Stage 1	7,931	2,016	20
Stage 2	7,640	2,307	23
Stage 3	7,669	2,278	23
Stage 4/ Effluent	7,560	2,387	29

(b) BOD

Sample	Soluble BOD (mg/l)	Cumulative BOD Removal (mg/l)	Cumulative Removal %
Influent	4,000	-	-
Stage 1	1,800	2,200	55
Stage 2	1,687	2,313	58
Stage 3	1,679	2,321	58
Stage 4/ Effluent	1,625	2,375	59

TABLE 4.9

ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 4-21 to 4-28-80, Unit A, undiluted retort water

Hydraulic Residence Time - 12 hours
BOD Loading Rate - 5.6 lb/(1000 $ft.^2$)(day)
Initial pH - 6.6

(a) COD

	mg/l		
Sample	Soluble COD	Cumulative COD Removal	Cumulative Removal %
Influent	9,826	-	-
Stage 1	7,374	2,452	25
Stage 2	7,190	2,636	27
Stage 3	7,107	2,719	28
Stage 4/ Effluent	7,010	2,816	29

(b) BOD

	mg/l		
Sample	Soluble BOD	Cumulative BOD Removal	Cumulative Removal %
Influent	3,983	-	-
Stage 1	1,859	2,124	53
Stage 2	1,779	2,204	55
Stage 3	1,638	2,345	59
Stage 4/ Effluent	1,714	2,269	57

(c) TOC

	mg/l		
Sample	Soluble TOC	Cumulative TOC Removal	Cumulative Removal %
Influent	2,050	-	-
Stage 1	1,650	400	20
Stage 2	1,600	450	22
Stage 3	1,500	550	27
Stage 4/ Effluent	1,600	450	22

TABLE 4.10

ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 6-10 to 6-13, Unit A, undiluted retort water

Hydraulic Residence Time - 9 hours

BOD Loading Rate - 7.6 lb/(1,000 ft.^{2})(day)

Initial pH - 6.6

(a) COD

	mg/l		
Sample	Soluble COD	Cumulative COD Removal	Cumulative Removal %
Influent	11,643	-	-
Stage 1	9,318	2,325	20
Stage 2	9,394	2,249	19
Stage 3	9,356	2,287	19.5
Stage 4/ Effluent	9,375	2,268	19.5

(b) BOD

	mg/l		
Sample	Soluble BOD	Cumulative BOD Removal	Cumulative Removal %
Influent	4,071	-	-
Stage 1	2,450	1,621	40
Stage 2	2,425	1,646	40
Stage 3	2,213	1,858	46
Stage 4/ Effluent	2,238	1,833	45

(c) TOC

	mg/l		
Sample	Soluble TOC	Cumulative TOC Removal	Cumulative Removal %
Influent	2,500	-	-
Stage 1	2,250	250	10
Stage 2	2,200	300	12
Stage 3	2,150	350	14
Stage 4/ Effluent	2,200	300	12

TABLE 4.11
ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 5-11 to 5-15-80, Unit A, undiluted retort water

Hydraulic Residence Time - 6 hours
BOD Loading Rate - 11.5 lb/(1000 ft.^{2})(day)
Initial pH - 6.6

(a) COD

Sample	Soluble COD (mg/l)	Cumulative COD Removal (mg/l)	Cumulative Removal %
Influent	9,888	-	-
Stage 1	8,543	1,345	14
Stage 2	8,638	1,250	13
Stage 3	8,411	1,477	15
Stage 4/ Effluent	8,317	1,571	16

(b) BOD

Sample	Soluble BOD (mg/l)	Cumulative BOD Removal (mg/l)	Cumulative Removal %
Influent	4,071	-	-
Stage 1	2,758	1,313	32
Stage 2	2,825	1,246	31
Stage 3	2,758	1,313	32
Stage 4/ Effluent	2,625	1,446	36

TABLE 4.12
ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 4-2-80, Unit D, 20:1 Dilution of Unit A effluent

Hydraulic Residence Time - 1.1 hours
BOD Loading Rate - 1.5 lb/(1000 ft.^{2})(day)

(a) COD

Sample	mg/l Soluble COD	mg/l Cumulative COD Removal	Cumulative Removal %
Influent	359	-	-
Stage 1	346	13	3.6
Stage 2	337	22	6.1
Stage 3/ Effluent	331	21	7.7

(b) BOD

Sample	mg/l Soluble BOD	mg/l Cumulative BOD Removal	Cumulative Removal %
Influent	85	-	-
Stage 1	70	15	17.6
Stage 2	70	15	17.6
Stage 3/ Effluent	64	21	25

TABLE 4.13

ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 4-27; 4-28; 5-5-80, Unit C, retort water diluted 20:1

Hydraulic Residence Time - 3.5 hours

BOD Loading Rate - 0.97 lb/(1000 ft.^{2})(day)

(a) COD

Sample	Soluble COD (mg/l)	Cumulative COD Removal (mg/l)	Cumulative Removal %
Influent	463	-	-
Stage 1	287	176	38
Stage 2	280	183	40
Stage 3/ Effluent	272	191	41

(b) BOD

Sample	Soluble BOD (mg/l)	Cumulative BOD Removal (mg/l)	Cumulative Removal %
Influent	180	-	-
Stage 1	24	156	87
Stage 2	22	158	88
Stage 3/ Effluent	20	160	89

TABLE 4.14
ROTATING BIOLOGICAL CONTACTOR RESULTS

Test Dates: 5-5 to 6-24-80, Unit C, retort water diluted 20:1

Hydraulic Residence Time - 2.6 hours

BOD Loading Rate - 1.4 lb/(1000 ft.^{2})(day)

(a) COD

	mg/l		
Sample	Soluble COD	Cumulative COD Removal	Cumulative Removal %
Influent	528	-	-
Stage 1	329	199	38
Stage 2	310	218	41
Stage 3/ Effluent	301	227	43

(b) BOD

	mg/l		
Sample	Soluble BOD	Cumulative BOD Removal	Cumulative Removal %
Influent	193	-	-
Stage 1	17	176	91
Stage 2	11	182	94
Stage 3/ Effluent	12	181	94

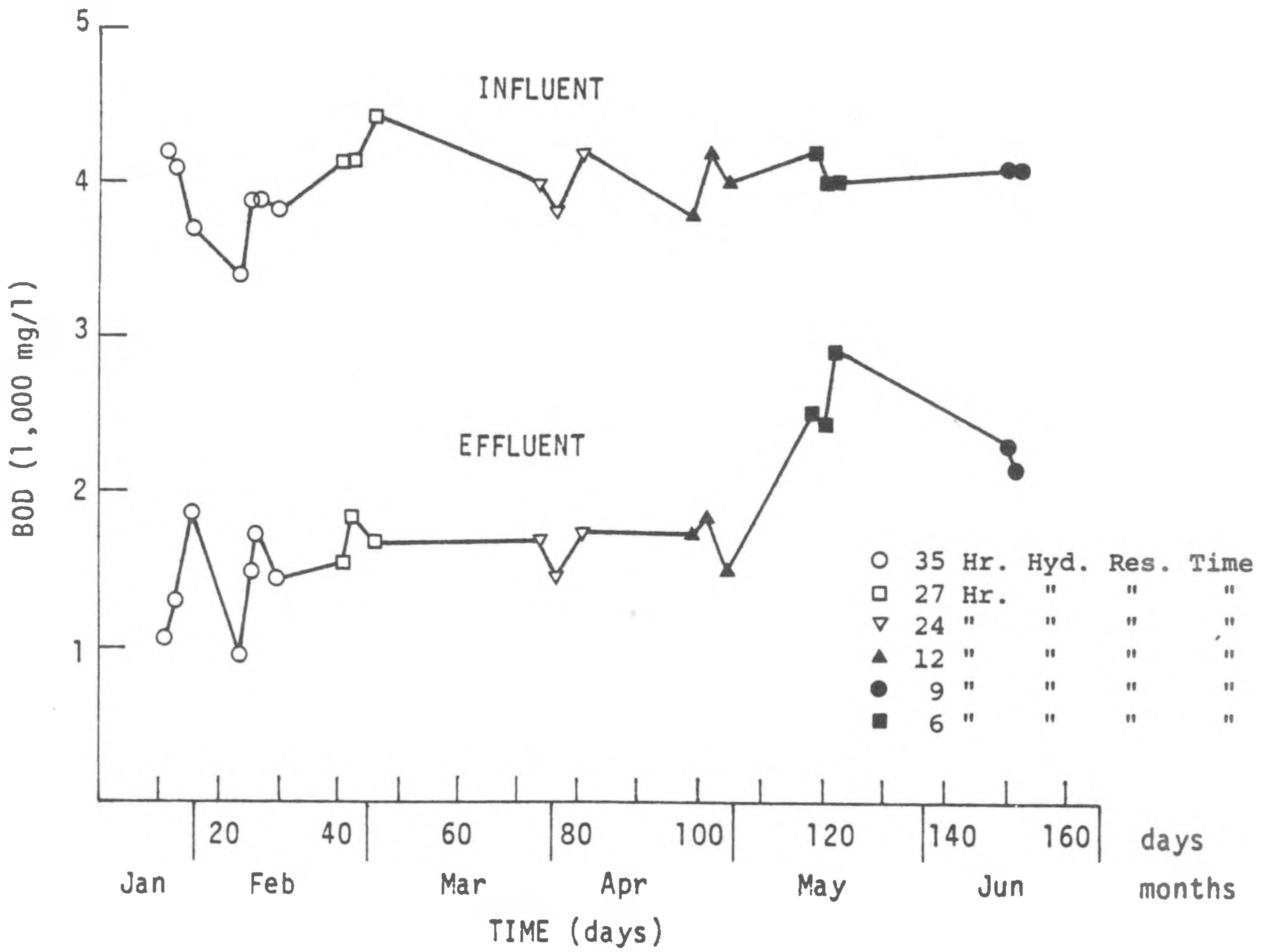


Figure 4-6. Changes in BOD with time for unit A, undiluted retort water.

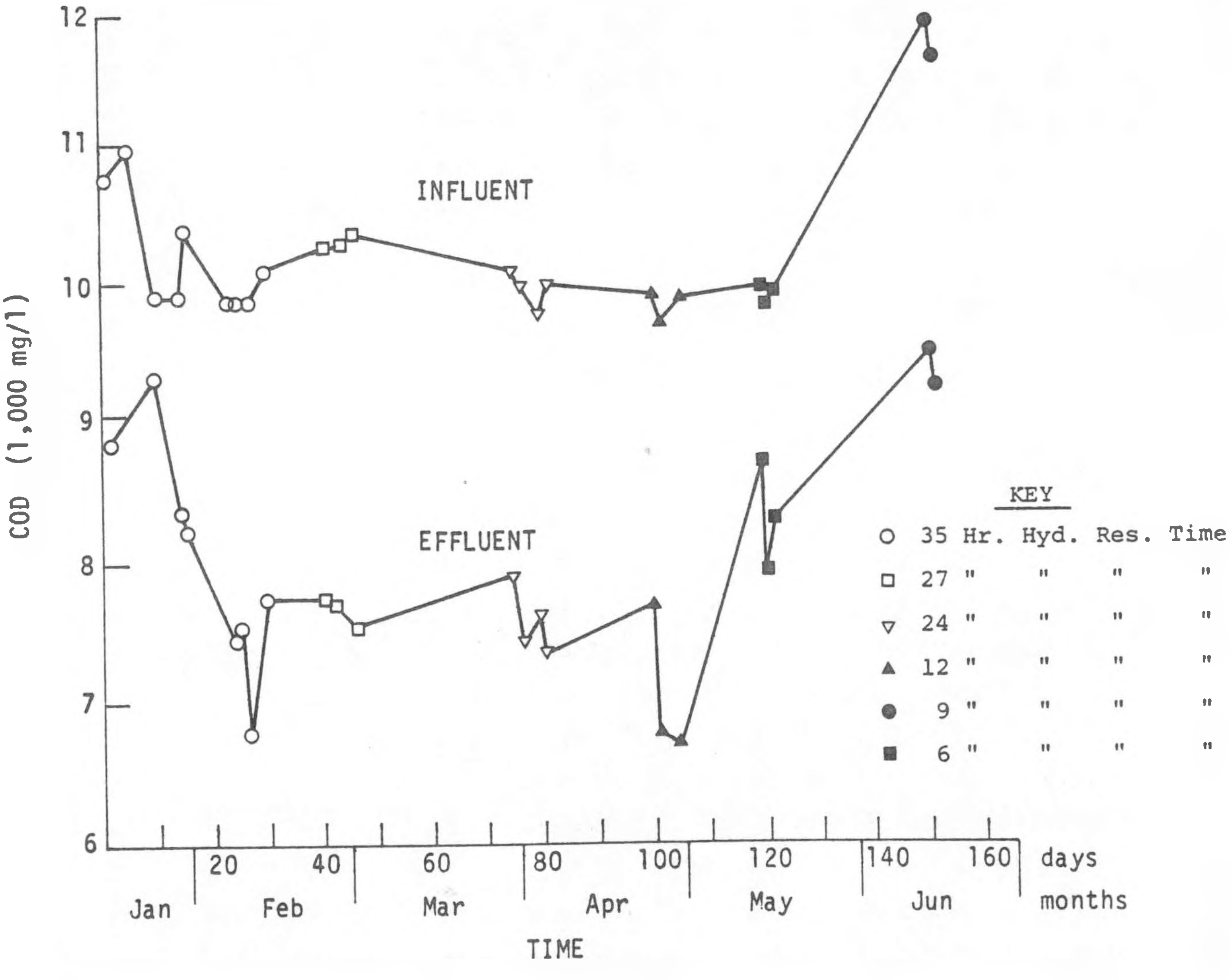


Figure 4-7. Changes in COD with time for Unit A, undiluted retort water.

increase in the organic loading rate.

4.3.6 Hydraulic Loading Rate

Retention time is set by the flow rate and the tank volume. The hydraulic residence times used in this study were calculated using the volumes and flow rates given in Table 4.4.

A parameter commonly used in RBC design is the hydraulic loading rate.[3] Common units used are gallons per ft^2 of disc area per day. The hydraulic loading rate at each residence time is given in Table 4.5. In unit A, treating straight retort water, the hydraulic loading rate was varied from 0.06 to 0.35 gpd/ft^2 while unit C, treating retort water diluted 20:1 was run at loading rates of 0.65 and 0.89 gpd/ft^2. The hydraulic loading rate of unit D, treating unit A effluent diluted 20:1, was set at 2.1 $gpd/ft.^2$

Both the hydraulic loading rate and the residence time fail to take waste strength into consideration. When results are reported in terms of hydraulic loading a given substrate loading must be assumed to be constant. The organic loading rate takes both flow and strength of a wastewater into account. Units commonly used are pounds of soluble BOD_5 per 1000 ft^2 per day. Since the principle mechanism of organic removal in RBCs is diffusion the loading is based on soluble BOD.

4.3.7 Organic Loading Rate

The organic loading rate is the most important parameter to be considered when an RBC system is designed to treat a high strength industrial waste such as retort water. In Figure 4-8 BOD removed is plotted against BOD applied. Organic loading is plotted over a wide range from 1.8 lbs/(1000 ft^2)(day) up to 11.4 lbs/1000 ft^2)(day). A linear fit was obtained for a loading rate up to 5.6 lbs/(1000 ft^2)(day). At higher organic loadings little additional removal was obtained as shown by a flattening out of the curve.

Figure 4-9 is a plot of % BOD removed as a function of BOD applied. The plot shows a relatively narrow variation in % BOD removal from a BOD loading of 1.8 to 5.6 lbs/(1000 ft^2)(day). The removal efficiency drops only slightly in this range as the organic load is increased. For each additional pound of BOD applied the removal efficiency drops by about 1%. Above a BOD loading rate of 5.6 lb/(1000 ft^2)(day) the curve drops off sharply with removal efficiency hitting a low of 36% at 11.4 lb/(1000 ft^2)(day) of BOD applied.

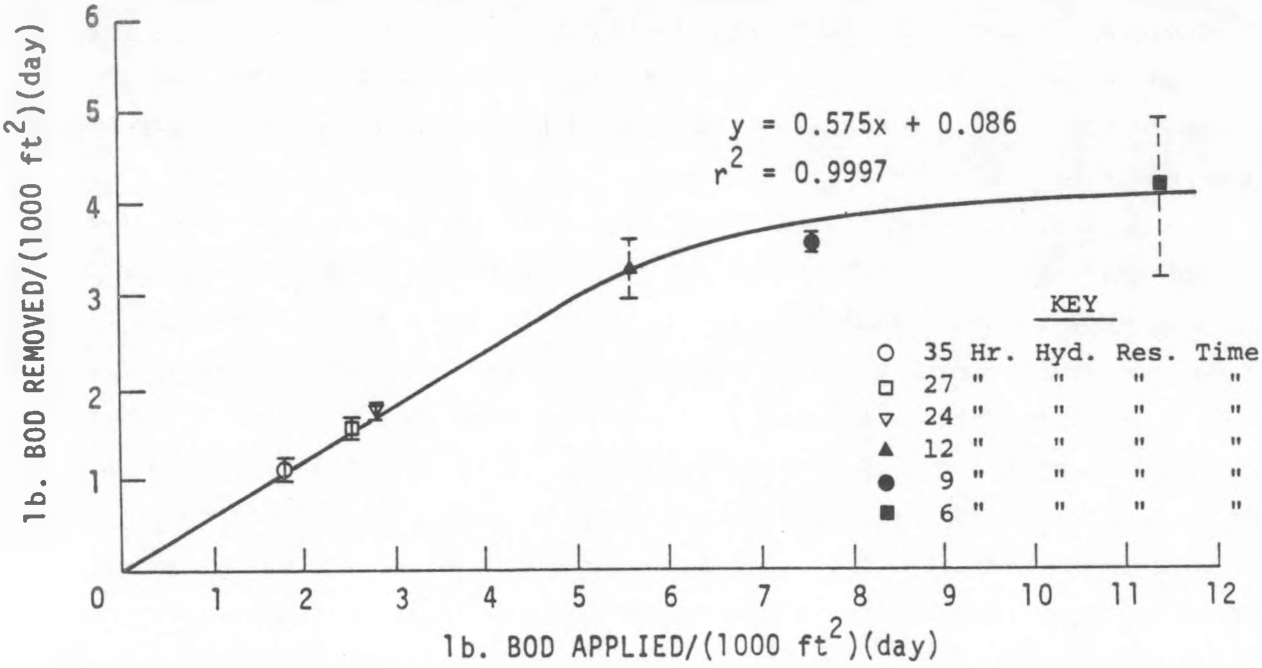


Figure 4-8. BOD removed as a function of BOD applied.

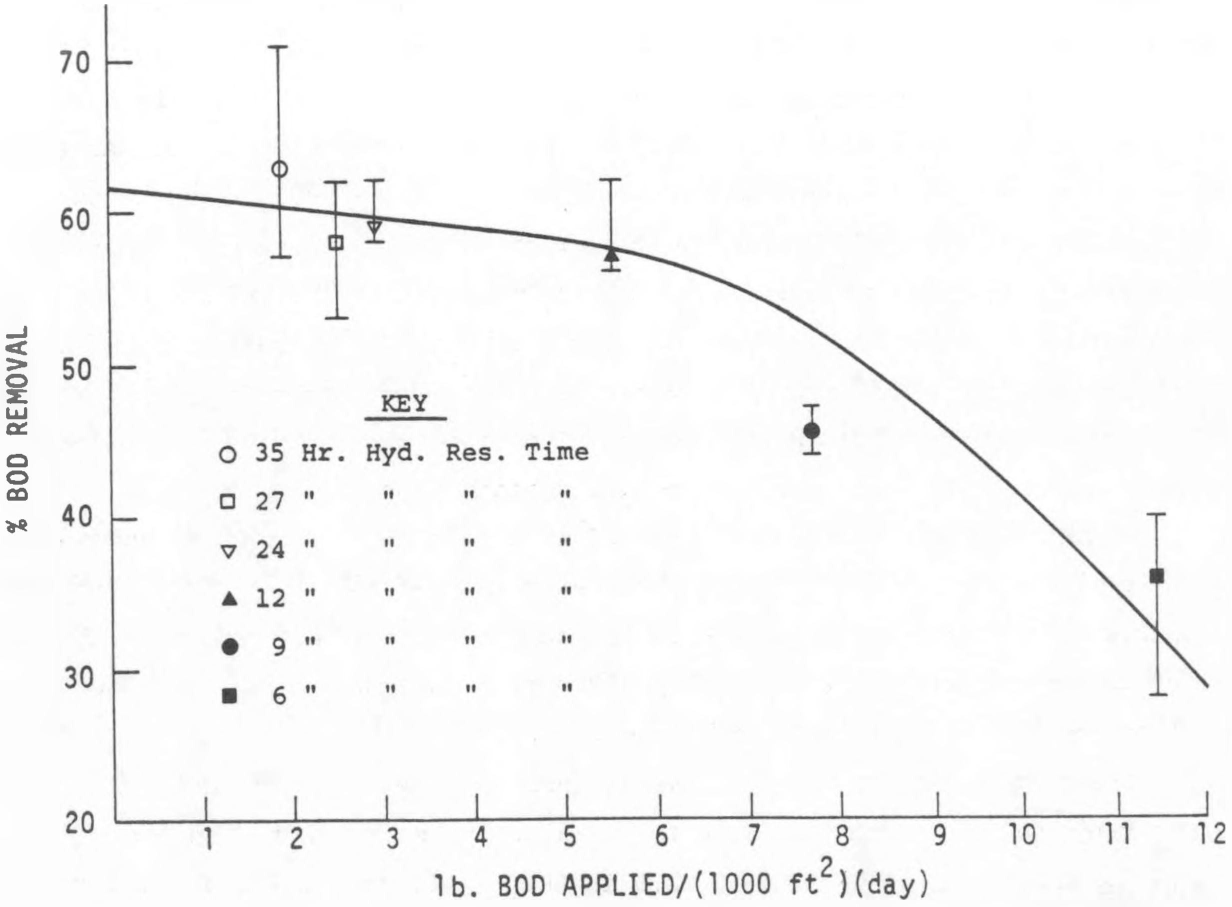


Figure 4-9. % BOD removed as a function of BOD applied.

From data presented in Figures 4-8 and 4-9 it is apparent that the RBC removal efficiency drops off drastically for BOD loadings above 5.6 lbs/ $(1000\ ft^2)$(day). This loading rate is well above the rates generally used when treating most wastewaters and overloading can be expected somewhere in this range.

The poor removal experienced at BOD loading rates less than 5.6 lbs/ $(1000\ ft^2)$(day) is probably characteristic of the retort water we tested. For municipal sewage, BOD removal by RBCs operating at loading rates in this range commonly exceed 90%. Our bench scale units used to treat the retort water barely achieved a 60% removal.

4.3.8 Effects of Staging

BOD and COD were measured in each stage and in the influent to determine the effects of staging. Figures 4-10 and 4-11 are plots of BOD by stage for each of the residence times used. The removal in Stage 1 averaged 93% of the total BOD removed. For hydraulic residence times of 35, 27, 24 and 12 hours the BOD in the first stage was reduced by an average of 2,205 mg/l equivalent to about 54% of the total BOO_5 present. As shown in Figure 4-11 only about 1600 and 1300 mg/l of BOD_5 are removed from the first stage at residence times of 9 and 6 hours respectively. First-stage BOD removal efficiency is 40% at a 9 hour residence time and 32% at a 6 hour residence time. COD by stage is plotted in Figures 4-12 and 4-13 for the six residence times used. An average of 82% of the COD which was removed, was removed in the first stage.

Stages 2, 3 and 4 achieved only a slight increase in organic removal over the first stage of treatment. Approximately 1 to 3 % of the total BOD removed was achieved in each of the last 3 stages. Although the final stages reduced the BOD only slightly they may be considered a polishing step in decreasing the effluent concentration. The last stages will also dampen shock loads due to hydraulic surges and organic loading peaks.

Figure 4-14 shows the BOD_5 removed as a function of the BOD_5 applied on a stage by stage basis. The data indicated that if the four stage unit were changed to a single stage unit with the same total surface area in each stage then up to approximtely 20 lbs $BOD_5/(1000\ ft^2)$(day) was applied to the RBC without a major reduction in BOD_5 removal rate.

Due to the logistical problems of supplying R-17 retort wastewater, larger hydraulic loading and organic loading rates were not possible. However an organic loading rate of 22.5 lb $BOD_5/(1000\ ft^2)$(day) with a 3 hour

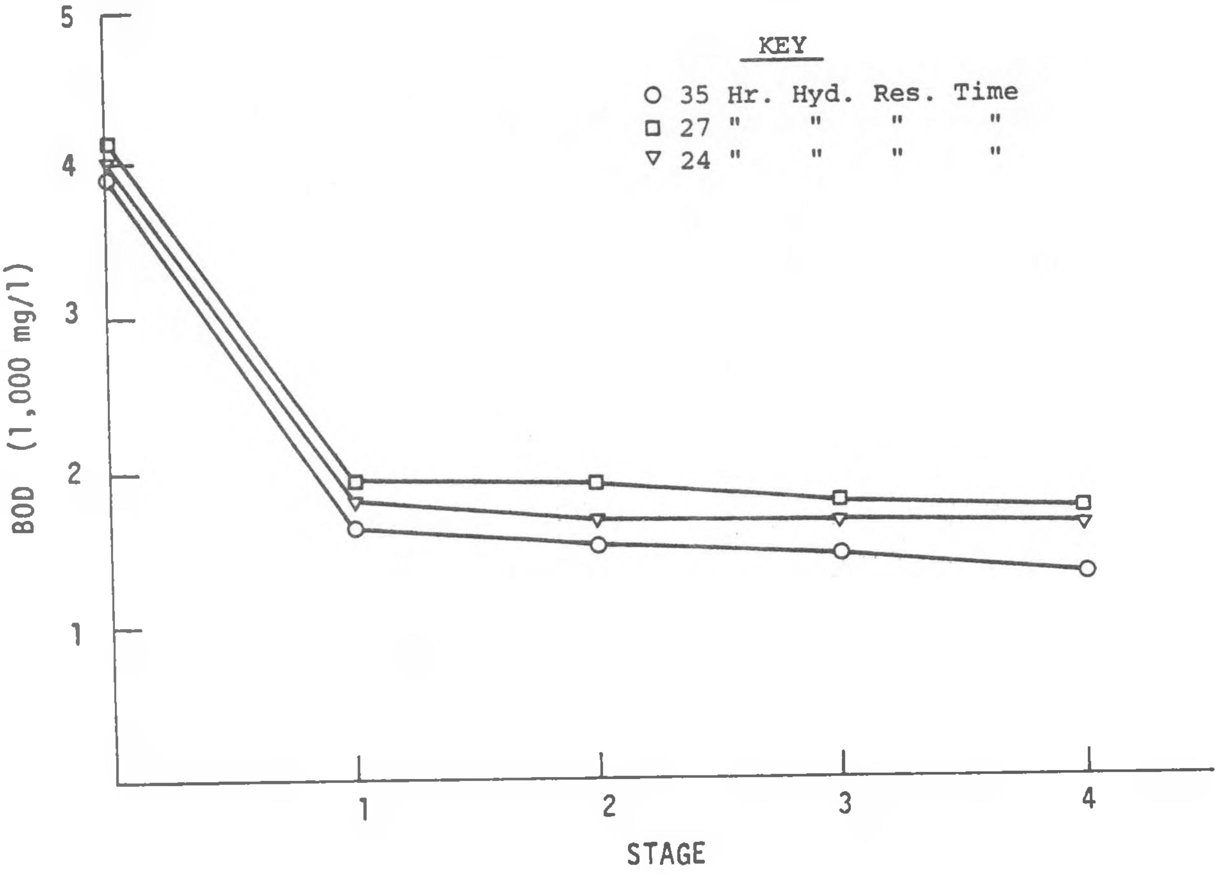


Figure 4-10. BOD by stage, (24 - 35 hour residence time).

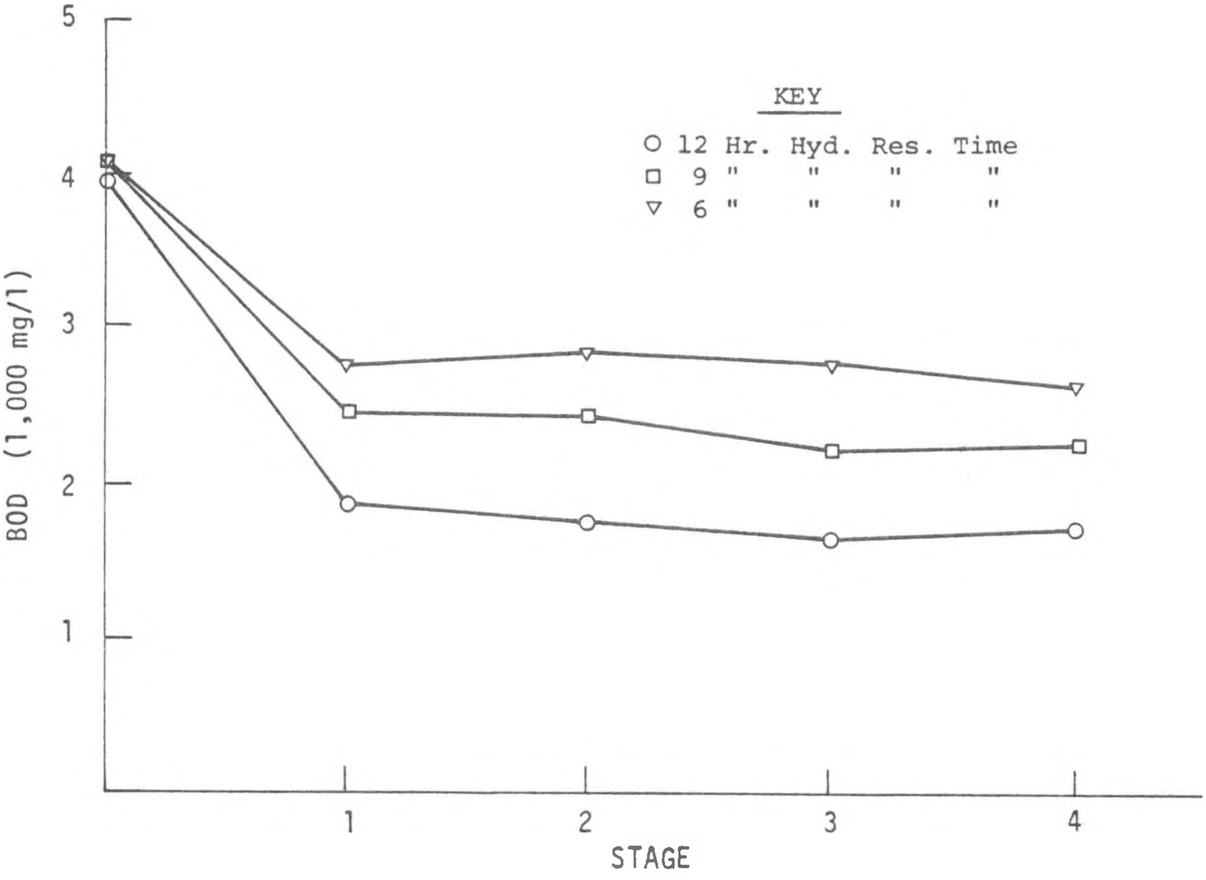


Figure 4-11. BOD by stage, (6 - 12 hour residence time).

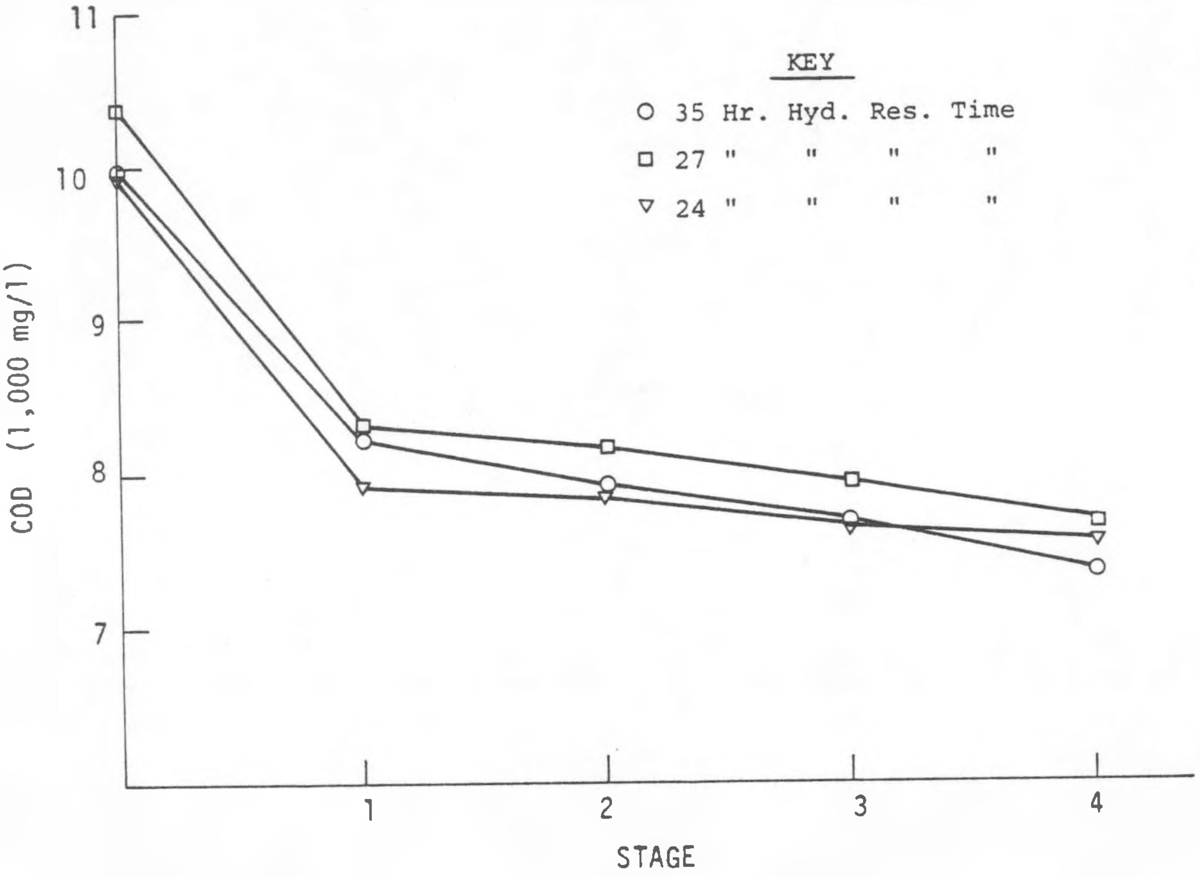


Figure 4-12. COD by stage, (24 - 35 hour residence time).

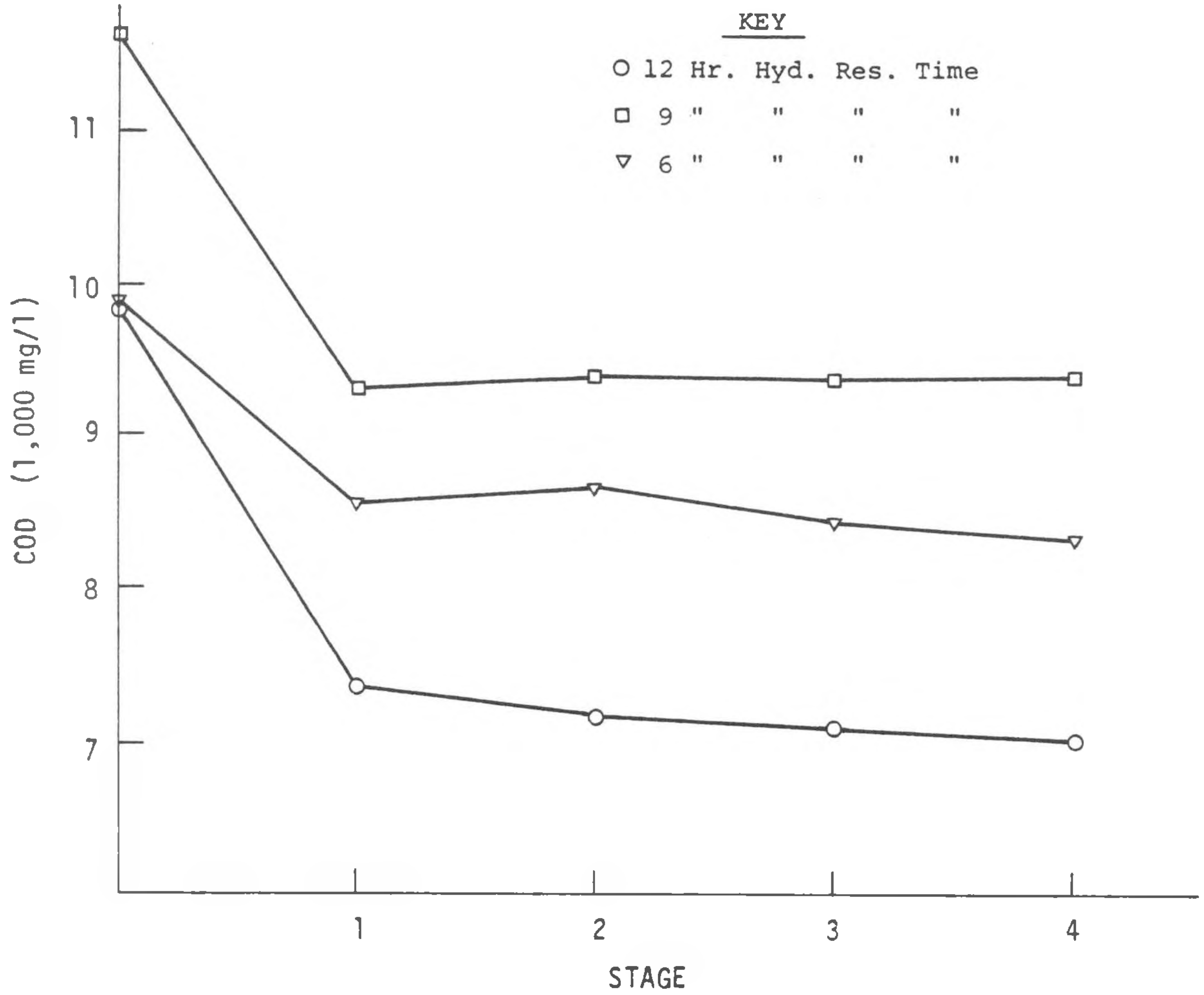


Figure 4-13. COD by stage, (6 - 12 hour residence time).

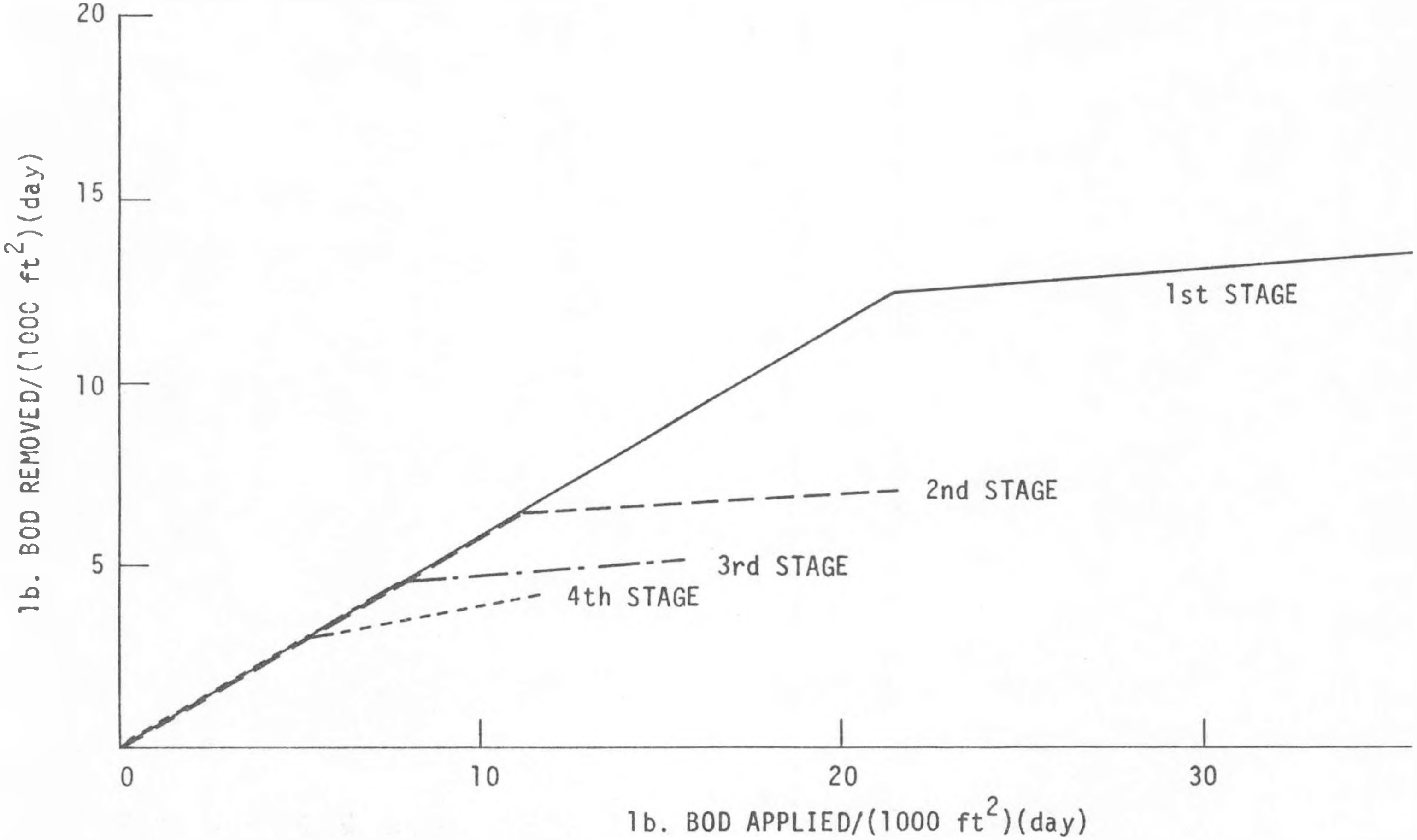


Figure 4-14. BOD removed as a function of BOD applied for various stages.

hydraulic residence time produced 54 percent BOD_5 removal. This data indicated that there is a portion of the soluble BOD_5 (50 to 60 percent) which will be readily removed by a fixed film RBC reactor within the design parameters investigated in this study. Higher BOD_5 removal efficiences were not recorded during this portion of the study. A more complete evaluation of BOD removal efficiency at these high organic rates would require a continous pilot scale evaluation.

4.3.9 Dissolved Oxygen

Dissolved oxygen data are recorded on Table 4.15 for residence times of 35, 24, 12, 9 and 6 hours. First-stage dissolved oxygen was found to be the highest (1 mg/l) at a 35 hour residence time. Dissolved oxygen rose to 4.5 mg/l in the 4th stage at a 35 hour detention time and 3.5 mg/l at a 24 hour residence time. At residence times of 12, 9 and 6 hours essentially anoxic conditions prevailed in all stages. In going from a 24 to a 12 hour residence time the BOD removal efficiency decreased only slightly, indicating that anoxic conditions have little effect on treatment efficiency.

Table 4.15 also lists organic loading rates and temperatures at which dissolved oxygen was measured. As shown, the dissolved oxygen in stage 4 dropped from 4.5 to 3.5 mg/l when the BOD loading rate was increased from 1.8 to 2.6 lbs/(1000 ft^2)(day). When the organic loading rate was increased to 5.6 lb/(1000 ft^2)(day) the dissolved oxygen dropped to 0.5 mg/l. The temperature was 21^oC at a 2.6 lb/(1000 ft^2)(day) BOD loading and 24^oC at a loading of 5.6. This may have affected the dissolved oxygen results by decreasing the solubility.

Figure 4-15 is a plot of dissolved oxygen concentration as a function of BOD loading rate. When the first stage loading rates or other cummulative stage loading rates were less than about 5 lb BOD_5/(1000 ft^2)(day) it was possible to maintain dissolved oxygen in the retort wastewater in those stages. As the BOD_5 loading rate increased over 5 lb BOD_5/(1000 ft^2)(day) dissolved oxygen concentrations decreased to less than 0.5 mg/l the minimum detectable concentration. The reduced dissolved oxygen concentration in the bulk liquid phase of the RBC reactors appears to have had only a minor effect on BOD removal rates.

Odors typically found with other organic wastes when treated under anoxic conditions were not present at any loading rate with the retort water. The water smelled strongly of crude oil before and after RBC treatment.

4.15

OXYGEN DATA

[illegible]	[illegible]		[illegible]	Rate [illegible]^2) (day)	Temp ($^\circ$C)	Stage	Dissolved Oxygen (mg/l)
					20	1	1.0
						2	Not Recorded
						3	Not Recorded
						4	4.5
					21	1	≤.5
						2	≤.5
						3	1.3
						4	3.5
					24	1	≤.5
						2	≤.5
						3	≤.5
						4	≤.5
					25	1	≤.5
						2	≤.5
						3	≤.5
						4	≤.5
					25	1	≤.5
						2	≤.5
						3	≤.5
						4	≤.5

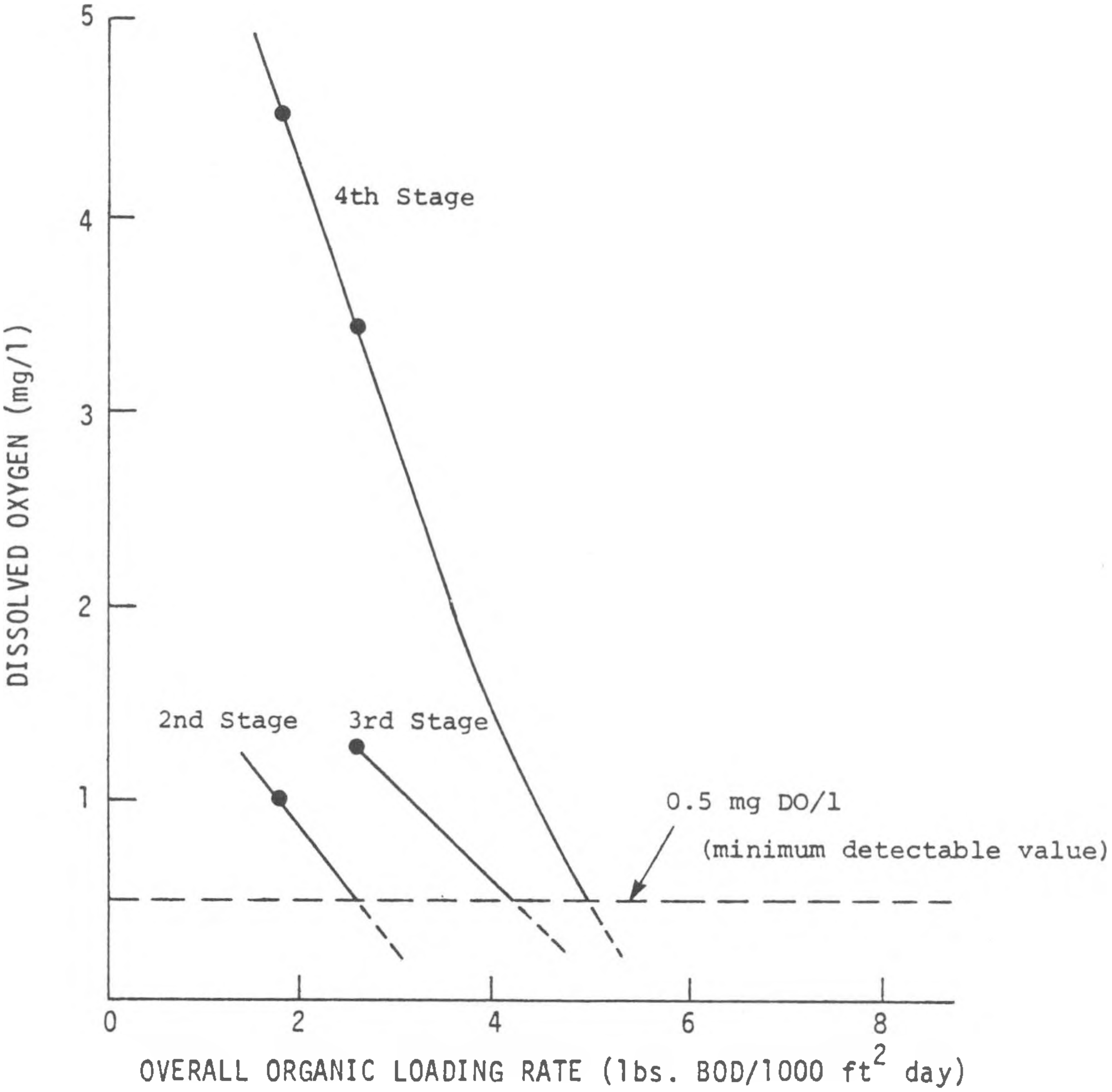


Figure 4-15. Dissolved oxygen as a function of overall organic loading rate.

4.3.10 pH

The retort water was fed into the RBC units after the pH was adjusted to neutral with phosphoric acid. As the water passed through the units the pH rose significantly. For hydraulic residence times of 35, 27 and 24 hours the pH rose to between 8.6 and 9.0 in the 4th stage. On March 31, 1980 the values of pH shown on Table 4.16 for unit A. were recorded. The greatest pH change occurred in the first stage.

It was thought that the high pH found might be inhibiting bacterial growth since the activity of most enzymes decreases as the pH is increased above neutral.[8] In order to identify any toxic effects the pH was adjusted to 6.6 at residence times of 12, 9 and 6 hours. The pH in stage 4 was then found to be between 7.5 and 8.0. However, when the pH was maintained at a lower level no increase in removal efficiency was noted.

4.3.11 Extended Aeration of RBC Effluent

To determine the extent to which organics could be removed from the RBC effluent by extended aeration a 10 liter sample was collected and aerated for 4½ months. Results of this test are shown in Table 4.17. Table 4.17 shows that extended aeration of RBC effluent will remove nearly 95% of the BOD. The amount of COD removed barely exceeded the BOD removal, indicating little or no removal of biorefractory organics.

4.3.12 Solids Production

Table 4.18 shows the amount of solids produced at each of the six loading rates used. Solids production ranged from 0.17 to 0.31 lb SS/lb of BOD removed. The largest amount of solids was produced at the shortest detention time as would be expected. However, accuracy of the data presented in Table 4.18 is questionable due to the variability of the influent suspended solids concentration. Influent suspended solids ranged from about 100 mg/l to 300 mg/l depending on the particular barrel of retort water used. It is possible that influent solids may have been destroyed biologically or redissolved after entering the RBC units thus increasing the error in a mass balance.

4.3.13 The Effect of 20:1 Dilution

At a BOD loading rate of 1.8 lb/(1000 ft^2)(day) only about 60% BOD removal was obtained. At this loading rate 90% BOD removal is common when treating most organic wastes. In an attempt to determine whether toxic inhibition might be causing such poor removal the effluent of unit A was diluted

TABLE 4.16

pH BY STAGE FOR 24 HR HYDRAULIC RESIDENCE TIME

Sample	pH	ΔpH
Influent	6.9	-
Stage 1	8.6	1.7
Stage 2	8.7	.1
Stage 3	8.75	.05
Stage 4	8.8	.05

TABLE 4.17

RBC EFFLUENT

DATE		BOD	COD
3/26/80	Before Aeration	2,225	8,420
8/ 6/80	After Aeration	123	6,101
	Change	2,102	2,319
	% Reduction	94.5	28

TABLE 4.18

SOLIDS PRODUCTION

Hydraulic Residence Time (Hrs)	lb SS Produced / lb BOD Removed	lb VSS Produced / lb BOD Removed
6	.31	.28
9	.26	.21
12	.17	.10
24	.18	.14
27	.21	.15
35	.24	.17

20:1 and fed into unit D as shown in Figure 4-5. Bacterial growth was visible after about 1 week, but the filamentous growth typical of healthy RBCs never developed.

Table 4.12 shows a typical set of data for unit D, treating unit A effluent diluted 20:1. The hydraulic residence time was adjusted to 1.1 hours, setting the BOD loading rate at 1.5 lb/(1000 ft.^{2})(day). Unit D removed 25% of the BOD and 7.7% of the COD remaining in the effluent of unit A. The removal efficiency for units A and D combined was 68% for BOD and 32% for COD.

A 20:1 dilution of the untreated retort water was fed through unit C as depicted in Figure 4-5. The hydraulic residence time was set at 3.5 hours making the BOD loading rate 0.97 lb/(1000 ft.^{2})(day). Bacteria began growing rapidly and after 2 weeks the discs in the first stage were covered with a thick growth. Growth on the second and third stages was significantly thinner than on the first stage.

BOD and COD removal using a 3.5 hour residence time is shown in Table 4.13. BOD removal efficiency was found to be 89% while 41% of the COD was removed. Table 4.14 is a summary of data using a 2.6 hour residence time. At this residence time 94% of the BOD and 43% of the COD were removed.

Removals using a 20:1 dilution of retort water were clearly greater than removals using undiluted retort water. Maximum BOD removal efficiency in unit C treating a 20:1 dilution of retort water was 94% while only a 60% removal efficiency was achieved in unit A treating undiluted retort water. The effluent BOD of unit A was reduced an additional 10% when it was diluted 20:1 and passed through unit D. Total removal for the combined units was 68% of the BOD, well below the removal efficiency achieved when treating straight retort water diluted 20:1.

Differences were noted between the growth on the discs of unit A, treating undiluted retort water, unit C, treating water diluted 20:1 and unit D, treating unit A effluent diluted 20:1. The discs treating a 20:1 dilution of retort were covered with a heavy growth of shaggy filamentous bacteria typical of healthy RBC units. Growth was thickest in the first stage and bridged adjoining discs in places. The growth became thinner in stage 2 and was thinnest in stage 3, the final stage. The growth was light brown in color. For unit A and unit D, the growth was dark brown in color and no filamentous growth was observed.

4.3.14 Color

Color was not removed or changed by the RBC treatment of undiluted retort water or 20:1 dilutions of retort water. For the undiluted water the effluent appeared a little cloudy due to an increase in suspended solids but was identical after filtering. Even in unit C, treating a 20:1 dilution of retort water there was no visible reduction in color, in spite of a 94% removal of BOD.

4.3.15 Conclusions

1. At the lowest BOD loading rate of 1.8 lb/(1,000 ft^2)(day) the RBC removed only 63% of the BOD. Effluent soluble BOD was still over 1300 mg/l. With the given removal efficiency and high effluent BOD the RBC process is not, by itself, a practical complete treatment for the R-17 retort water.
2. At a BOD loading rate of up to 5.6 lb/(1,000 ft^2)(day) the RBC still removed nearly 60% of the BOD and the RBC may prove to be practical as an intermediate or pre-treatment step.
3. Only a small increase in treatment efficiency (10%) was gained by diluting RBC effluent 20:1 and passing the diluted effluent through another RBC unit. Poor growth on the discs and poor removal indicated toxic inhibition.
4. By diluting the retort waste 20:1, about 94% of the BOD can be removed from R-17 retort water. No signs of inhibition were noted. The dilution water was freshwater, not recycled water.
5. The pH rose significantly as the retort water passed through the RBC unit. When the initial pH was adjusted to 7.0 the pH rose to between 8.5 and 9.0 by the 4th stage. By adjusting the initial pH to 6.6 the pH in stage 4 can be kept between 7.5 and 8.0
6. If the RBC unit is to be used as a pretreatment step the most economical application would be to operate parallel single stage reactors. Increasing the loadings from 5.6 to 21 lb BOD_5(1,000 ft^2)(day) would result in a 54% BOD_5 removal efficiency and would reduce the estimated capital cost by 70% and the power requirement by 50%.

4.4 Air Activated Sludge (AS) and Oxygen Activated Sludge (OS)

4.4.1 Introduction

The purposes of this part of the experimental study were:

1. To evaluate BOD removal using air and oxygen activated sludge;
2. To investigate the applicability of the Monod type model for substrate utilization and to evaluate the coefficients of the model;
3. To examine the dewatering characteristics of the activated sludge.

A wide variety of values of the major parameters, (F/M ratio, mean cell residence time, hydraulic residence time, etc.) were tested.

Throughout the study the poor characteristics of the water were noted. There was an oil film which persisted even after filtering through paper. The deep brown color persisted at 500:1 dilution after filtration. The gasoline odor was always present.

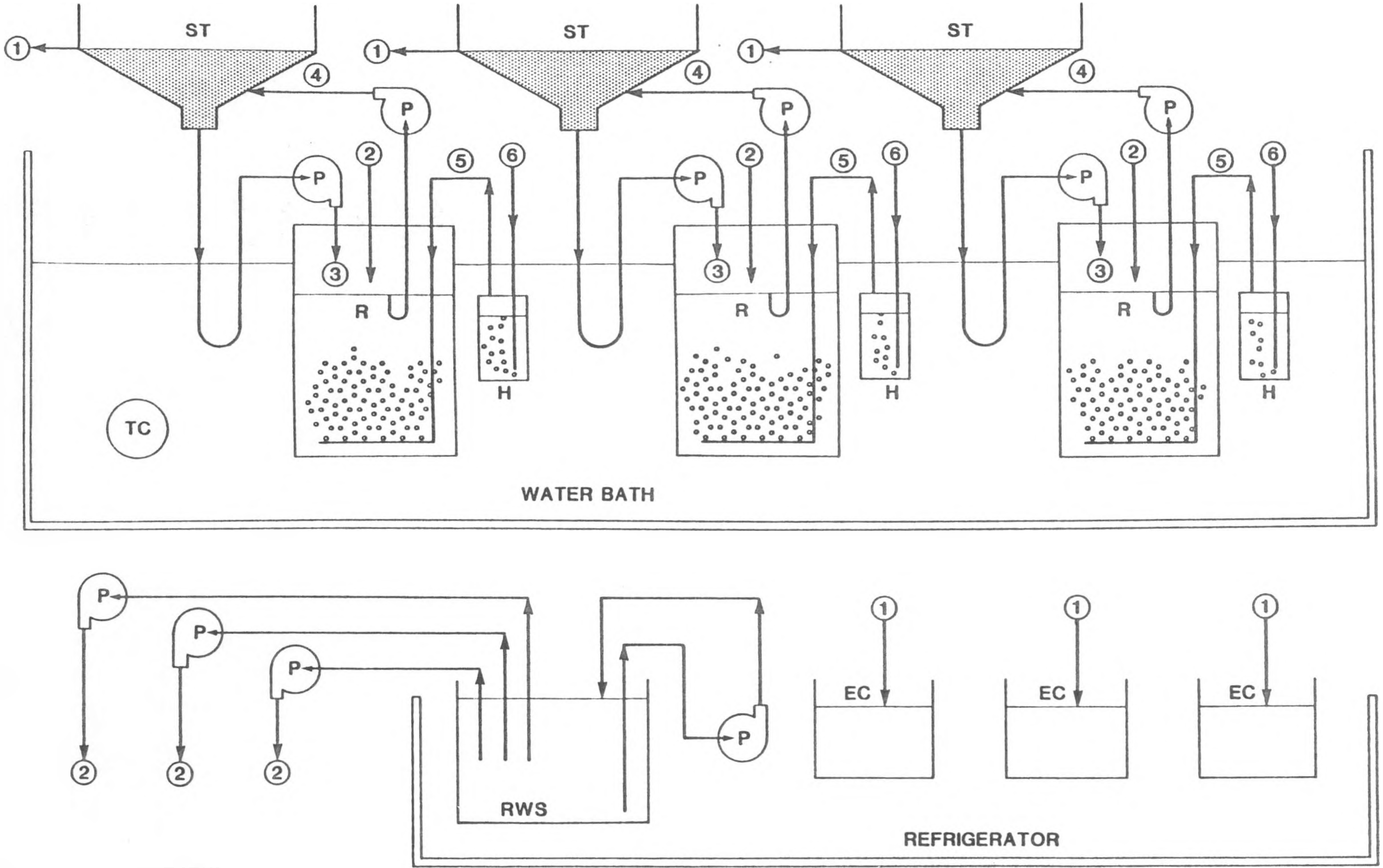
4.4.2 Experimental Apparatus and Procedure

Experimental Apparatus

Both the air and oxygen studies had the same experimental set up which is shown in Figure 4-16. Three activated sludge units were placed in a water bath and all experiments were conducted at 25°C. The volumes of reactors I, II, and III were 2.8 l, 3.0 l, and 2.25 l for the air activated sludge, and 2.7 l, 3.2 l, and 2.35 l for the oxygen activated sludge. The settling tanks, which had 40° sides, had volumes of 2.9 l. Pretreated retort water was used as feed influent. Weekly, 40 liters of retort water were prepared and stored in a refrigerated holding tank. All treated effluent water was continuously collected and stored in a refrigerated holding tank. The influent was constantly mixed to assure the uniformity of suspended solids in the substrate supplied. Influent, effluent and return sludge flow rates were proportioned to approximate steady state flow by the use of time controlled pumps.

Experimental Procedure

Each week a batch of the R-17 retort water was stripped of ammonia, filtered, pH adjusted, and then refrigerated. Samples of each batch were taken from the refrigerated feed influent, each of the reactors, and each clarifier, so that a mass balance could be established. These samples were



LEGEND

① Effluent from settling tank to effluent collectors (gravity)
② Influent from raw water storage to reactors (forced)
③ Recirculated sludge from settling tank to reactor (forced)
④ MLSS to settling tank (forced) controlling mixed liquor level in reactor
⑤ Air (or oxygen) from humidifier to reactor
⑥ Air (or oxygen) from air source to reactor

P	Pump
R	Reactor (enclosed)
H	Humidifier
ST	Settling tank
TC	Temperature control
EC	Effluent collector
RWS	Raw water storage

Figure 4-16. Experimental activated sludge apparatus

taken at the start and end of every run, along with effluent samples which were collected every other day. All samples were refrigerated prior to analysis. The sludge attached to the walls of the reactors was washed down and resuspended on a daily basis. The length of a run varied from 3 to 6 days. This sampling procedure was chosen to minimize the effects of raw water quality variation from batch to batch. As stated in section 4.1, the quality of the R-17 retort water fluctuated from barrel to barrel. This water quality fluctuation in the influent made a steady state difficult to establish, and mass balances hard to evaluate.

4.4.3 Equations

Using average values of the measured parameters balances were established using the following equations. All the terms used in the following equations are defined in Appendix 4.

1. Concentration of MLVSS:

$$X_R = \frac{X_i^R + X_{i+1}^R}{2} \qquad (4\text{-}1)$$

2. Concentration of substrate in the reactor:

$$L_R = \frac{L_i^R + L_{i+1}^R}{2} \qquad (4\text{-}2)$$

3. Sludge retention time (SRT) or mean cell residence time:

$$\Theta_c = \frac{V_R X_R}{Q(X_{EF} - X_{IN}) + V_{S.T.}(X_{i+1}^{S.T.} - X_i^{S.T.})/t} \qquad (4\text{-}3)$$

4. Net specific sludge growth rate:

$$\mu = \frac{1}{\Theta_c} \qquad (4\text{-}4)$$

5. Sludge growth rate:

$$\frac{X}{t} = \mu X_R \tag{4-5}$$

6. Substrate utilization rate:

$$\frac{S}{t} = \frac{V^R(L_i^R - L_{i+1}^R) + V^{S.T.}(L_i^{S.T.} - L_{i+1}^{S.T.}) + V^{EF}(L_{IN} - L_{EF})}{V_R t} \tag{4-6}$$

7. Specific substrate utilization rate:

$$U = \frac{\frac{\Delta S}{\Delta t}}{X_R} \tag{4-7}$$

8. Run time:

$$t = \frac{24(D_{i+1} - D_i) + (T_{i+1} - T_i)}{24} \tag{4-8}$$

9. Flow rate through the treatment system:

$$Q = \frac{V^{EF}}{t} \tag{4-9}$$

10. Hydraulic residence time in reactor:

$$\Theta_H = \frac{V^R}{Q} \tag{4-10}$$

11. Food-to-microrganism ratio:

$$\frac{F}{M} = \frac{L_{IN}Q}{V^R X_R} \tag{4-11}$$

12. Nominal treatment efficiency:

$$E_n = \frac{L_{IN} - L_{EFF}}{L_{IN}} \times 100\% \qquad (4\text{-}12)$$

13. Overall treatment efficiency:

$$E_o = \frac{\left(\frac{s}{t}\right) V^R \ t}{V^R L_i^R + V^{S.T.} L_i^{S.T.} + V^{EF} L_{IN}} \times 100\% \qquad (4\text{-}13)$$

14. The oxygen uptake rate (OUR) was measured from the slope of the dissolved oxygen curve as a function of time, in mg/(1)(min).

15. Specific oxygen uptake rate i.e. OUR per unit concentration of MLVSS

$$OUR' = \frac{OUR(1440)}{X_R} \qquad (4\text{-}14)$$

16. Oxygen consumption per unit sludge produced:

$$OC_M = \frac{OUR'}{\frac{\Delta X}{\Delta t}} \qquad (4\text{-}15)$$

17. Oxygen consumption per unit substrate utilized:

$$OC_F = \frac{OUR'}{\frac{\Delta s}{\Delta t}} \qquad (4\text{-}16)$$

18. The Monod type coefficients were found from:

$$\mu = YU - k_d \qquad (4\text{-}17)$$

and

$$\frac{1}{u} = \frac{K_s}{k} \frac{1}{L^R} + \frac{1}{k} \qquad (4\text{-}18)$$

19. Oxygen consumptions per unit weight of MLVSS per day were approximated by:

$$OUR' = U + bk_d \tag{4-19}$$

20. Specific sludge resistance was measured using a Buchner funnel and Wathman No. 1 filter paper under a vacuum of 15.4" Hg. The viscosity of a filtrate was assumed to be equal to 1 centipoise. During filtration the time to vacuum break was measured. The relationship used:

$$\frac{t}{v} = c(V) - d \tag{4-20}$$

while the specific resistance was calculated as:

$$r = 4.274 \times 10^8 \; \frac{C}{(MLSS)} \left(\frac{sec^2}{g}\right) \tag{4-21}$$

4.4.4 Analytical Procedures

All analyses were performed according to Standard Methods for the Examination of Water and Wastewater, 14th edition[7], except measuring specific resistance of sludge. The routine measurements included:

1. Temperature of water bath and reactors
2. Volumes of reactors and effluent
3. pH of influent, reactors and effluent
4. BOD in reactors, settling tanks, influent and effluent
5. Suspended solids and volatile suspended solids in influent, effluent, reactors and settling tanks
6. COD in influent, reactors, settling tanks and effluent
7. TOC in influent, reactors, settling tanks and effluent
8. Time of each run

4.4.5 Experimental Results

BOD and COD Relationship in the Activated Sludge Process

The average BOD_5 and COD concentrations for a number of test runs are summarized in Table 4.19. These data represent sampling dates when both BOD_5 and COD analyses were run on a given sample, and valid data collected. The data indicated that the influent retort water had an average BOD_5 concentration of 3,830 mg/l, average COD concentration of 9,103 mg/l, and a

TABLE 4.19

BOD AND COD CONCENTRATIONS FOR SHALE OIL RETORT WATER USING ACTIVATED SLUDGE TREATMENT

AIR ACTIVATED SLUDGE

INFLUENTS			EFFLUENTS		
BOD_5 (mg/l)	COD (mg/l)	DATE	BOD_5 (mg/l)	COD (mg/l)	REACTOR NO.
3413	8570	2/16	-	-	-
4810	9858	2/23	858	6905	1
		2/28	2875	8222	2
		2/23	995	8859	3
4618	9290	3/02	-	-	1
		3/02	3379	7457	2
		3/02	1842	8624	3
3925	9897	3/09	1006	7000	1
		3/09	2150	7170	2
		3/09	1522	8019	3
4100	9302	3/15	-	-	
4173	9383	AVG. CONC.	1828	7782	
		OXYGEN ACTIVATED SLUDGE			
2800	7384	7/10	548	5905	1
		7/10	1230	6536	2
		7/10	350	5020	3
3200	9330	7/13	820	7982	1
		7/13	840	8008	2
		7/13	305	6997	3
4200	-	7.19	638	8008	1
		7/19	1290	8676	2
		7/19	330	6997	3
3900	8493	7/25	570	-	1
		7/25	1500	-	2
		7/25	405	-	3
3700	9806	7/31	570	-	1
			1260	-	2
			730	-	3
3,560	8,753	AVG. CONC.	730	7084	
3,830	9,103	TOTAL AVG CONC. FOR INFLUENT			

COD/BOD ratio equal to 2.38.

The effluent data for the first phase of the activated sludge study in which air was used as the oxygen supply showed an average BOD_5 concentration of 1,828 mg/l, average COD concentrations of 7,782 mg/l and a COD/BOD ratio of 4.26. The average BOD removal was 56 percent, and average COD removal was only 17 percent using air activated sludge.

During the second phase of the activated sludge study, when pure oxygen was used in the aeration tanks the average BOD_5 effluent concentration was 730 mg/l, the COD effluent concentration was 7084 mg/l, and the COD/BOD ratio was 9.84. The average BOD removal was 80 percent and COD removal 19 percent.

These values are average concentrations and do not represent optimum treatment conditions; however, the high residual COD concentrations in the effluent indicated that COD was not necessarily the best parameter to use for the measurement of the process performance. The data listed in Table 4.19, is plotted in Figure 4-17. The line of best fit, were calculated using the least squares method. The data indicates that the BOD to COD correlation is rather poor for both influent ($r = 0.64$) and effluent ($r = 0.40$) values. The data also shows the high residual COD concentrations which remain after treatment.

In order to determine what portion of the shale oil retort water was biodegradable, a long term aeration experiment was conducted. Two (2) liters of the influent retort water were diluted to eight (8) liters to reduce any toxic effects and were seeded with acclimated activated sludge. The initial retort water had a COD concentration of 10,800 mg/l prior to dilution and 2,700 mg/l when diluted at the start of the experiment. The initial BOD_5 was approximately 4000 prior to dilution, and equivalent to 1000 mg/l when the experiment started. The COD concentrations are plotted in Figure 4-18. Following six months of aeration,the final COD was 1,650 mg/l while the resulting BOD_5 was 22 mg/l. This long term aeration experiment indicated that even when 98 percent of the BOD_5 was removed, approximately 50 percent of the initial COD remained as residual.

The results agree with the data plotted in Figure 4-17, which indicated that even with better BOD removals, 5,000 mgCOD/l residual remained in the effluent samples. Because of the large COD effluent residuals, BOD_5 concentrations were selected as the best parameter to measure biological treatment using activated sludge.

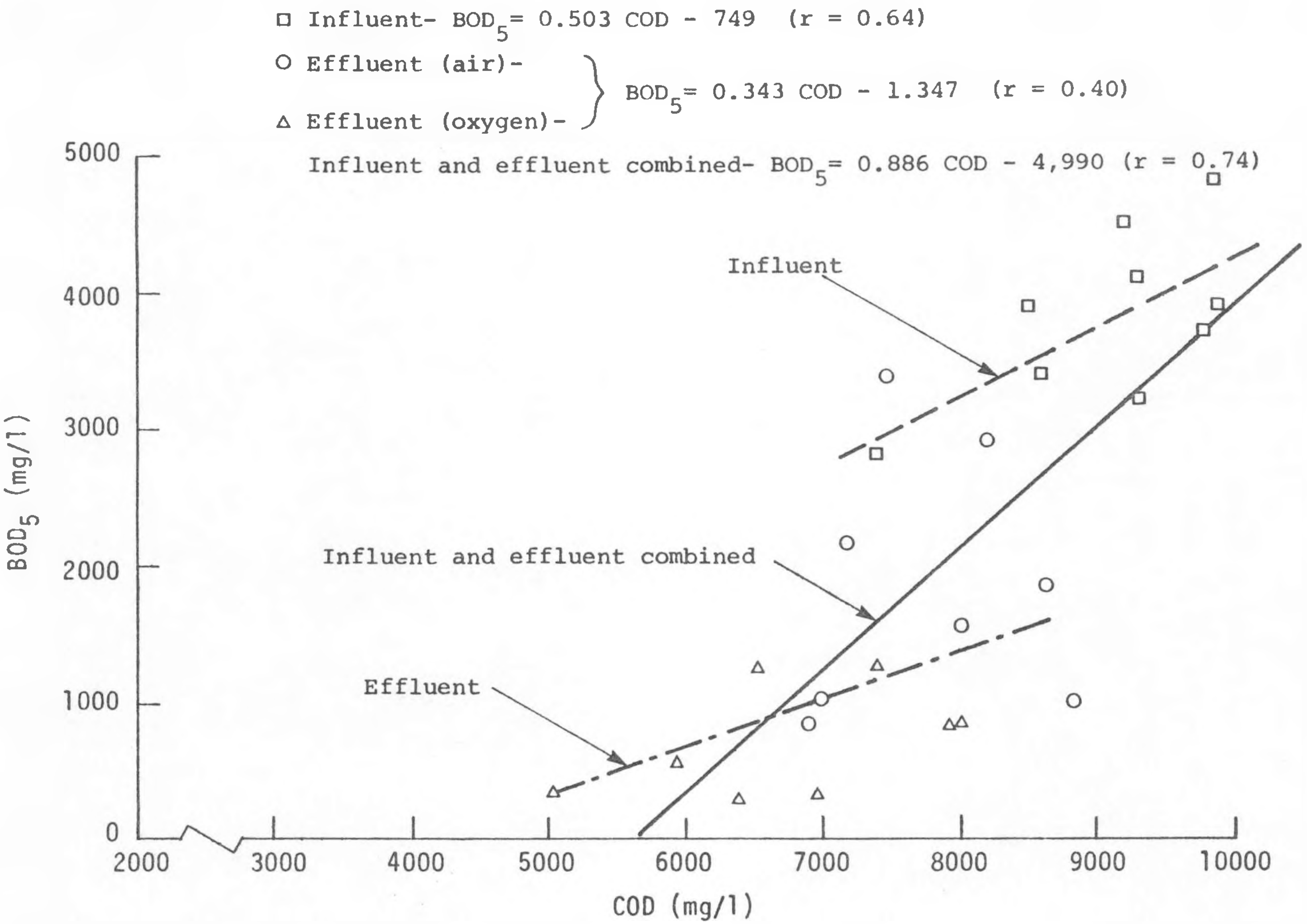


Figure 4-17. BOD_5 and COD correlation for shale oil retort water.

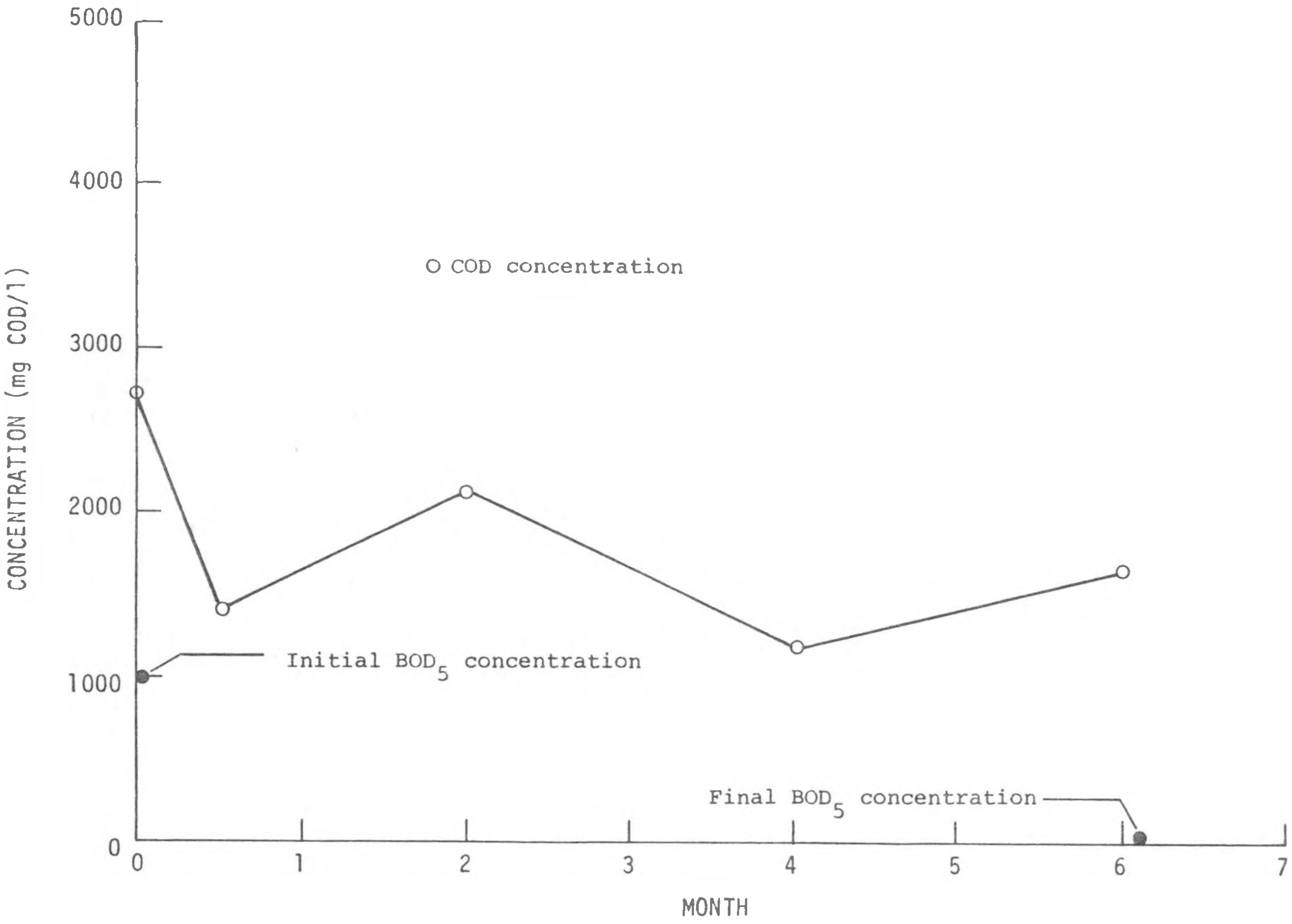


Figure 4-18. Long term aeration results using a 4:1 dilution of influent retort water.

Treatment Performance

Phase 1 - Air Activated Sludge Study

The BOD_5 influent and average effluent concentrations are shown in Figure 4-19. These results are from phase 1 of the study when the activated sludge units used air for both mixing and oxygen supply The effluent BOD_5 concentration varied from a low of 250 mg/l to a high of 2,875 mg/l depending on the mode of operation.

In addition to BOD_5, the ultimate BOD (BOD_L) concentrations were evaluated for selected influent and effluent concentrations. These results are listed in Table 4.20. The reactors with MLVSS concentrations ranging between 950 mg/l to 1,500 mg/l, and hydraulic residence time (HRT) of two (2) days or less produced equal effluents in terms of BOD_L. The reactor with the highest MLVSS and HRT produced the lowest BOD_L concentration (1,520 mg/l).

The BOD reaction rate k_e, (see Reference 15 for detailed definition) varied between influent and effluent, and there was not a general trend in terms of k_e variation between influent and effluent samples. The previously reported COD/BOD ratios do increase with biological treatment as is expected, BOD_L concentrations are reduced with treatment, while k_e values vary. This indicates that complex intermediate biochemical reactions were being carried out in the reactors and complete oxidation of BOD was not obtained using air activated sludge.

The incomplete oxidation of the shale oil retort water, and intermediate bio-oxidations can be seen using the data plotted in Figure 4-20. The graph of BOD_5 removal vs F/M ratio shows a decline in BOD_5 removal at both high and low F/M ratios. However, in an activated sludge system the highest BOD_5 removals should be obtained at the lowest F/M ratios. With BOD_L values, the lowest F/M ratios did show the maxium BOD removal.

Four observations may thus be summarized as follows:

1.) BOD_L and BOD_5 removals do not agree at both high and low F/M ratios,

2.) COD/BOD_5 ratios follow the expected trend commonly observed with activated sludge systems,

3.) k_e values in some of the effluent samples increased when compared to influent samples,

4.) BOD_L removals increased with lower F/M ratios.

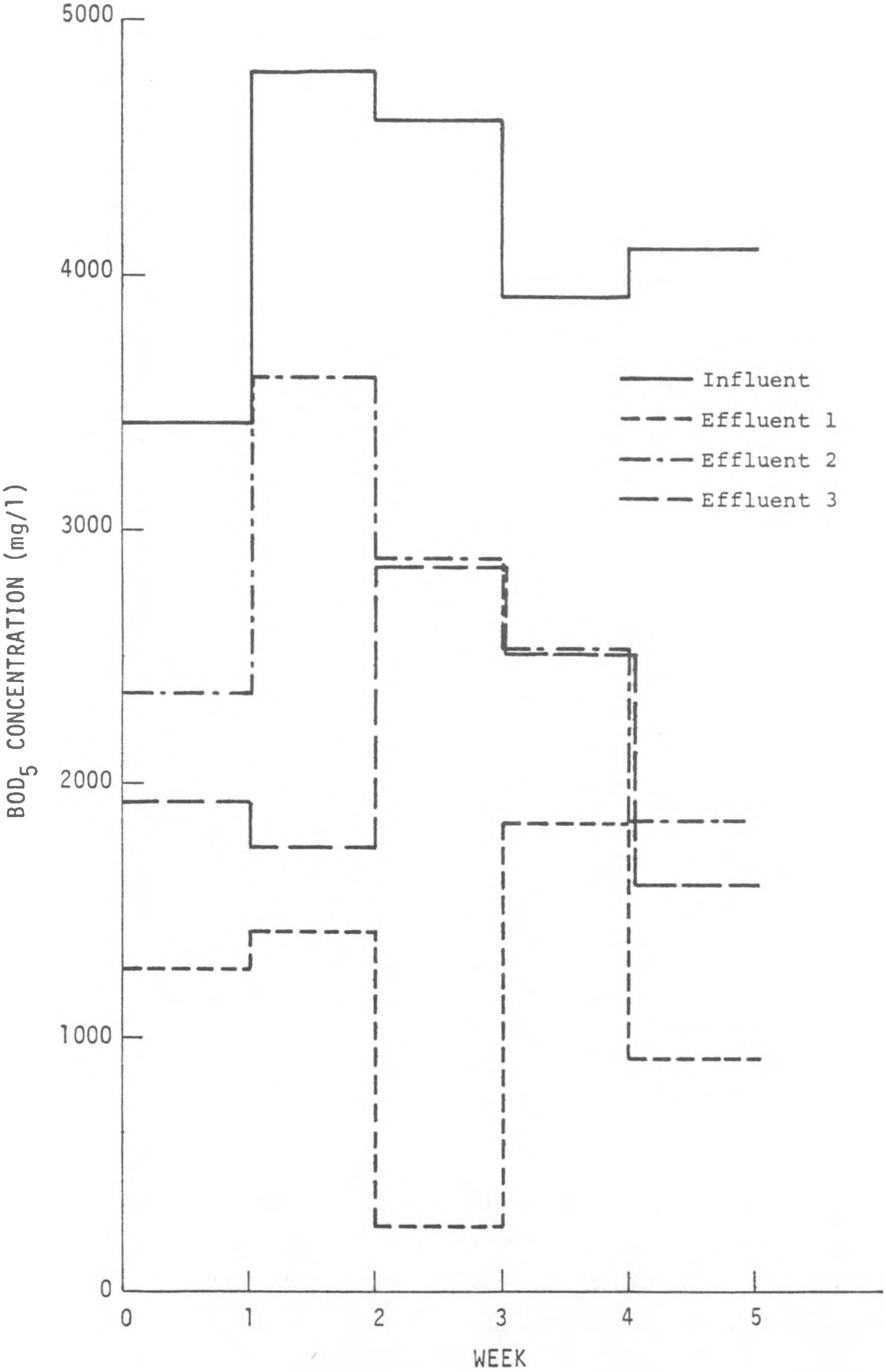


Figure 4-19. BOD concentration as a function of time for activated sludge study using air.

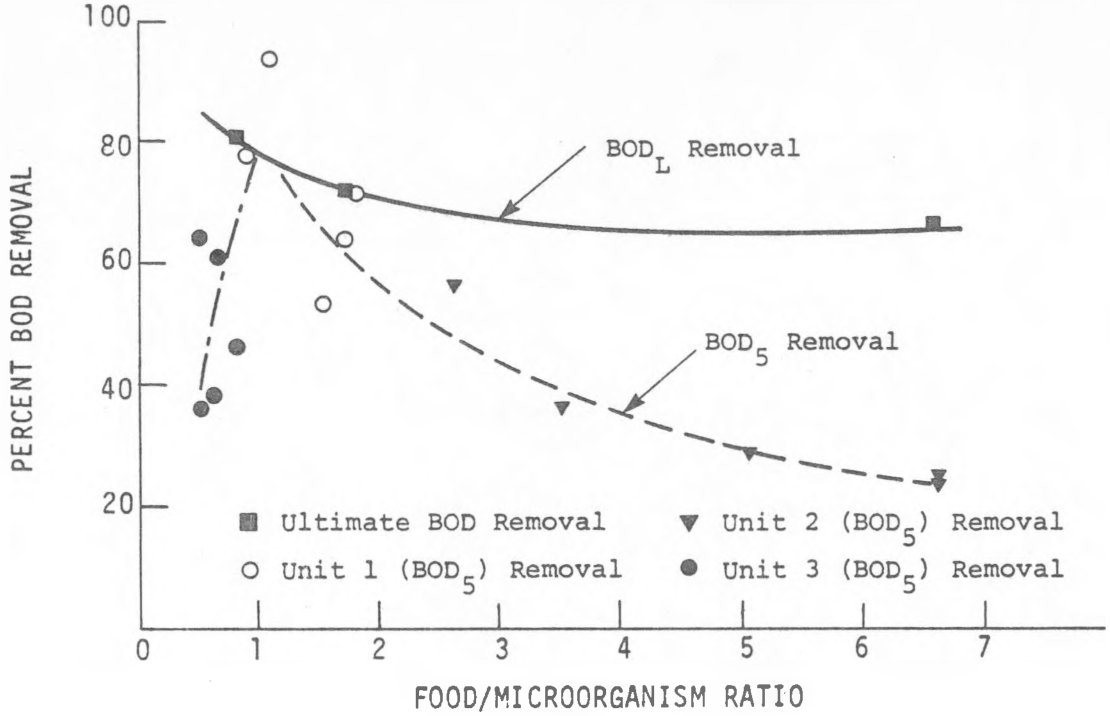


Figure 4-20. Percent BOD removal as a function of food to microorganism ratio

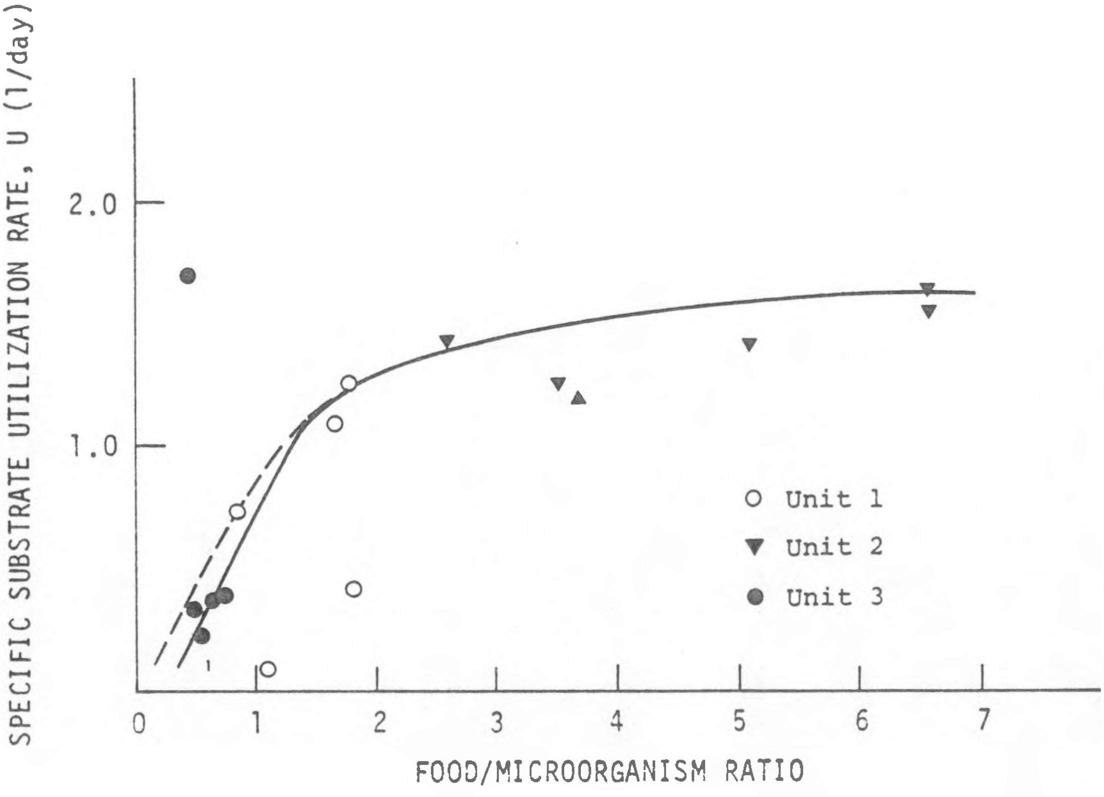


Figure 4-21. Specific substrate utilization as a function of food to microorganism ratio

TABLE 4.20

ULTIMATE BOD CONCENTRATIONS AND SELECTED TREATMENT PARAMETERS FOR SHALE OIL RETORT WATERS USING AIR ACTIVATED SLUDGE TREATMENT

	REACTOR 1	REACTOR 2	REACTOR 3	INFLUENT
SRT, θc, (days)	6	3.5	30	-
HRT, θ, (days)	2	1	3.6	-
MLVSS (mg/l)	1,500	950	2,500	-
k_e (day^{-1})	0.10	0.20	0.19	0.12
BOD_L (mg/l)	2,580	2,750	1,520	7,500
% BOD_L REMOVAL	66	63	80	-
F/M RATIO	1.73	6.57	0.79	-

These observations indicate that BOD_L will give the best evaluation of shale oil retort water treatment with the air activated sludge process. If only BOD_5 values are used variations caused by increases in the k_e values and intermediate substrate formation under different treatment conditions will interfere with correlation.

The summary of other treatment parameters is given on Table 4.21. The data plotted in Figure 4-21 indicated an increasing substrate utilization rate up to an F/M ratio of 2.0 As F/M increased above 2 the substrate utilization rate reached a relatively constant value of approximately 1.5/day. The upper limit was probably imposed by oxygen limitation associated with the high F/M ratios in an air activated sludge system.

In-situ measurements of dissoved oxygen concentrations remained below 2 mg/l throughout the air activated sludge study period. When the concentration of oxygen in the reactor is below 1 mg/l, oxygen-limiting conditions can exist. Due to the enclosed nature of the biological reactor, and cyclic mode of operation, exact measurements of dissovled oxygen concentrations in the mixed liquors were not possible. However, the indication that the reactors were anoxic at high F/M ratios is also supported by the decline in sludge growth rate at F/M values above 2.0 (Figure 4-22). Additional air supply was not possible, due to excessive foaming within the aeration tank which caused the biomass to be pushed out of the tank.

Phase 2 - Oxygen Activated Sludge Study

During the oxygen activated sludge study, O_2 gas was used as both the source of oxygen and for mixing. The higher oxygen transfer produced excess dissolved oxygen in the biological reactors. Although the oxygen flow was set to the minimum value which assured a uniform suspension of all the solids in the reactors the average concentration of dissolved oxygen in the reactors was in a range of 15 mg/l throughout phase 2. Low intensity of aeration eliminated foaming and promoted formation of heavier, settling flocs.

The time variation of BOD_5 for the influent and effluent of reactors 1, 2 and 3 for the pure oxygen process is shown in Figure 4-23. Influent BOD_5 concentrations ranged from 4,200 to 2,900 mg/l, while the effluent BOD_5 concentrations ranged from 1,500 mg/l to 300 mg/l. The nominal treatment efficiency (from Equation (4-12)) is shown in Figure 4-24 and the overall treatment efficiency (from Equation (4-13)) is shown in Figure 4-25. The

TABLE 4.21

SUMMARY OF TREATMENT PARAMETERS FOR AIR ACTIVATED SLUDGE

WEEK	F/M RATIO (d^{-1})	PERCENT BOD_5 REMOVAL	MEAN CELL RESIDENCE TIME Θ_c (d)	SPECIFIC SUBSTRATE UTILIZATION RATE U (d^{-1})	SLUDGE GROWTH RATE $\frac{\Delta x}{\Delta t}$ (mg/(l) (d)
UNIT 1					
1	1.73	63	5.2	1.08	159
2	1.13	85	5.1	1.07	283
3	6.58	25	3.3	1.64	184
4	0.74	54	9.1	0.39	199
5	0.91	78	8.3	0.71	223
UNIT 2					
1	6.57	24	3.5	1.55	123
2	5.11	28	3.2	1.41	260
3	0.51	64	21.0	0.33	82
4	3.50	36	5.6	1.26	208
5	2.58	56	3.8	1.44	350
UNIT 3					
1	0.79	43	19.8	0.35	86
2	1.78	71	4.0	1.26	267
3	0.47	38	51.0	0.18	37
4	0.58	37	35.8	0.22	56
5	0.63	61	17.0	0.38	124

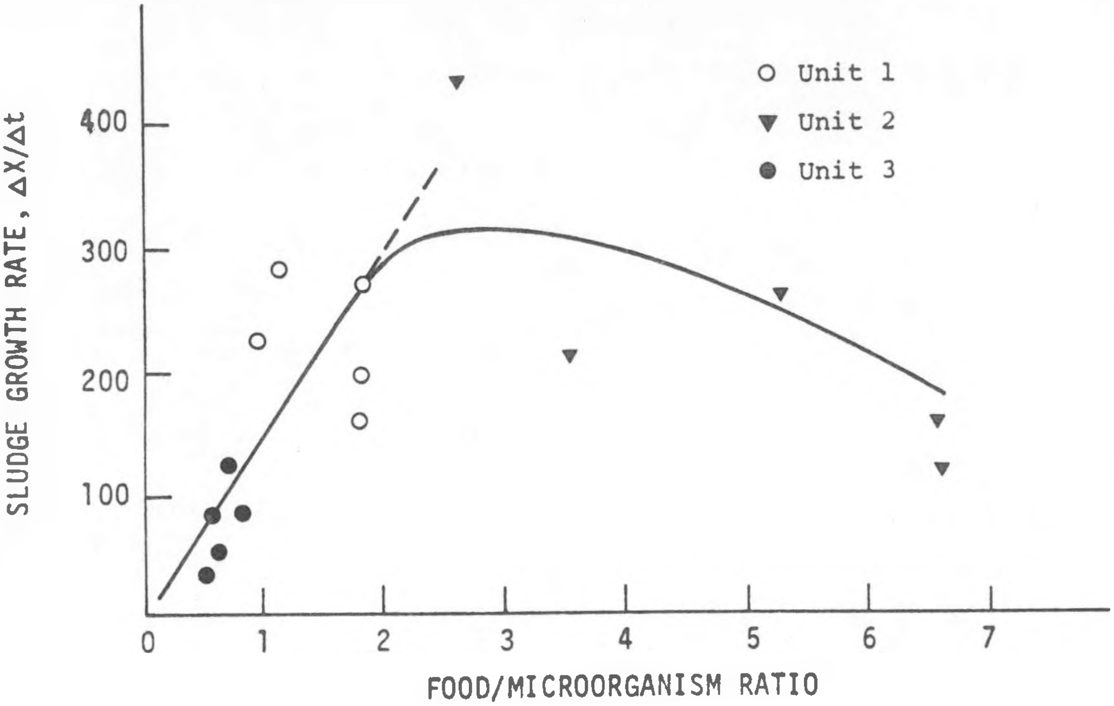


Figure 4-22. Sludge growth rate as a function of food to microorganism ratio.

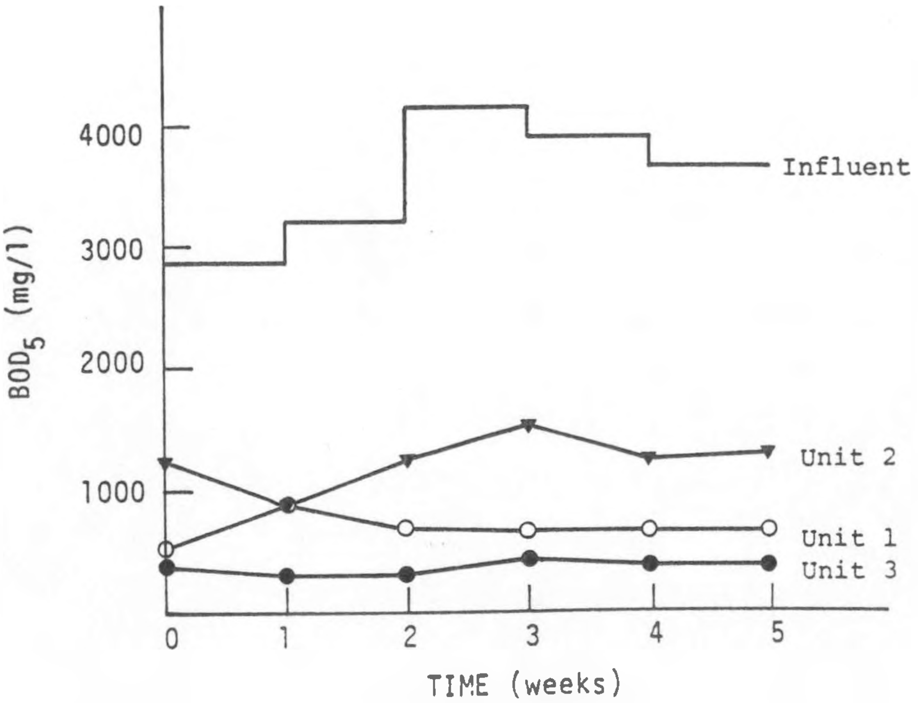


Figure 4-23. BOD_5 of influent and effluent for reactors 1,2, and 3-oxygen activated sludge.

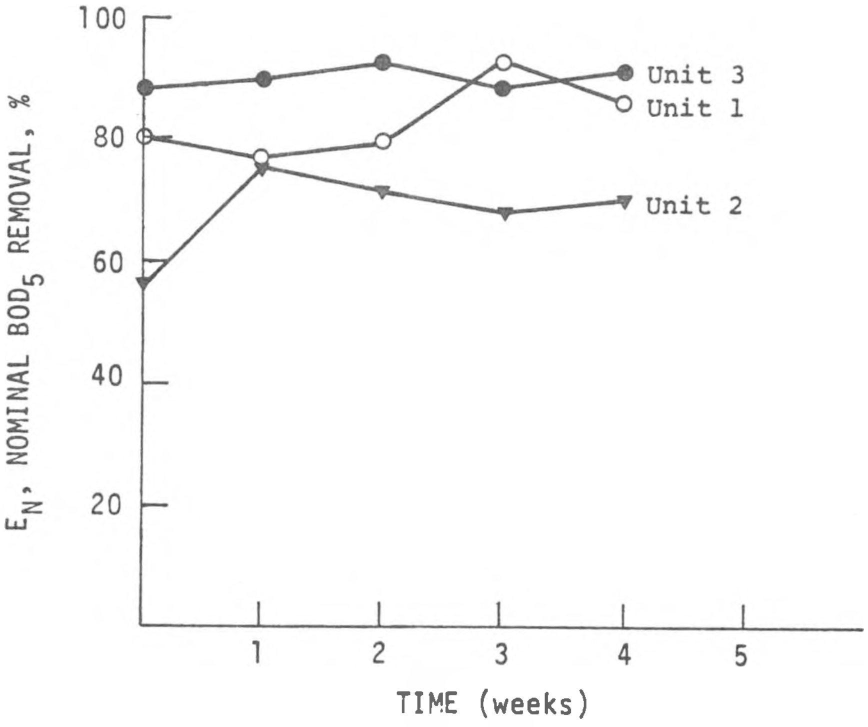


Figure 4-24. Nominal BOD_5 removal from equation (4-12)- oxygen activated sludge

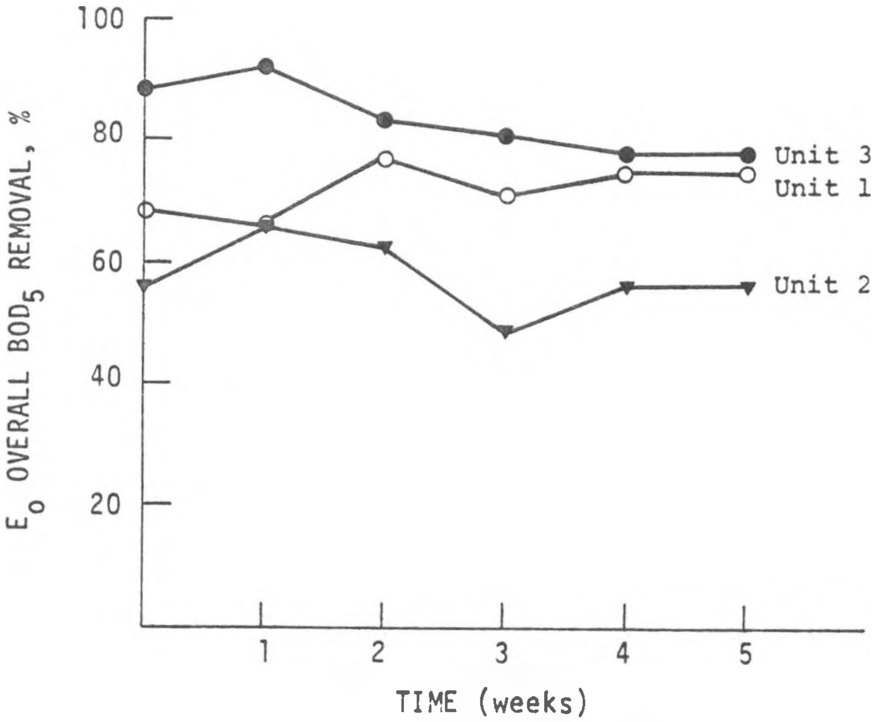


Figure 4-25. Overall BOD_5 removal from equation (4-13)- oxygen activated sludge

data indicate that despite the variation in the strength of the influent the quality of the effluent remained stable and overall BOD_5 removal was consistently higher than that reached with air activated sludge.

BOD_5 removals by oxygen activated sludge with F/M ratios between 0.6 to 2.2 are plotted in Figure 4-26. This F/M range represents a practical organic loading for oxygen systems. The nominal BOD_5 removal efficiencies for F/M ratios between 1.0 and 2.0 ranged from 80 to 60 percent. These were similar to the BOD_5 removals for air activated sludge. For F/M ratios below 1.0, the BOD_5 removals appeared to increase to above 80 percent, however oxygen activated sludge systems are seldom designed at the lower F/M ratios.

BOD_5 and BOD_L removal for air activated sludge (Figure 4-20) was the same as oxygen activated sludge for F/M ratios of 1 to 2.

The data plotted in Figure 4-27 indicated that the correlation between F/M and U up to 1 mg BOD_5/(mg MLVSS)(d) was a linear relationship approximating a 45^o slope. This indicates that for the pure oxygen process the removal of BOD_5 supplied will be mostly complete for F/M ratios below one. In addition, the comparison of the data presented in Figure 4-27 to similar data for air plotted in Figure 4-21, indicate that the specific substrate utilization rates were the same for F/M ratios up to about 2.

Data plotted on Figures 4-28 and 4-22 indicate that there is no significant difference between air and oxygen aeration in terms of waste sludge production for systems working with the same F/M ratios (0.5 to 2.0).

Throughout phase 2 (oxygen activated sludge) the value of the F/M ratio did not increase above 2.2, despite the fact that shorter hydraulic residence times were used in this phase of the study. As both the substrate utilization rate and sludge growth rates were the same in both systems for F/M ratios between 0.5 to 2.0. The oxygen supply and sludge foaming problems appear to be the major design considerations for the treatment of retort water by activated sludge processes. If aerobic condition can be maintained in the aeration tank then a F/M design loading of 2 appears feasible.

pH

In order to minimize the effect of pH on the treatment process the influent was adjusted to pH 7 as described in section 4.2. The pH results are presented in Figures 4-29 and 4-30. The pH in the reactor increased during the air aeration experiment to values above 7.0, while during the oxygen aeration the pH increase was substantially lower. No correlation of

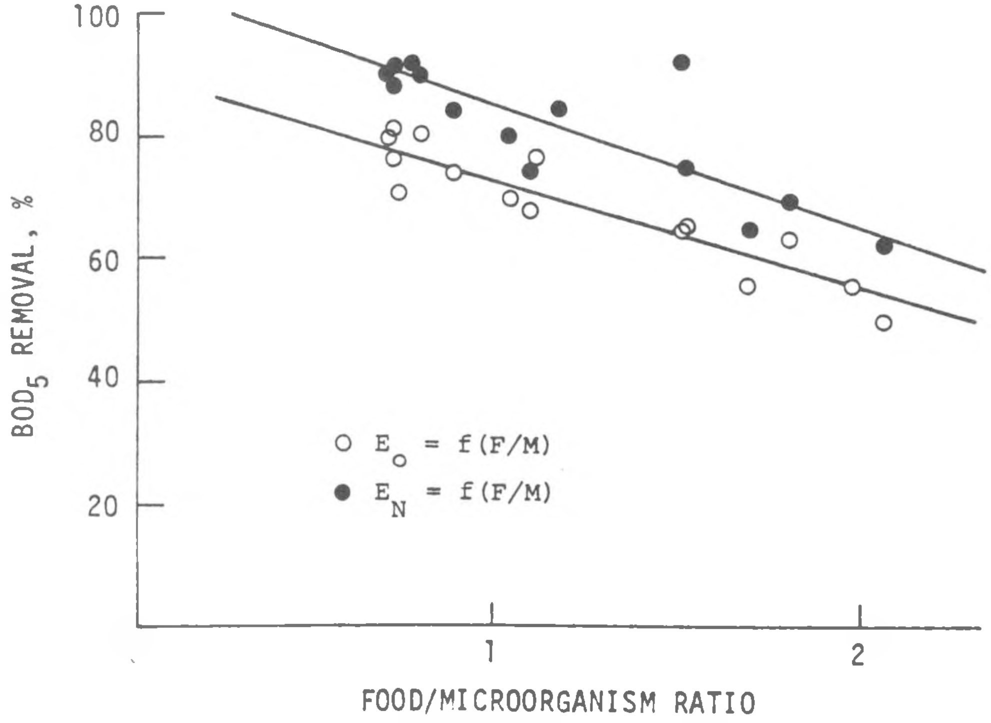


Figure 4-26. BOD_5 removal as a function of food to microorganism ratio- oxygen activated sludge

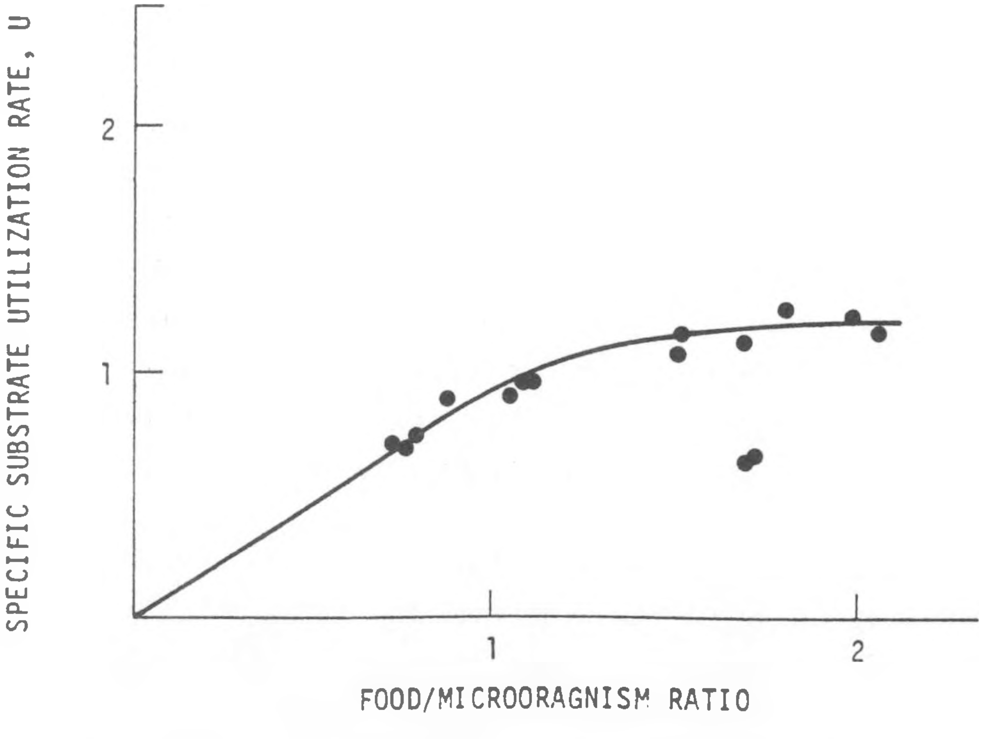


Figure 4-27. Specific substrate utilization rate as a function of food to microorganism ratio- oxygen activated sludge

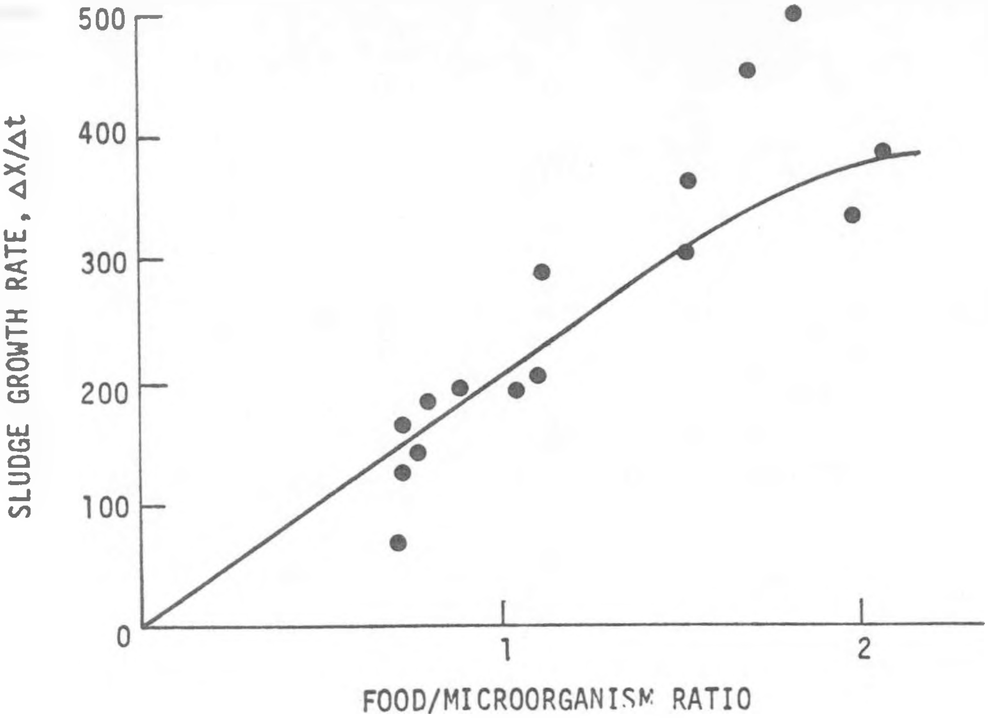


Figure 4-28. Sludge growth rate as a function of food to microorganism ratio- oxygen activated sludge

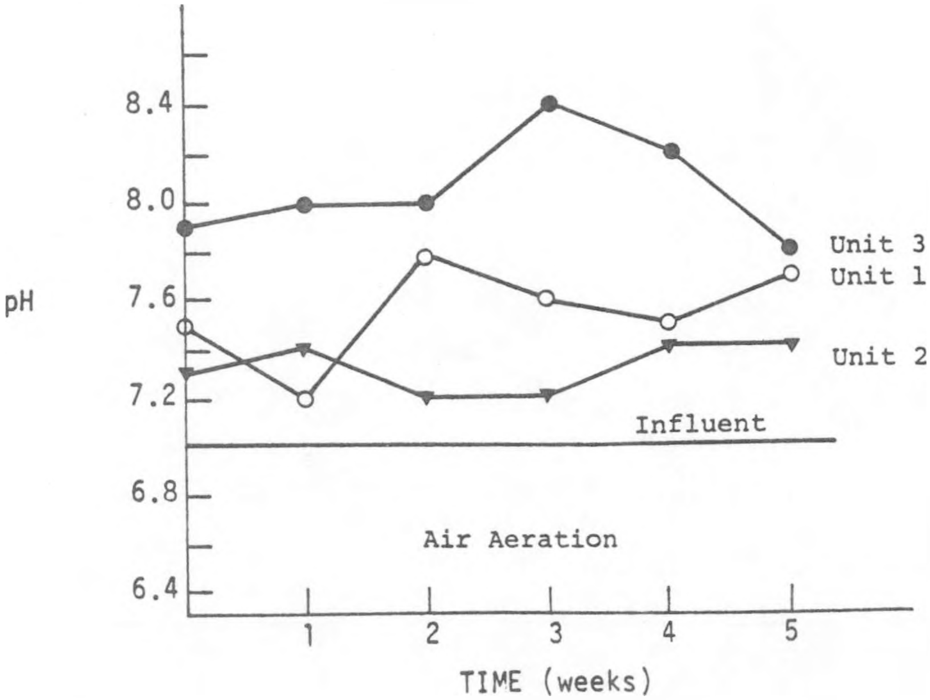


Figure 4-29. Variation of pH in reactors using air for aeration.

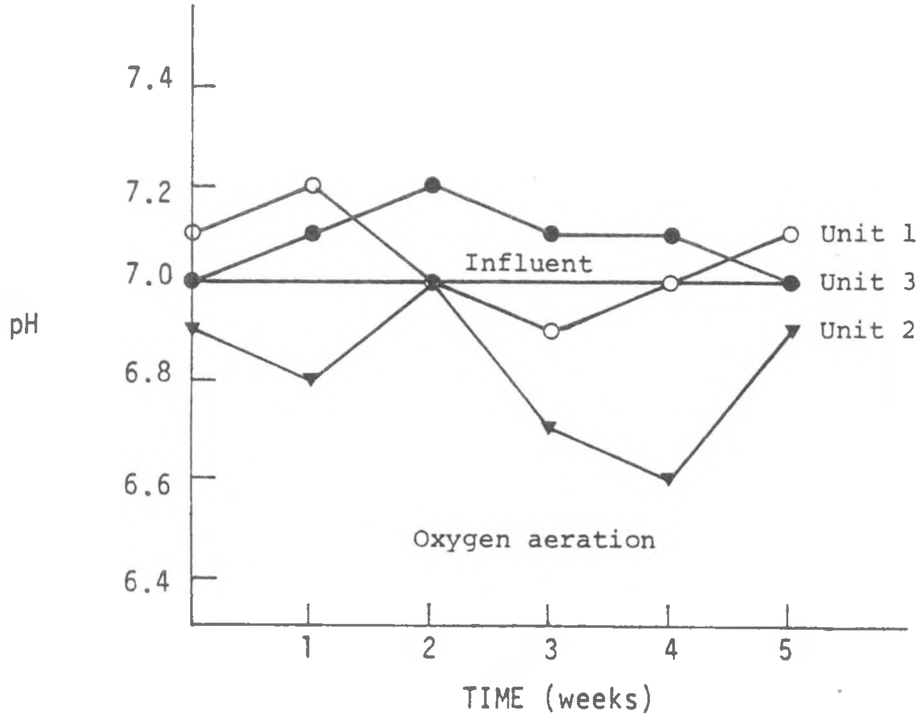


Figure 4-30. Variation of pH using pure oxygen for aeration.

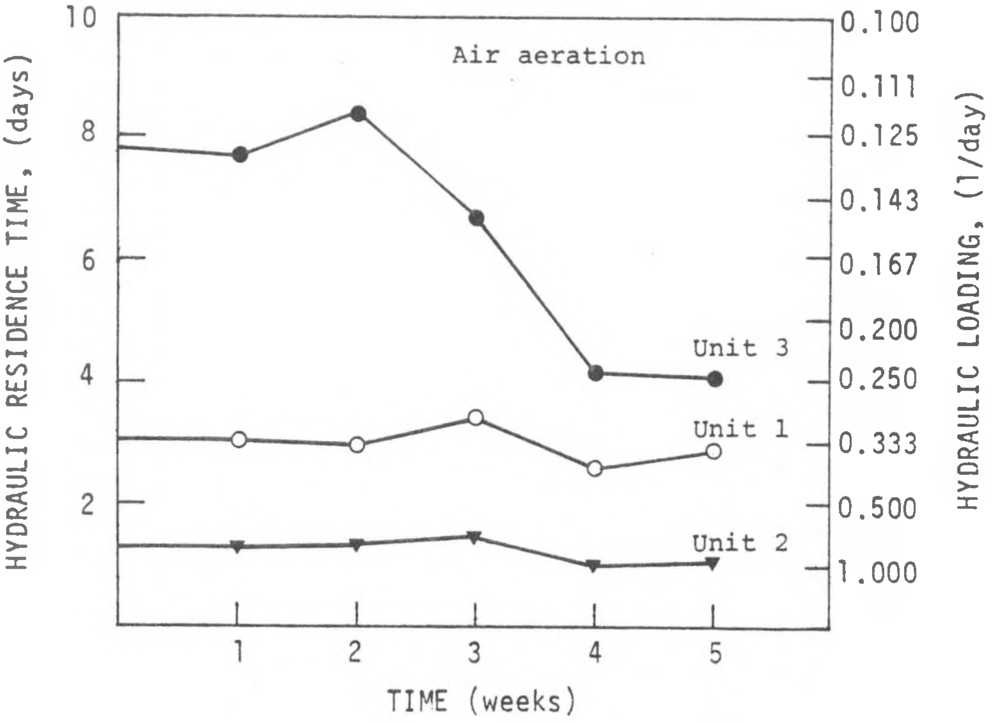


Figure 4-31. Hydraulic residence time and hydraulic loading for reactors 1, 2, and 3 during air aeration.

pH with any other parameter was established.

Loading Rates

Throughout this study the characteristics of the influent and influent supply rate were kept constant for a given run. The other parameters varied and were averaged for the duration of a run (i.e, for 3 or 6 days). Hydraulic loading was kept fairly constant while the loading of BOD per unit of volume of reactor and per unit weight of MLVSS per day varied. These variations may be encountered in the actual treatment plant operation.

The plots of hydraulic loadings vs. time are shown on Figures 4-31 and 4-32. The results indicate, that except for reactor 3 during the air aeration phase, hydraulic loading in a given reactor was essentially constant.

Oxygen Consumption

The concentration of dissolved oxygen in the reactors during the period when air was used as the source of oxygen, was low. In order to measure the oxygen up take rate (OUR), a sample of mixed liquor was taken from a reactor and saturated with pure oxygen at the start of the OUR measurement. The OUR measured by this method is only an estimation. The figures obtained were averaged. These averaged results and corresponding substrate utilization rates are presented in Table 4.22, and the oxygen requirements per unit weight of BOD_5 removed are calculated.

TABLE 4.22

OXYGEN CONSUMPTION IN AIR ACTIVATED SLUDGE SYSTEM

REACTOR	$\Delta S/\Delta t$ (mg/(l)(d))	OUR (mg/(l)(min))	mg O_2/mg BOD_5 removed
1	0.95	1500	1.096
2	1.5	2400	1.111
3	0.65	1000	1.068

The dissolved oxygen concentrations changed drastically when pure oxygen was used. The concentration of dissolved oxygen in all the reactors never dropped below 15 mg/l which made measurement of OUR easy and reliable. The data obtained during this period are shown in Table 4.23.

In an aeration tank oxygen is consumed for two purposes, namely for oxidation of the BOD and for endogenous respiration. It is not known how total oxygen consumed is distributed between these two tasks and what is the

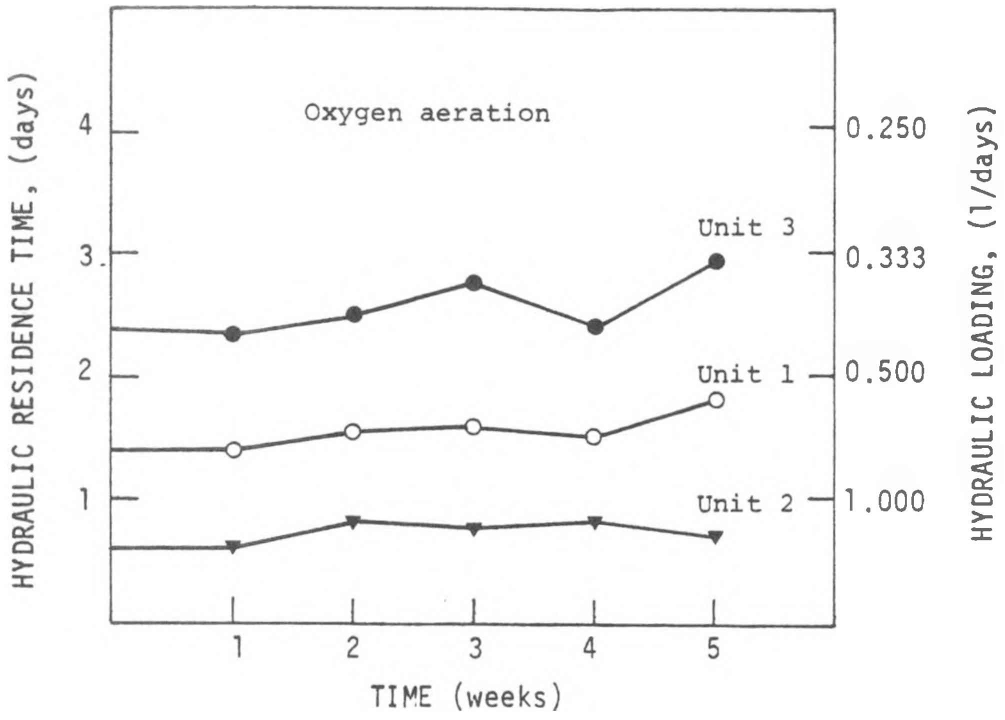


Figure 4-32. Hydraulic residence time and hydraulic loading for reactors 1,2, and 3 during pure oxygen aeration.

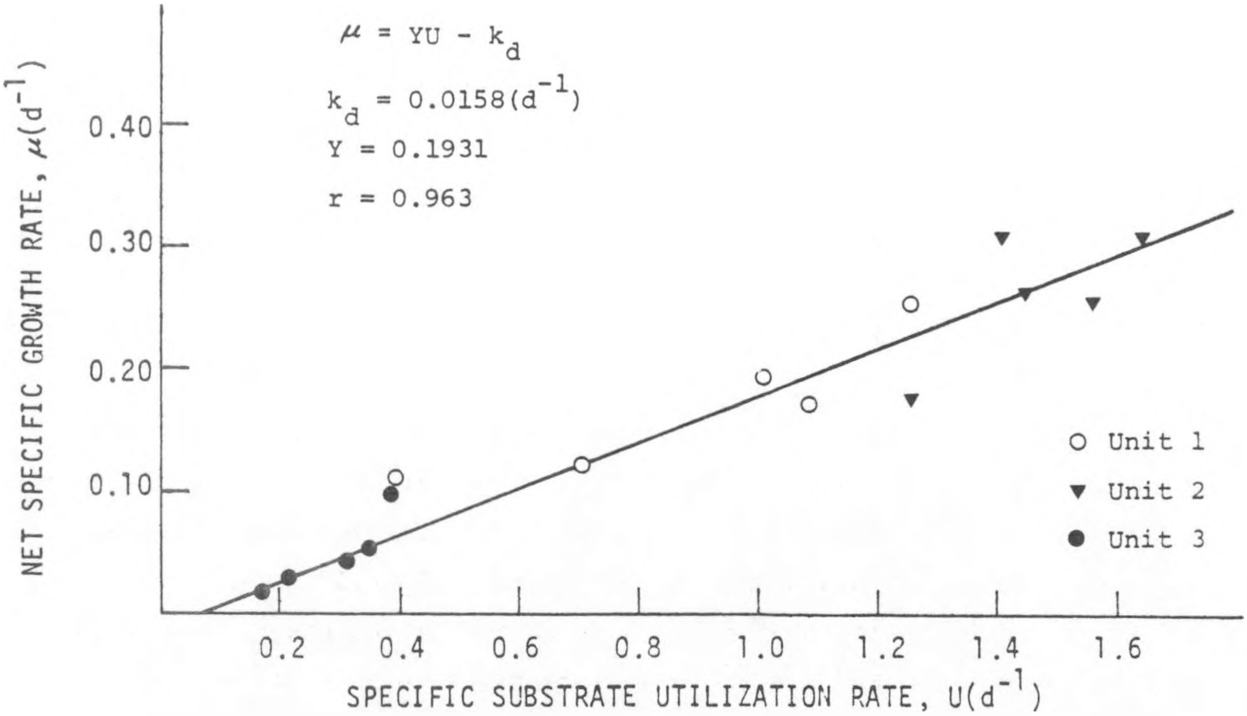


Figure 4-33. Net specific growth rate as a function of specific substrate utilization for air aeration activated sludge units.

TABLE 4.23

OXYGEN CONSUMPTION IN OXYGEN ACTIVATED SLUDGE SYSTEM

	REACTOR 1			REACTOR 2			REACTOR 3		
WEEK	u*(d^{-1})	OUR'(d^{-1})	mg O_2/mg BOD_5 removed	u*(d^{-1})	OUR'(d^{-1})	mg O_2/mg BOD_5 removed	u*(d^{-1})	OUR'(d^{-1})	mg O_2/mg BOD_5 removed
1	0.886	1.014	1.144	1.235	1.396	1.130	0.700	0.824	1.177
2	0.940	1.064	1.132	1.156	1.243	1.075	0.640	0.752	1.175
3	0.945	1.042	1.103	1.255	1.309	1.043	0.655	0.768	1.172
4	1.062	1.101	1.037	1.155	1.204	1.042	0.720	0.830	1.153
5	0.875	1.018	1.163	1.115	1.183	1.061	0.675	0.785	1.163

*U = specific substrate utilization rate order of each reaction. A number of publications suggest a linear model of zero order[9,10,11]. Such a model was tried in this case. The data obtained were analyzed to see how well they fit Equation (4-19). The coefficient "a" was found to be 0.933 and coefficient "b" was found to be 5.34. The correlation coefficient was r = 0.988, indicating a high degree of fit for this type of substrate and activated sludge.

Specific Sludge Resistance

One of the important considerations of biological treatment is sludge production and sludge treatability. The biological sludge required long settling times (sometimes longer than the aeration period) and very low overflow rate in the clarifiers, in order to prevent sludge washout. Because of the dispersed nature of sludge, parameters such as settleability or sludge volume index were poor. The specific resistance of a thickened sludge was chosen as the sole parameter to evaluate the ability of sludge to give up water. At the termination of the activated sludge studies, the mixed liquor from all three units was tested for specific resistances. Each sludge was thickened prior to testing. Results are presented in Table 4.24.

TABLE 4.24

SPECIFIC RESISTANCE OF ACTIVATED SLUDGE

REACTOR	SLUDGE CONCENTRATION (g/l)	VOLUME OF SLUDGE (ml)	C (EQUATION (4-20))	r (EQUATION (4-21)) (sec^2/g)
1	31.24	135	0.5957	8.15
2	35.61	200	0.1425	1.71
3	27.15	120	1.0947	17.23

These results show that these sludges are similar to typical activated sludge as reported in the literature[15]. It also appears that the longer the sludge retention time (from 3.5 to 30 days) the larger is the specific resistance to filtration type dewatering.

4.4.6 Model Coefficients

The results for air activated sludge are shown on Table 4.25. On the assumption that the Monod model is applicable the results were plotted according to Equations (4-17) and (4-18) on Figures 4-33 and 4-34. The calculations

TABLE 4.25

SUMMARY OF TREATMENT PARAMETERS FOR AIR ACTIVATED SLUDGE

DATE OF RUN	UNIT NUMBER	H.R.T. θ_H (days)	SLUDGE AGE, θ_c (days)	MLVSS, X (mg/l)	BOD_5 IN REACTOR, S (mg/l)	μ (1/day)	U (1/day)	1/U (day)	1/S (1/mg)
2/16 - 2/23	1	3.00	5.2	928	319	0.171	1.08	0.92	0.00319
2/16 - 2/23	2	1.37	3.5	430	1500	0.258	1.55	0.64	0.00067
2/16 - 2/23	3	7.81	19.8	1698	262	0.051	0.38	2.87	0.00381
2/23 - 3/ 2	1	2.99	3.9	1045	520	0.256	1.26	0.79	0.00192
2/23 - 3/ 2	2	1.38	3.3	600	2630	0.306	1.64	0.61	0.00038
2/23 - 3/ 2	3	8.97	21.3	1792	223	0.047	0.33	3.04	0.00448
3/2 - 3/ 9	1	3.39	5.1	1450	408	0.195	1.07	0.93	0.00245
3/2 - 3/ 9	2	1.40	3.2	840	3090	0.310	1.41	0.71	0.00032
3/2 - 3/ 9	3	7.14	50.7	1900	125	0.020	0.18	5.66	0.00797
3/9 - 3/15	1	2.67	9.1	1812	139	0.110	0.39	2.54	0.00719
3/9 - 3/15	2	1.04	5.6	1175	1665	0.177	1.26	0.79	0.00050
3/9 - 3/15	3	4.13	35.8	2000	115	0.028	0.50	4.56	0.00877
3/15 - 3/22	1	2.79	8.3	1858	142	0.120	0.71	1.42	0.00702
3/15 - 3/22	2	1.09	3.8	1650	943	0.262	1.44	0.69	0.00106
3/15 - 3/22	3	4.06	17.0	2105	58	0.059	0.38	2.60	0.01724

were based on five day BOD values. Because of the variations in the relationship between ultimate BOD and five day BOD for the various reactors, the values of k and K_s are not well defined. The calculated coefficients for growth yield and decay are:

$$k_d = 0.0158(d^{-1}); \quad Y = 0.1931$$

with correlation coefficient, r = 0.963.

Figure 4-34 illustrates some of the various ways in which the values of K_s and k could be determined. For all 15 data points in Table 4.25 the values for the coefficients are:

$$k = 1.03 \text{ (day}^{-1})$$

and

$$K_s = 206 \text{ (mg/l BOD}_5)$$

with a correlation coefficient, r = 0.62.

If four points from reactor 3 are discarded then the values for the same coefficients are

$$k = 1.52 \text{ (day}^{-1}) \text{ and } K_s = 85 \text{ (mg/l BOD}_5)$$

with a correlation coefficient r = 0.895.

The results of the oxygen aeration experiments are summarized in Table 4.26. The data listed in Table 4.26 are plotted in Figures 4-35 and 4-36. BOD_5 was also used as the basis for the mathematical model in this case. The variation in F/M ratio for the pure oxygen aeration was within a narrow range (0.70 to 2.06) so the results should be applied in the same range. As shown in Figures 4-35 and 4-36, coefficients for the oxygen activated sludge were calculated as: y = 0.16; k_d = 0.0307 (d^{-1}) with r = 0.915, while k = 1.51 and K_s = 370 mg/l with r = 0.938.

The model coefficients evaluted above are summarized in Table 4.27A. On Table 4.27B are shown similar coefficients for coke over wastewater and coal conversion wastewater for comparison.

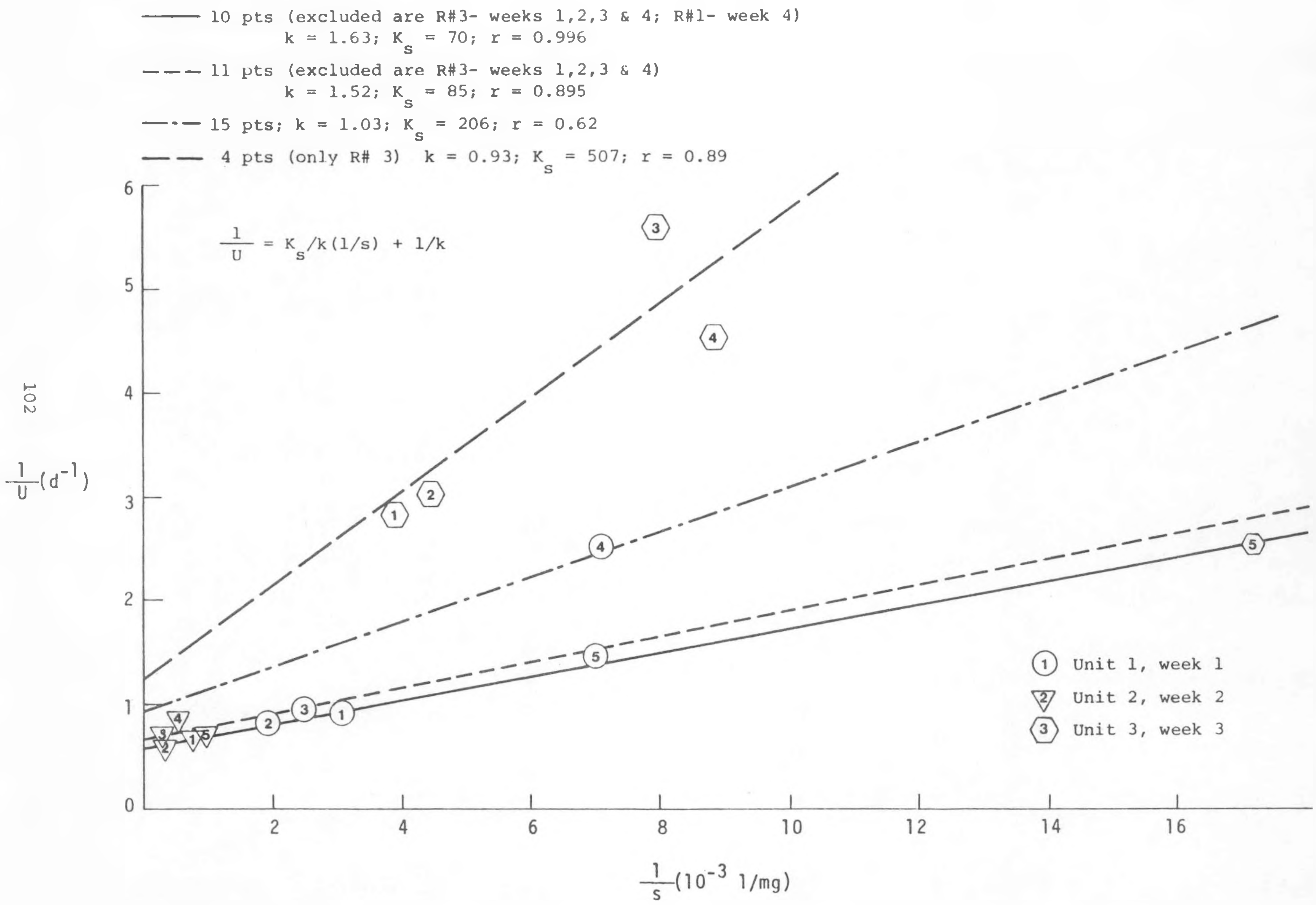


Figure 4-34. Plot of experimental data to determine K_s and k for air activated sludge units.

TABLE 4.26

SUMMARY OF TREATMENT PARAMETERS FOR OXYGEN ACTIVATED SLUDGE

DATE OF RUN	UNIT NUMBER	H.R.T. θ_H (days)	SLUDGE AGE, θ_c (days)	MLVSS, X (mg/l)	BOD$_5$ IN REACTOR, S (mg/l)	μ (1/day)	U (1/day)	1/U (day)	1/S (1/mg)
7/ 7 - 7/10	1	1.41	9.8	1905	578	0.102	0.89	1.13	0.00173
7/ 7 - 7/10	2	0.65	6.5	2175	1170	0.153	1.24	0.81	0.00085
7/ 7 - 7/10	3	235	13.3	1650	340	0.075	0.70	1.43	0.00294
7/13 - 7/16	1	1.55	9.3	1875	720	0.108	0.94	1.06	0.00139
7/13 - 7/16	2	0.82	7.1	2560	960	0.141	1.16	0.86	0.00104
7/13 - 7/16	3	2.50	13.2	1830	305	0.076	0.64	1.56	0.00328
7/19 - 7/23	1	1.60	8.2	2355	630	0.122	0.95	1.06	0.00159
7/19 - 7/23	2	0.79	5.9	2960	1250	0.169	1.25	0.80	0.00080
7/19 - 7/23	3	2.75	12.8	2120	315	0.078	0.66	1.53	0.00317
7/25 - 7/28	1	1.53	5.6	1690	458	0.180	1.06	0.95	0.00218
7/25 - 7/28	2	0.85	5.8	2225	1440	0.174	1.16	0.86	0.00069
7/25 - 7/28	3	2.40	11.1	2060	310	0.090	0.72	1.39	0.00322
7/31 - 8/3	1	1.81	11.7	2310	772	0.085	0.88	1.14	0.00129
7/31 - 8/3	2	0.71	6.6	3105	1200	0.150	1.12	0.89	0.00083
7/31 - 8/3	3	2.94	11.8	1665	285	0.085	0.68	1.48	0.00351

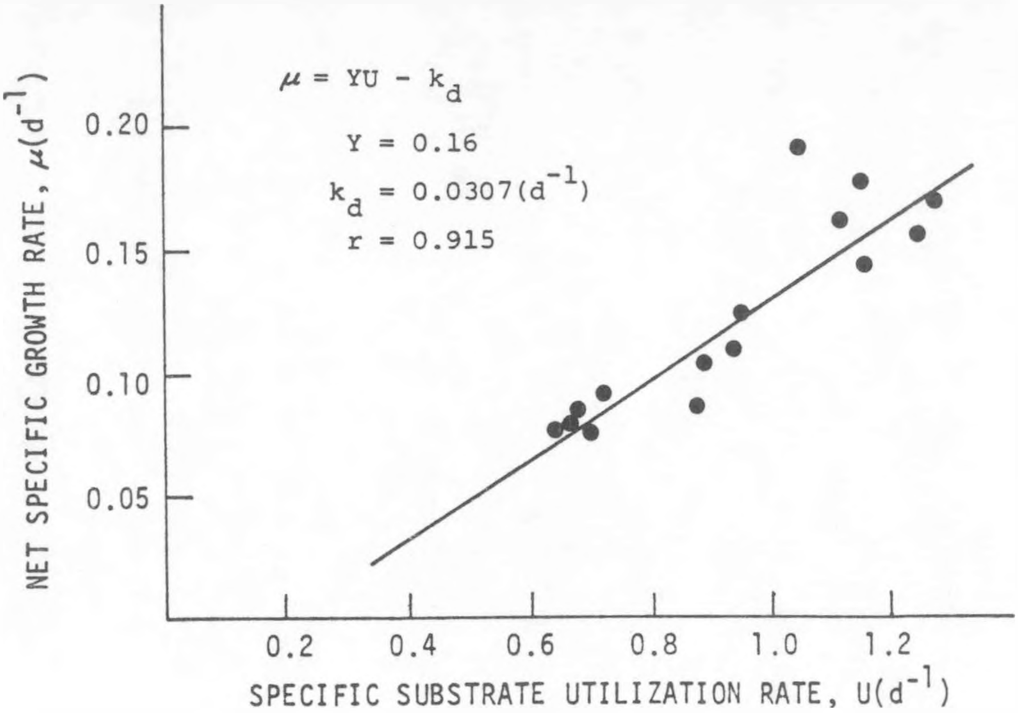


Figure 4-35. Net specific growth rate as a function of specific substrate utilization for pure oxygen activated sludge units.

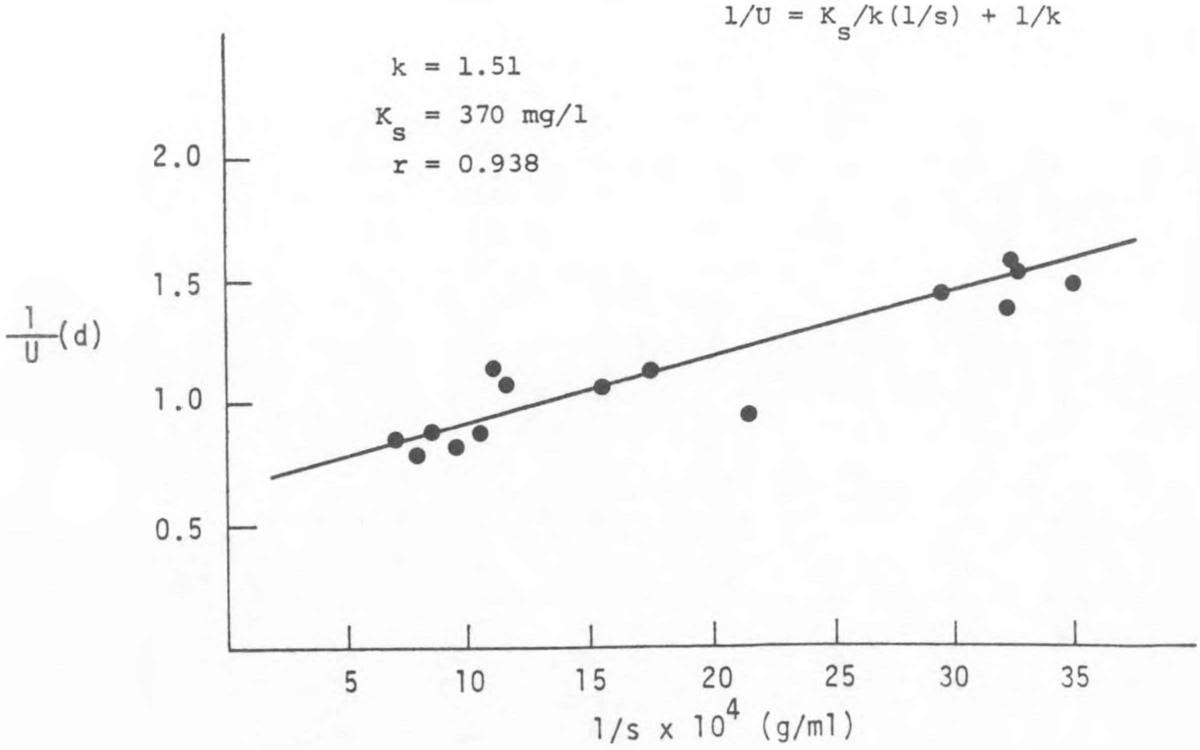


Figure 4-36. Plot of experimental data to determine K_s and k for pure oxygen activated sludge units.

TABLE 4.27A

MODEL COEFFICIENTS

	Air Activated Sludge	Oxygen Activated Sludge
k $\left(\frac{\text{mg BOD}_5}{\text{mg MLVSS} \cdot \text{day}}\right)$	1.03 - 1.52	1.51
K_s (mg/l BOD_5)	206 - 85	370
Y $\left(\frac{\text{mg MLVSS}}{\text{mg BOD}_5}\right)$	0.193	0.16
kd (day^{-1})	0.0158	0.0307
T °C	25	25
pH	7	7
Analysis		
BOD	3,300	3,300
COD	10,800	10,800

TABLE 4.27B

BIOKINETIC CONSTANTS

	Coke Oven Liquor	H-Coal Wastewater	Synthane Wastewater	Coal Gasification	Coal Liquefaction
k, g soluble BOD/g MLVSS day	1.8	∿ 0.3	∿ 1	0.46	0.39
K_s, mg BOD/l	0.34	∿ 30	∿ 266	5	14
Y, g VSS/g BOD processed	0.2	0.48	0.37	0.53	0.61
k_d, day^{-1}	0.17	0.03	0.033	0.02	0.02
T, °C	27-32	25	-	4	24
pH	-	-	-	neutral	7.5
Ref.	39	38	40	41	41
Analysis					
BOD mg/l	4,000-6,000	1,900-2,600	-	19,000	1,200
COD	7,000	3,100-4,200	5,700	13,000	1,500
Phenol	2,000	750-1,500	1,200	1,400	300

4.4.7 Conclusions

The results of the experiments show that

1. BOD_5 or, under certain circumstances, BOD_L should be used as the control parameter for the biotreatment of shale oil retort water. COD and probably TOC cannot serve the same purposes.
2. Approximately half of the COD in the retort water studied is non-biodegradable.
3. The retort water studied can be treated without dilution by an activated sludge process if pretreatment is provided to reduce ammonia concentration, neutralize pH, and supply adequate phosphorous nutrient.
4. Using an activated sludge process the concentration of BOD_5 of shale oil retort water can be reduced up to 80%. The nominal BOD_5 removal ranges from 80% to 60% corresponding to a food to microorganism ratio of 1.0 to 2.0.
5. Within the range of food to microorganism ratio from 0.5 to 2.0, no significant difference was observed between air and oxygen activated sludge systems in terms of soluble BOD removal efficiency, specific substrate utilization rate, sludge production, and oxygen consumption.
6. Use of oxygen in place of air appeared to improve the settleability of sludge, increase the stability of the activated sludge treatment, and decrease the pH in the bioreactor.
7. The process of biological treatment of shale oil retort water can be modeled by the Monod method.
8. Coefficients founds for the Monod type model are statistically sound and can be used for estimation of a number of treatment parameters such as:
    - sludge growth rate
    - BOD utilization rate
    - BOD of treated effluent
    - sludge age
9. Oxygen uptake rate can be estimated.
10. The results of sludge specific resistance test indicated that the sludges are similar to typical activated sludge.

4.5 Activated Sludge with Powdered Activated Carbon (PAC-AS)

4.5.1 Introduction

In the course of treating oil shale retort water with bench-scale activated sludge units it was found that while it was possible to remo up to 50% of the influent COD with an aeration time of a few days, one difficulty encountered was the highly-dispersed sludge that was not easily separated from the effluent. To solve this problem, attention was focused on powdered activated carbon (PAC) because of its potential as a weighting agent. Furthermore, PAC, with its superior adsorptive capacities, was thought to be able to remove pollutants in addition to those degraded by the activated sludge. Recent reports[12,13,14] on PAC added to activated sludge systems indicated that an effluent quality compatible with granular-carbon tertiary treatment was technically feasible and cost-effective when it was applied to various types of industrial wastewater such as oil refinery wastes and textile wastes. In those applications sludge settleability was also observed to improve with some, but not all, types of PAC.

Before conducting bench-scale, PAC-added activated sludge (PAC-AS) experiments on oil shale retort water, three objectives were specified:

(1) To determine the effectiveness of the PAC-AS system, specifically the removal efficiency of BOD_5, COD and TOC;

(2) To assess the dewatering characteristics of the resulting sludges.

As the study progressed and the results of a concurrent rotating biological contactor (RBC) process became available, the investigation was expanded to evaluate the treatment sequence of the RBC unit followed by the PAC-AS unit, and thus an additional objective was

(3) To investigate the combined effectiveness of the RBC-PAC-AS sequence. The dewatering properties of the resulting sludge would also be assessed.

4.5.2 The Wastewater and the Carbon

The wastewater was as described in section 4.1, pretreated as described in section 4.2

Many types of PAC were made available to us by manufacturers. The samples of PAC used in this study were chosen because of the specific surface area, the density, and their adsorption isotherms. After a preliminary screening four samples of PAC were selected for adsorption isotherm tests. They are shown in Table 4.28.

The results were summarized in Table 4.29 and plotted in Figure 4-37A using the Freundlich isotherm formula. The fitted line in Figure 4-37 resulted from a regression analysis of the data for AMOCO PX-21; this was done because one data point was found to be far off the line. AMOCO PX-21 was selected as the PAC for our experiments and more extensive adsorption isotherm test was run on AMOCO PX-21. The results are plotted in Figure 4-37B. The fitted values and the straight line shown in Figure 4-37B are also the results of a regression analysis.

4.5.3 Equipment and Procedure

Equipment

The treatment scheme shown in Figure 4-38 was used. It consisted of two sets of equipment run in parallel, one as control and the other with PAC addition. A schematic flow diagram of the continuous flow PAC-AS system is shown in Figure 4-39.

Unless otherwise noted, the following descriptions of the experimental apparatus apply to both systems. Peristalic pumps operated by 30-min cycle timers were used for the raw feed, return sludge, and PAC-slurry. All the pressure tubing for liquid delivery was made of Tygon. The raw water feed bottle was a glass container having a volume equivalent to a 5 day feed supply. From the feed bottle the feed retort water was pumped at a constant rate to the reactor which had an effective volume of 6.67 liters for the PAC-AS unit and 6.53 liters for the control unit. Air was supplied from a central air compressor. Also fed into the PAC-AS reactor was Type PX-21 PAC-slurry which came from a cylindrical container equipped with a timer-controlled mixing device. This device was used to ensure that the PAC-slurry was well mixed before it was pumped into the reactor. The settling unit had a volume of about 2 liters, from which the settled sludge was returned at a rate of about 1 liter/day, which was equivalent to a recirculation of about 55% on the average.

Start-up

The seed activated sludge was obtained from the Easterly Wastewater Treatment Plant, East Marlboro, Mass., where a combined municipal and industrial wastewater was being treated. Stripped retort water was mixed with a nutrient broth to ensure that the necessary nutrients were available.

TABLE 4.28

PAC SPECIFICATION*

PARAMETER	CALGON TYPE NAP	ICI TYPE HDC	AMOCO TYPE PX-21	WESTATE TYPE CC 601P
Surface Area (m^2/g, BET)	1,525	550	3,183	1,100-1,250
Bulk Density (g/cc)	-	-	0.30	.48-.52
Pore Volume (cc/g)	-	-	.15(>15^{o}A) 2.08(<10^{o}A)	.65
Tamped Density (g/ml)	-	.70	-	-
Iodine No.	1,265	-	2,933	-
Molasses No.	550	95	12	-
Ash (wt %)	15	-	-	-
Moisture (wt %)	2	5.5	-	3.0
CCl$_4$ Adsorption (wt %)	92	-	-	60.0
Screen size				
<#100 mesh, wt %	90	-	99.7	-
<#325 mesh, wt %	-	70	72.7	-
<#350 mesh, wt %	70	-	-	-
lb/ft.^{3}	-	44	-	30

---

*Information in this table were provided by the manufacturers.

TABLE 4.29

PAC-ADSORPTION ISOTHERM TEST RESULTS

1½ hr. mixing, pH = 7.0, T = 17°C

PAC DOSAGE (mg/l)	RESIDUAL TOC (mg/l)	TOC ADSORBED (mg/l)	X/M (mg TOC Adsorped /gm PAC)	REMARK
000	2,800	-	-	
500	2,600	200	400	Calgon
1,000	2,575	225	225	Type NAP
1,500	2,300	500	333	
2,000	2,125	675	337.5	
000	2,800	-	-	
500	2,575	225	450	ICI
1,000	2,400	400	400	Type HDC
1,500	2,350	450	300	
2,000	2,250	550	275	
000	2,800	-	-	
500	2,250	550	1,100	AMOCO
1,000	2,250	550	550	Type PX-21
1,500	2,000	800	533	
2,000	1,750	1,050	525	
000	2,800	-	-	
500	2,200	600	1,200	Westate
1,000	1,950	850	850	Type CC 601P
1,500	1,900	900	600	(coconut
2,000	1,900	900	450	shell)

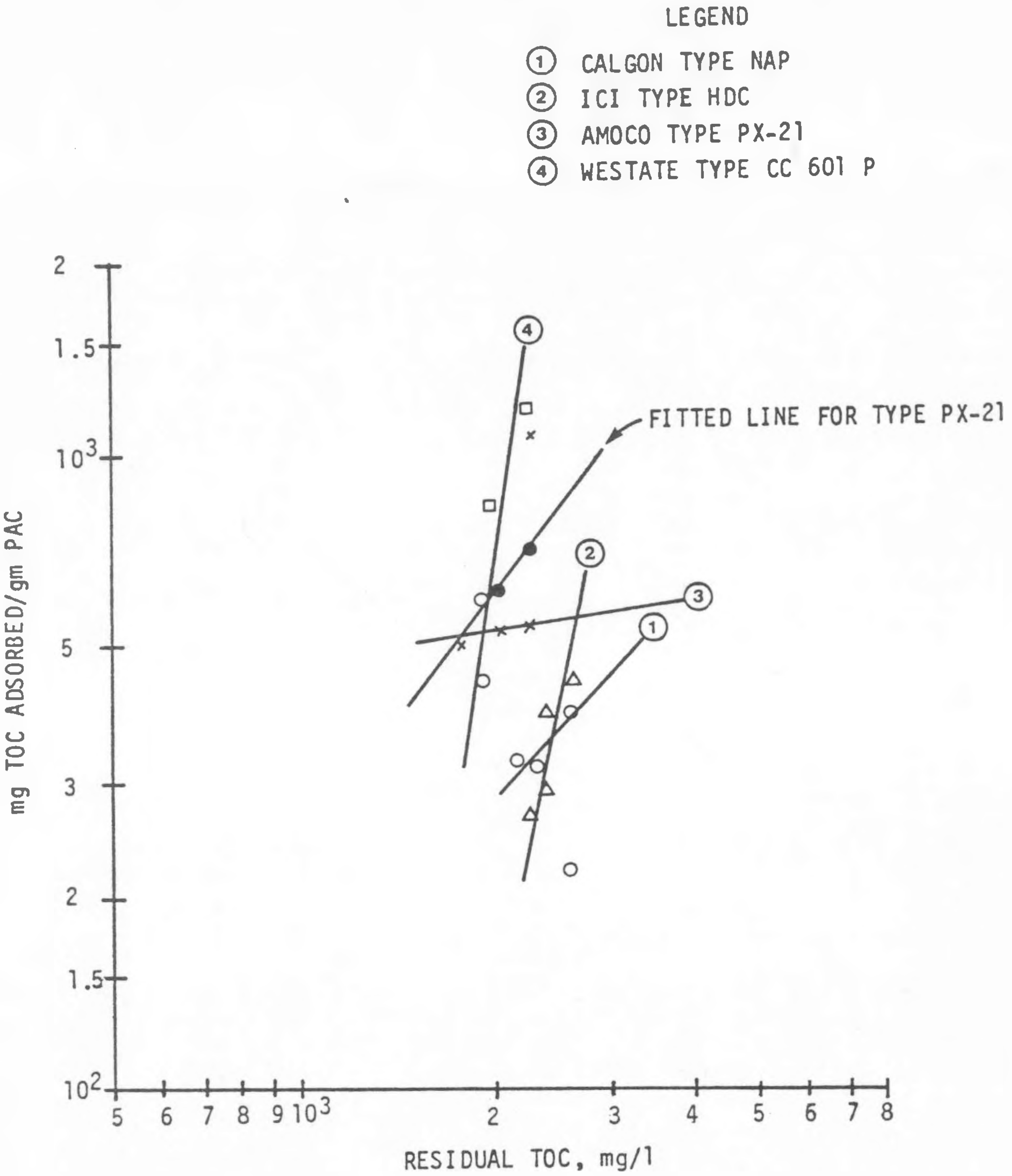


Figure 4-37A. Freundlich Isotherms for four types of PAC.

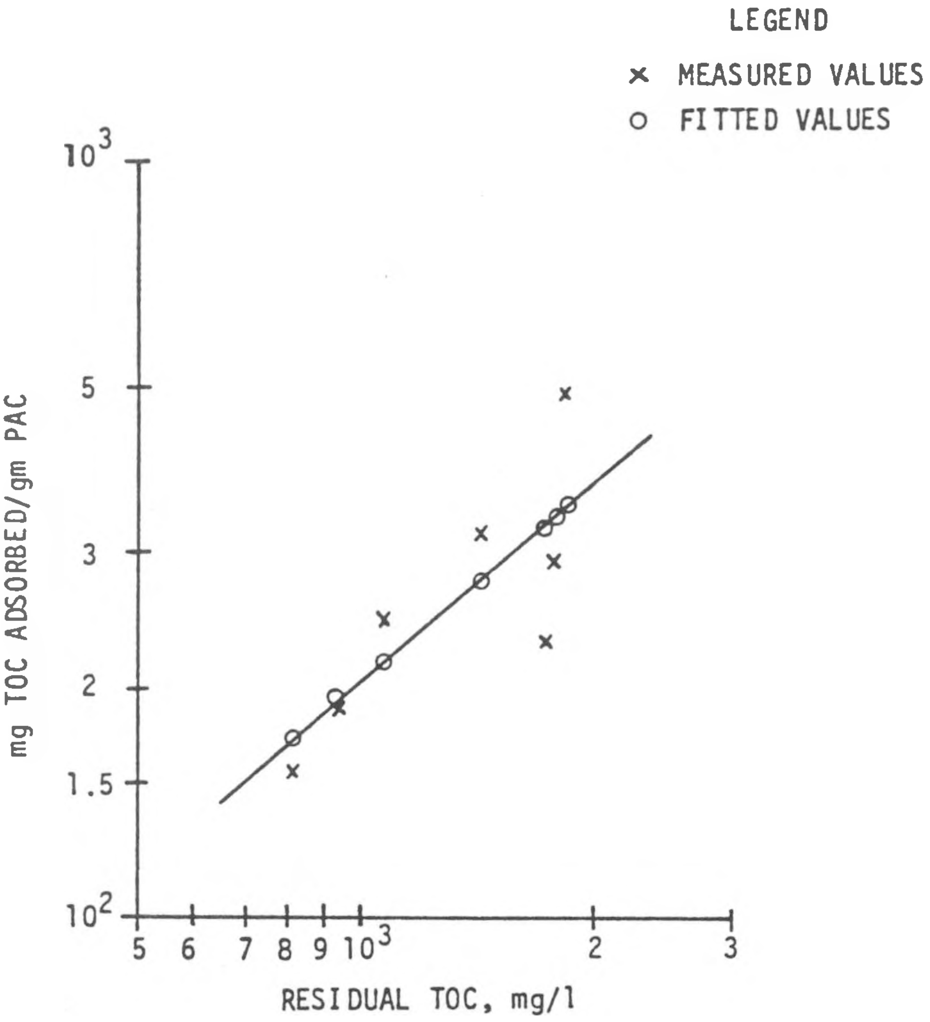
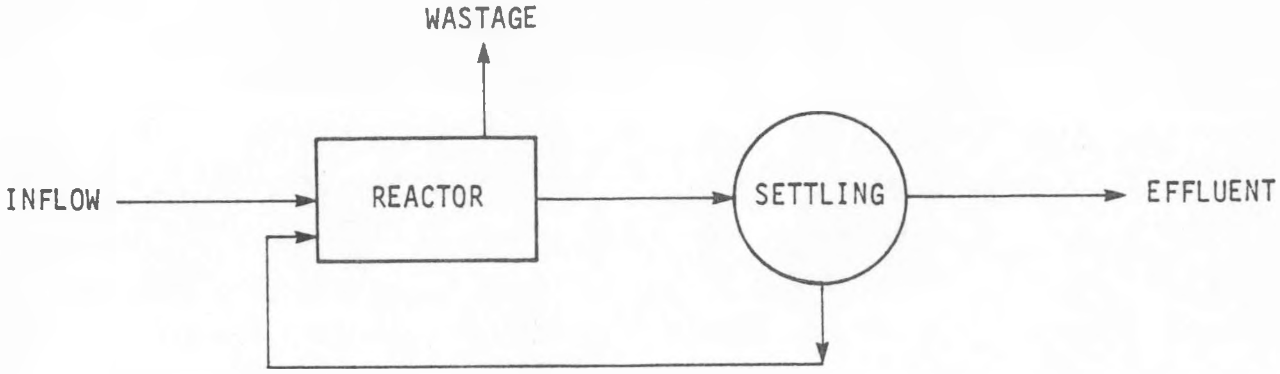


Figure 4-37B. Freundlich Isotherm for Amoco PAC Type PX-21.



CONTROL AS SYSTEM

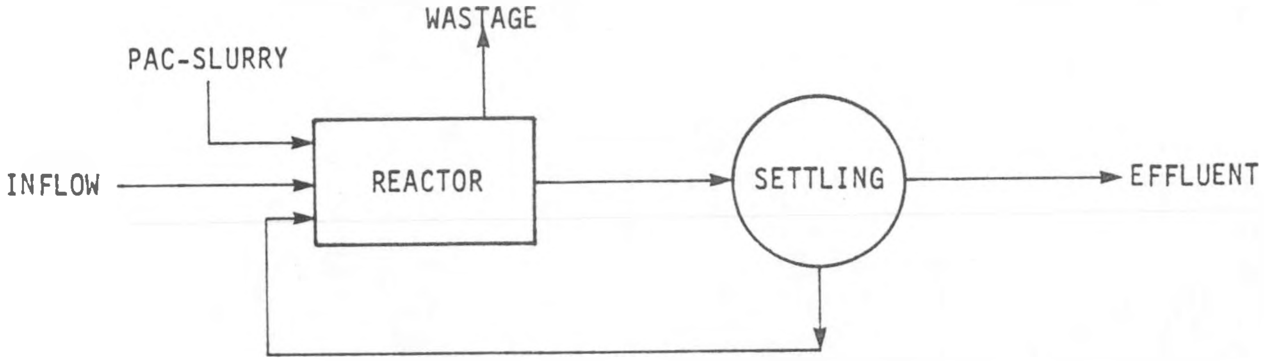


Figure 4-38. Treatment scheme.

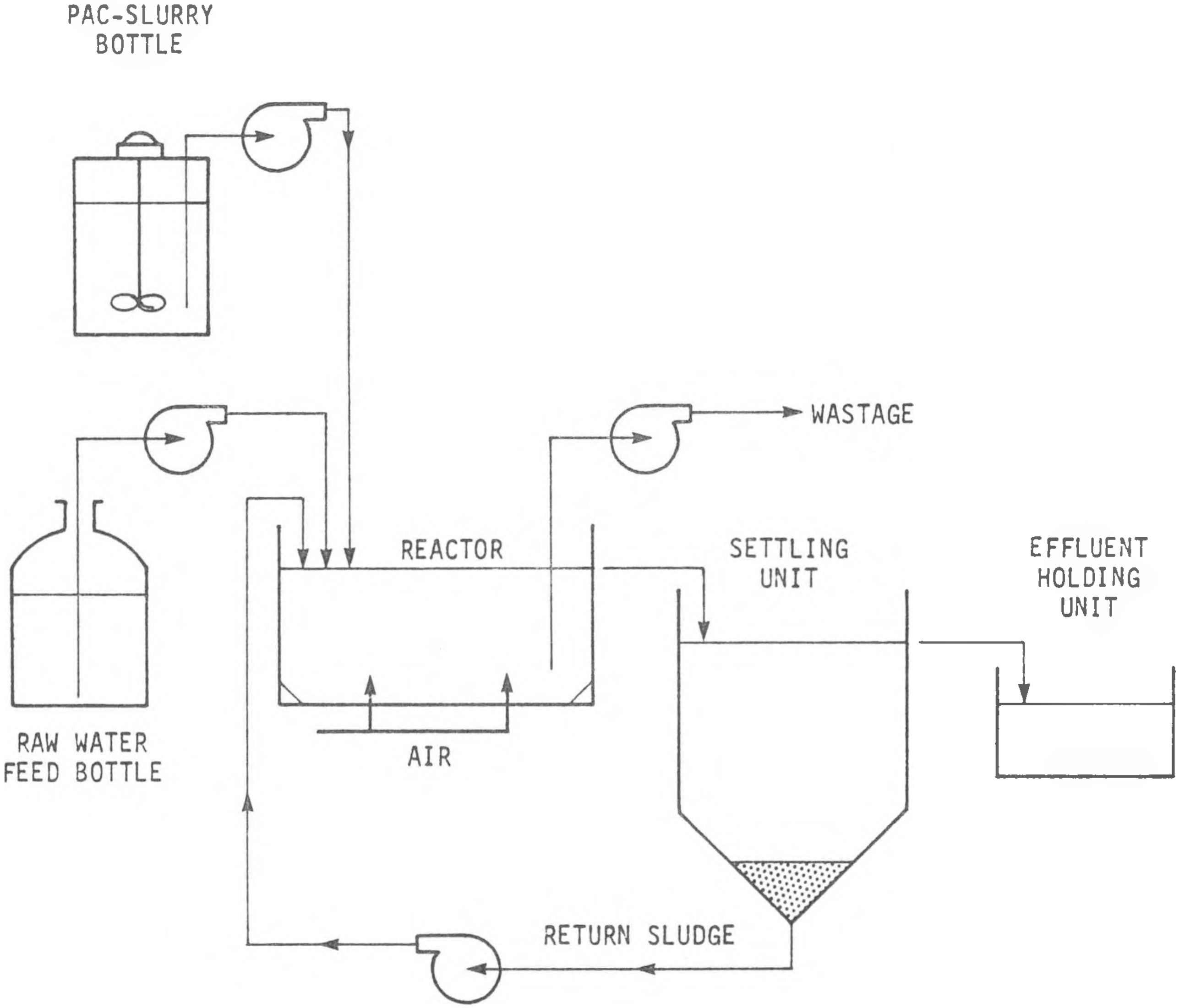


Figure 4-39. Schematic diagram of PAC-AS system.

The mixture was diluted with tap water and mixed with the seed sludge in a glass container to which compressed air was supplied. After some months of acclimation the sludge growth was plentiful and seemed to be viable by microscopic examination. The mixed liquor was then distributed to the two reactors and continuous application of the feed retort water was begun.

PAC-slurry Preparation

To remove impurities that might exist the PAC was first washed with deionized water, then held in boiling water for about one hour, cooled, washed three times and finally delivered to the feed container. There, deionized water was added and the concentration of the slurry was determined.

Sludge Wasting

Sludge was wasted directly from the reactor and its solids concentrtion was considered equal to the value determined for the mixed liquor.

Sampling

When the system was running the oxygen uptake rate (OUR) was constantly checked to make sure that the sludge was viable. The OUR was also used as a means of detecting steady-state conditions. Generally, when the OUR reached a constant level, the system was considered to have attained its steady-state conditions and samples were taken from the influent, the effluent and the mixed liquor for analysis. The samples were filtered through Whatman GF-C fiber glass paper to ensure that only a soluble substrate was obtained. During steady-state periods samples were taken twice a week and analyses of the influent and the effluent BOD_5, COD and TOC were usually made on the same day. If preservation of the samples was necessary, they were preserved according to standard practice. pH and temperature were recorded daily.

4.5.4 Continuous Flow RBC-PAC-AS Procedure

In this mode of combined operation influent to the PAC-AS system came from the concurrent operation of the four-stage RBC unit number A. During the period when the combined system was in operation, the RBC unit was maintained at the operation conditions shown in Table 4.30.

The apparatus and operating procedures of the PAC-AS unit for the combined system were the same as described above except for the following differences:

TABLE 4.30

FOUR-STAGE RBC OPERATION CONDITIONS AND EFFLUENT CHARACTERISTICS

OPERATION CONDTIONS:

Hydraulic residence Time = 12 - 18 hours
Bod_5 loading rate = 5.6 - 3.8 lb/(1,000 ft.^{3})(day)
COD loading rate = 13.7 - 9.3 lb/(1,000 ft.^{3})(day)

EFFLUENT:

BOD_5 = 1,600 - 1,950 mg/l
COD = 8,000 - 8,800 mg/l
TOC = 1,500 - 2,100 mg/l

(1) Instead of using a separate reactor and settling unit, a combined reactor and clarifier was used as shown schematically in Figure 4-40, with an effective total volume of 4.07 liters.

(2) A different but commercially available type of PAC was selected from the isotherm tests described in Section 4.5.3. The selected PAC, Calgon NAP, had the second largest specific surface area and seemed to perform better at low residual TOC than the other two types of PAC which were also commercially available.

(3) Seed sludge was readily available from the biological reactors already in operation. A portion of the activated sludge from the control unit containing about 1,500 mg/l of MLSS was put into the reactor. As soon as air was supplied, the feed water and PAC-slurry pumps were also activated. Sludge wasting was not begun until the carbon concentration of the mixed liquor (MLCSS) reached a preselected level.

4.5.5 Analytical Methods

Analytical procedures in the 14th Edition of the "Standard Methods"[7] were followed whenever possible. Specific resistance of the sludge was measured using the Buchner-funnel vacuum filtration method. The determination of carbon concentration in both effluent and mixed liquor were adopted from reference 16, and employed nitric acid as a digestion agent in a procedure outlined in Appendix 5. An aliquot (10 ml for mixed liquor, 10 ml or more for effluent) of sample was mixed with 20 ml of concentrated nitric acid. The mixture was heated at near-boiling temperature for about 90 minutes or until the remaining volume was approximately 10 ml. After cooling, suspended solids and suspended ash were determined as shown in Appendix 5.

4.5.6 System Performance

Steady-state data were collected for the AS and PAC-AS systems during the steady-state periods 4/6/80 to 9/10/80 and 6/12/80 to 7/18/80, and for the RBC-PAC-AS system during the period 6/12/80 to 7/18/80. Tables 4.31 to 4.34 show the operation conditions and the system performance in

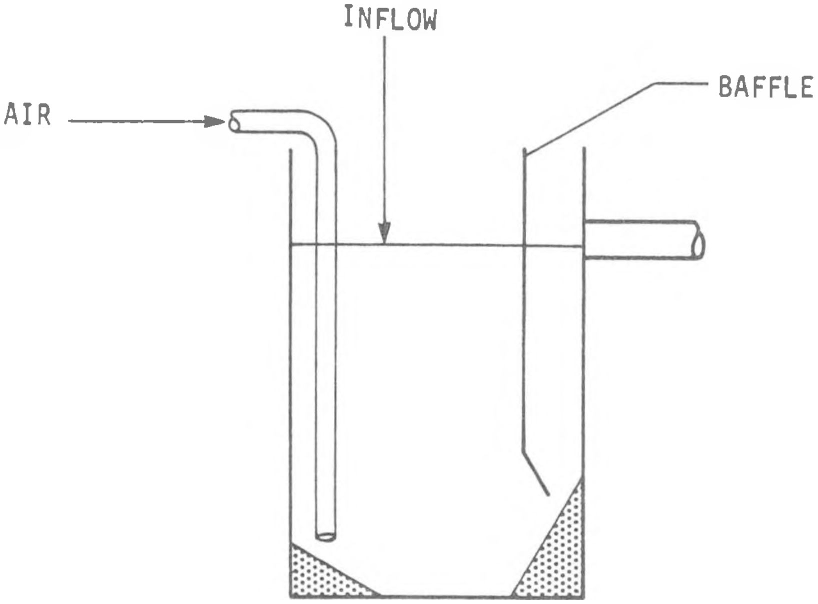


Figure 4-40. Eckenfelder-type reactor.

TABLE 4.31

OPERATING CONDITIONS AND PERFORMANCE OF THE AS SYSTEM

OPERATING CONDITIONS AND PERFORMANCE OF THE AS SYSTEM

DATE	INFLOW ml/day	OUTFLOW ml/day	WASTAGE ml/day	SLUDGE AGE θ_c	TEMP °C	BOD_5, mg/l		COD, mg/l		TOC, mg/l		MLSS mg/l	MLVSS mg/l	EFF. SS mg/l	EFF. VSS mg/l
						Inf.	Eff.	Inf.	Eff.	Inf.	Eff.				
4/06	1700	1300	75	6.10	20.5	3,840	1,830	9,956	8,132	2,560	2,160	1,280	640	620	490
4/12	1700	1450	0	7.50	21.5	3,840	1,680	10,138	7,910	2,320	1,880	1,280	785	620	470
4/19	1700	1300	110	7.11	22	3,780	1,740	10,083	8,022	2,360	1,960	750	715	525	445
4/21	1700	1300	110	7.69	23	3,660	1,620	9,936	7,949	2,280	1,880	1,180	730	540	415
5/03	1700	1300	110	7.15	24	3,690	1,650	9,800	7,762	2,400	2,000	1,485	720	805	445
5/10	1700	1300	110	6.77	21.5	3,792	1,710	9,878	7,762	2,400	1,980	1,230	730	690	480
6/16	1500	1500	0	8.35	27.5	3,975	1,470	10,891	8,122	2,250	1,760	2,140	965	940	503
6/19	1700	1500	0	8.62	24	3,863	1,365	10,891	8,049	2,200	1,700	2,050	1,020	975	515
6/23	1700	1500	0	8.82	25	3,769	1,350	10,778	7,841	2,175	1,660	1,913	1,060	913	523
6/26	1700	1500	0	8.90	28	3,694	1,395	10,644	7,809	2,100	1,600	1,825	1,028	775	503
6/30	1700	1500	0	9.56	21	3,619	1,290	10,453	7,775	2,075	1,590	1,795	995	753	453
7/03	1700	1500	0	9.26	24	3,469	1,215	10,242	7,604	2,038	1,560	1,870	1,010	793	475
7/07	1700	1500	0	10.41	23	3,226	1,050	10,154	7,333	2,038	1,530	1,888	1,095	780	458
7/10	1700	1500	0	10.93	25	3,132	1,020	10,236	7,302	2,075	1,560	1,843	1,100	780	438
7/15	1700	1500	0	10.06	26	3,301	1,110	10,169	7,451	2,050	1,560	1,780	1,040	693	450
7/18	1700	1500	0	9.88	27.5	3,076	1,080	9,844	7,191	2,025	1,560	1,763	1,005	723	443

TABLE 4.32

OPERATING CONDITIONS AND PERFORMANCE OF THE PAC-AS SYSTEM

(First Period)

DATE	4/6	4/12	4/19	4/21	5/3	5/10
Substrate Inflow (ml/dav)	1,850	1,800	1,900	1,900	1,900	1,900
PAC Inflow (ml/day)	200	200	200	200	200	200
Outflow (ml/day)	1,500	1,500	1,320	1,400	1,400	1,400
Wastage (ml/day)	80	65	125	115	115	115
PAC Dosage (mg/l)	339	337	352	758	821	835
Sludge Age θ_c (days)	17.37	30.69	26.75	29.13	17.52	16.92
Temperature($^{\circ}$C)	18	19	20	20	21	19
pH	7.7	7.7	7.4	7.3	6.8	6.9
BOD_5(mg/l)						
Influent	3,840	3,840	3,780	3,660	3,690	3,792
Effluent	1,230	1,110	1,080	1,020	1,110	1,206
COD (mg/l)						
Influent	9,956	10,138	10,083	9,936	9,800	9,878
Effluent	4,484	4,224	4,195	4,048	4,234	4,547
TOC (mg/l)						
Influent	2,560	2,320	2,360	2,280	2,400	2,400
Effluent	1,280	1,040	1,080	1,040	1,160	1,200
MLSS (mg/l)	9,070	9,280	9,655	10,730	12,815	12,200
MLVSS (mg/l)	7,610	7,940	8,260	9,120	10,835	10,420
MLCSS (mg/l)	4,300	4,337	4,437	5,274	7,353	7,116
MLBSS (mg/l)	3,310	3,603	3,823	3,846	3,482	3,304
Effluent SS (mg/l)	1,785	1,715	1,250	1,635	1,935	2,030
Effluent VSS (mg/l)	1,133	730	490	860	1,145	1,080
Effluent CSS (mg/l)	247	208	130	547	484	421
Effluent BSS (mg/l)	671	522	360	313	661	659

TABLE 4.33

OPERATING CONDITIONS AND PERFORMANCE OF THE PAC-AS SYSTEM

(Second Period)

DATE	6/16	6/19	6/23	6/26	6/30	7/3	7/7	7/10	7/15	7/18
Substrate Inflow (ml/day)	1,850	1.850	1,850	1,850	1.850	1.850	1.850	1,850	1.850	1.850
PAC Inflow (ml/day)	200	200	200	200	200	200	200	200	200	200
Outflow (ml/day)	1,050	1.050	1,050	1,050	1,050	1,050	1.150	1,150	1.150	1.150
Wastage (ml/day)	330	330	330	330	330	330	240	240	240	240
PAC Dosage (mg/l)	2.110	2,050	2,050	2.280	2,710	2,860	2,170	1,520	1.540	1,500
Sludge Age θ_c (days)	18.17	17.53	17.14	16.95	16.77	17.73	23.10	25.12	25.49	26.0
Temperature (°C)	24	20	21.5	25	18	22	21	22	23	24
pH	7.6	7.5	7.2	6.9	7.05	6.9	7.2	6.8	7.0	7.4
BOD_5 (mg/l)										
Inf.	3,975	3.863	3,769	3,694	3.619	3.469	3,226	3.132	3.301	3.076
Eff.	810	780	720	735	735	690	615	570	570	555
COD (mg/l)										
Inf.	10,891	10.891	10,778	10,664	10.453	10,242	10,154	10,236	10,169	9,844
Eff.	3,397	3,545	3,497	3,371	3,387	3,194	3,029	2,935	3,008	2,945
TOC (mg/l)										
Inf.	2.250	2,200	2,175	2,100	2,075	2,038	2,038	2.075	2,050	2,025
Eff.	680	700	650	640	600	560	540	500	500	510
MLSS (mg/l)	24,010	23,615	22,373	21,945	22,140	24,090	25,980	24,830	23,933	22,943
MLVSS (mg/l)	22.555	21,875	20,915	20.835	21.270	22.315	22.805	23,580	22,665	21,810
MLCSS (mg/l)	12,440	12.081	11.358	11,363	11,842	12.658	13.321	12,755	11.553	11,058
MLBSS (mg/l)	10.115	9,794	9.557	9,472	9,428	9,657	10,484	10,825	11.112	10,752
Effluent SS (mg/l)	1.578	1,893	2,105	1,975	1,965	1,878	1,998	1,865	1,905	1,933
Effluent VSS (mg/l)	925	1,070	1,115	1,170	1,340	1,220	1.270	1,040	1,043	918
Effluent CSS (mg/l)	568	600	576	597	731	795	826	800	834	763
Effluent BSS (mg/l)	357	470	539	573	609	425	444	240	209	155

TABLE 4.34

OPERATING CONDITIONS AND PERFORMANCE OF THE RBC-PAC-AS SYSTEM

DATE	6/16	6/19	6/23	6/26	6/30	7/3	7/7	7/10	7/15	7/18
Substrate Inflow (ml/day)	1,340	1,340	1,340	1,340	1,340	1,340	1,340	1,340	1,340	1,340
PAC Inflow (ml/day)	360	360	360	360	360	360	360	360	360	360
Outflow (ml/day)	1,230	1,230	1,230	1,230	1,230	1,230	1,330	1,330	1,330	1,330
Wastage (ml/day)	320	320	320	320	320	320	220	220	220	220
PAC Dosage (mg/l)	1,580	1,720	1,530	1,690	1,700	1,820	1,870	1,600	1,500	1,520
Sludge Age θ_c (days)	10.34	10.43	11.10	12.02	12.24	12.59	17.82	16.36	16.05	15.67
Temperature °C	22	22	24	27	20	24	23	24	26	26
pH	8.3	7.8	7.6	7.4	7.25	7.1	7.35	7.1	7.2	7.0
BOD_5 (mg/l)										
Inf.	1,950	1,950	1,935	1,920	1,845	1,815	1,725	1,680	1,650	1,620
Eff.	840	810	735	690	615	570	525	480	495	480
COD (mg/l)										
Inf.	8,639	8,639	8,755	8,738	8,432	8,264	8,192	8,189	8,135	8,013
Eff.	4,024	3,987	3,851	3,576	3,317	3,194	3,030	3,003	3,076	3,082
TOC (mg/l)										
Inf.	2,080	1,980	1,860	1,830	1,690	1,560	1,560	1,560	1,600	1,580
Eff.	960	880	740	650	530	430	410	440	440	440
MLSS (mg/l)	11,740	12,613	13,250	13,105	13,750	14,553	14,123	13,700	12,850	12,058
MLVSS (mg/l)	9,315	10,205	10,460	11,290	11,545	11,875	12,645	12,225	11,570	10,995
MLCSS (mg/l)	4,966	5,582	5,526	5,895	5,989	6,150	6,476	6,213	5,597	5,245
MLBSS (mg/l)	4,349	4,623	4,934	5,395	5,556	5,725	6,169	6,012	5,973	5,750
Effluent SS (mg/l)	1,433	1,493	1,323	1,245	1,210	1,180	1,208	1,398		1,385
Effluent VSS (mg/l)	715	730	540	395	360	460	490	425	425	440
Effluent CSS (mg/l)	455	466	353	313	303	445	450	295	274	268
Effluent BSS (mg/l)	260	264	187	82	57	15	40	130	151	172

chronological order. Tables 4.35 and 4.36 summarize the performance and operation conditions in average term. Figures 4-41, 4-42, and 4-43 are plots of organic removal efficiences against mean cell residence time (θ_c). The numerical data used for these plots are tabulated in Tables 4.37, 4.38 and 4.39. For each treatment system the removal efficiences of BOD_5, COD and TOC increased as the sludge age, θ_c, increased, and leveled off as θ_c increased beyond a certain value. The biggest transition occurred in RBC-PAC-AS system (Figure 4-43) where the removal efficiency of TOC increased from about 60% to roughly 72% as θ_c increased from 11 days to 14 days. BOD_5 and COD also show similar trends. In this case, it would be clear that optimal θ_c for the RBC-PAC-AS system lies in a relatively narrow range around 14 days. For the other two systems it does not seem to be so distinct.

It is worth noting that Figure 4-42 shows that for each set of results, two distinctive curves could be fitted. One set of curves corresponded to the second period (6/16/80 to 7/18/80) of operations in which the average MLCSS was maintained at a much higher level (about 12,000 mg/l) than in the first period (4/6/80 to 5/10/80) with an average MLCSS of 5500 mg/l. The two periods of operation are treated separately in the following data analyses.

The addition of PAC into the AS system improved system performance. Influent and effluent BOD_5, COD and TOC concentrations are plotted on a probability basis in Figures 4-44, 4-45 and 4-46. PAC-addition in the PAC-AS system clearly led to an additional removal efficiency (ΔE) compared with the control AS system. On a 50% probability level a PAC dosage of 2090 mg/l resulted in a ΔE of 18.3% in BOD_5, 45.1% in COD and 50.6% in TOC. When PAC dosage was reduced to 570 mg/l, the ΔE's in BOD_5, COD and TOC were 6.9%, 35% and 26.7% respectively. In both cases ΔE's for BOD_5 were lower than for COD and TOC. Further comparison reveals the following interesting points:

(1) The AS system seemed to be the most unstable among the three systems as its effluent BOD between 10% and 90% probability levels had a much wider spread than those in the other system.

(2) The RBC-PAC-AS system showed somewhat more variable performance in all three parameters than the PAC-AS

TABLE 4.35

AVERAGE PERFORMANCE

SYSTEM	FLOW	BOD_5		COD		TOC	
		mg/l	% Removal	mg/l	% Removal	mg/l	% Removal
AS	Influent	3,608	-	10,257	-	2,209	-
	Effluent	1,411	60.9	7,751	24.4	1,746	21.0
PAC-AS	Influent	3,767 (3,512)*	-	9,965 (10,432)*	-	2,387 (2,105)*	
	Effluent	1,126 (678)*	70.1 (80.7)*	4,289 (3,230)*	57.0 (69.0)*	1,133 (588)*	52.5 (72.1)
PAC-AS section of the combined system	Influent	1,809	-	8,400	-	1,730	-
	Effluent	624	65.5	3,414	59.4	592	65.8
RBC-PAC-AS combined system	Influent	3,500	-	10,400	-	2,300	-
	Effluent	624	82.2	3,414	67.2	592	75.3

*Values in parenthesis are for the period 6/16/80 to 7/18/80 during which time MLCSS was approximately 12,000 mg/l, while the others are for MLCSS approximately 5,500 mg/l in the PAC-AS system.

TABLE 4.36

SUMMARY OF OPERATING CONDITIONS

	AS SYSTEM	PAC-AS-SYSTEM 4/6 - 5/10/80	PAC-AS-SYSTEM 6/16 - 7/18/80	RBC-PAC-AS SYSTEM
Hydraulic Residence, days	3.84	3.56	3.61	3.04
θ_c days	6.10 to 10.93	16.92 to 30.69	16.77 to 26.0	10.34 to 17.82
Temp., °C	20.5 to 28	18 to 21	18 to 25	20 to 27
pH	7.0 to 9.2	6.8 to 7.7	6.8 to 7.6	7.0 to 8.3
MLSS, mg/l	1630	10,630	23,590	13,170
MLVSS, mg/l	915	9,030	22,160	11,310
MLBSS, mg/l	-	3,560	10,120	5,450
MLCSS, mg/l	-	5,470	12,040	5,860
PAC Dosage, mg/l	-	570	2,090	1,620

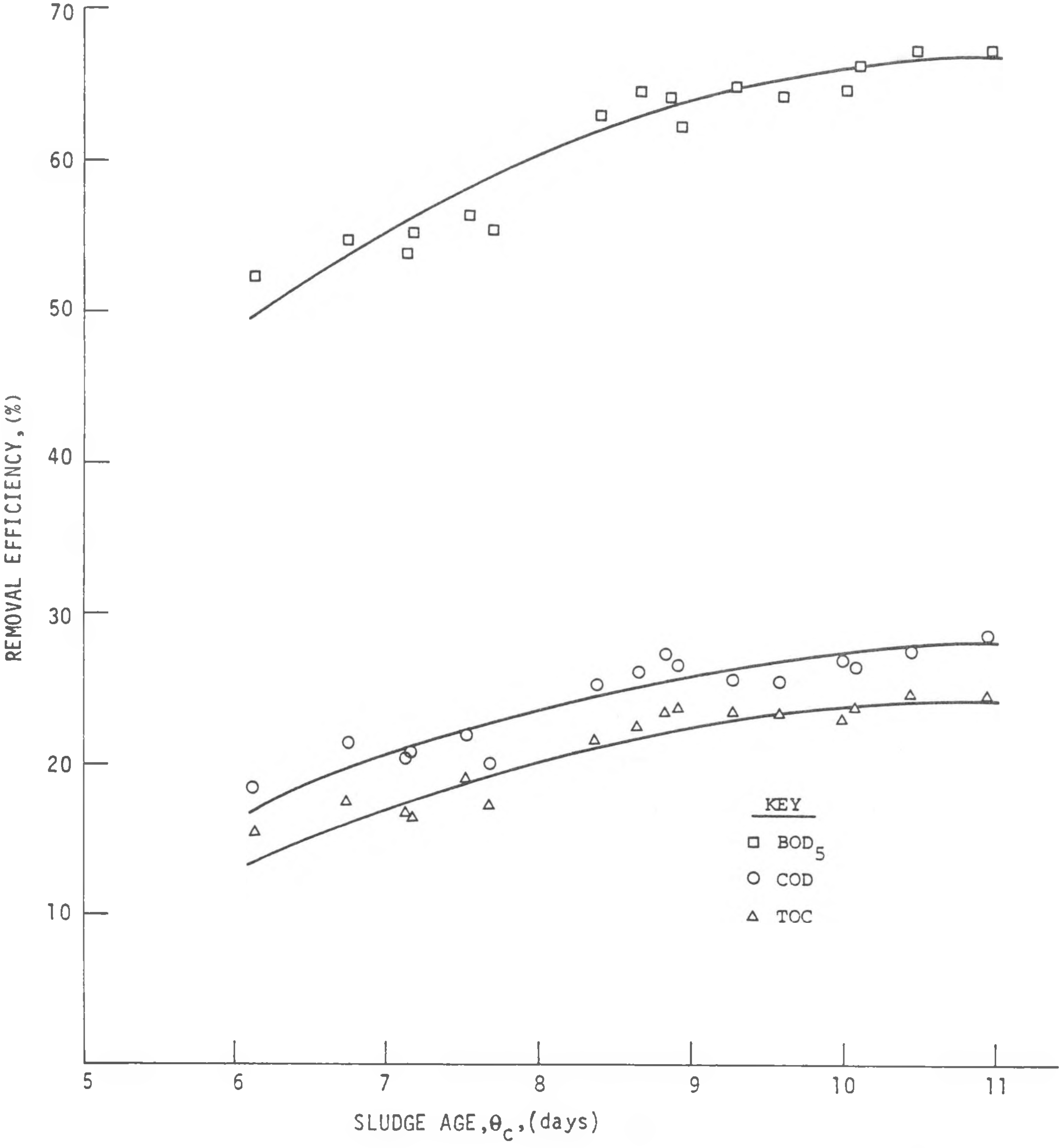


Figure 4-41. Effect of sludge age on removal efficiency in the AS system.

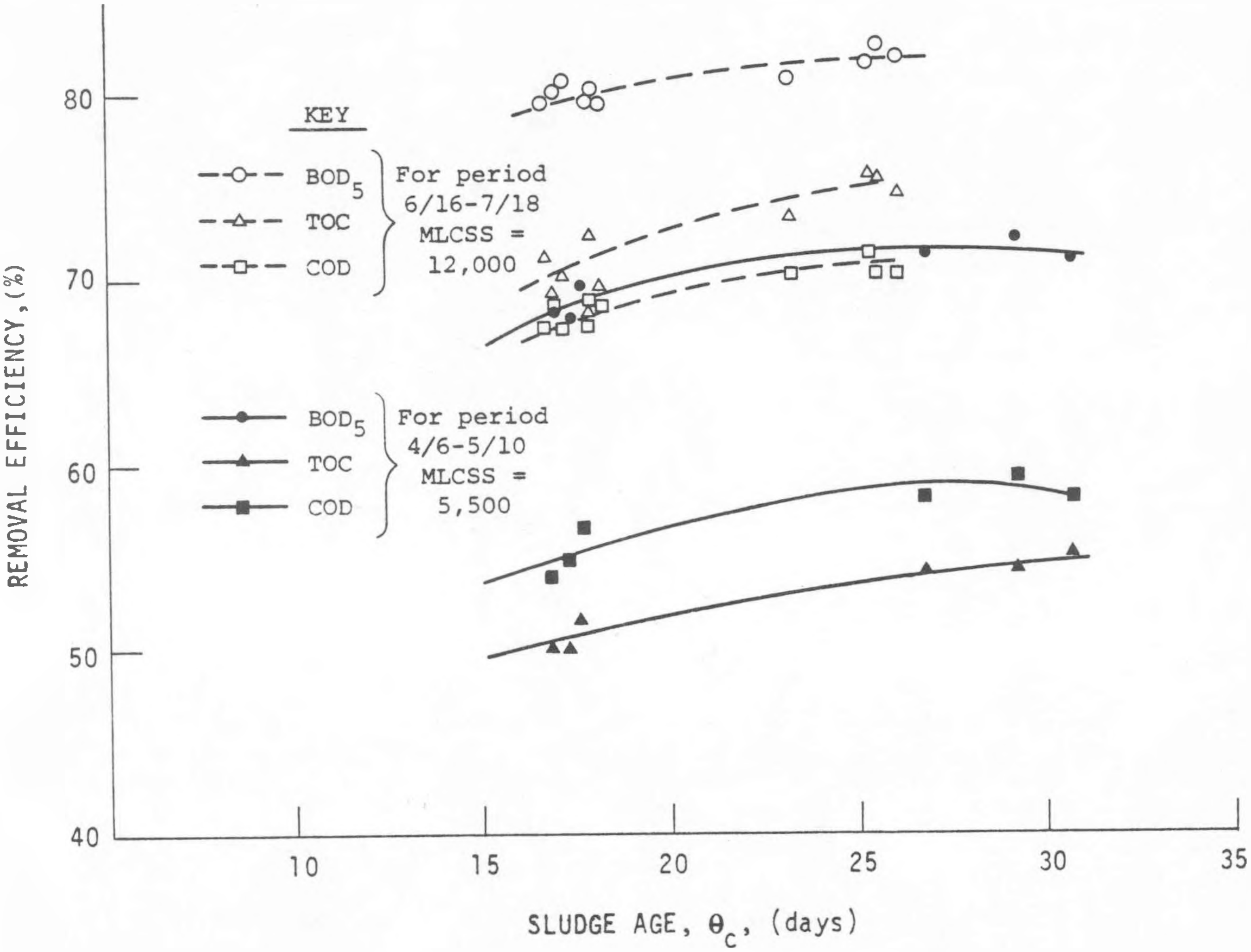


Figure 4-42. Effect of sludge age on removal efficiency in the PAC-AS system.

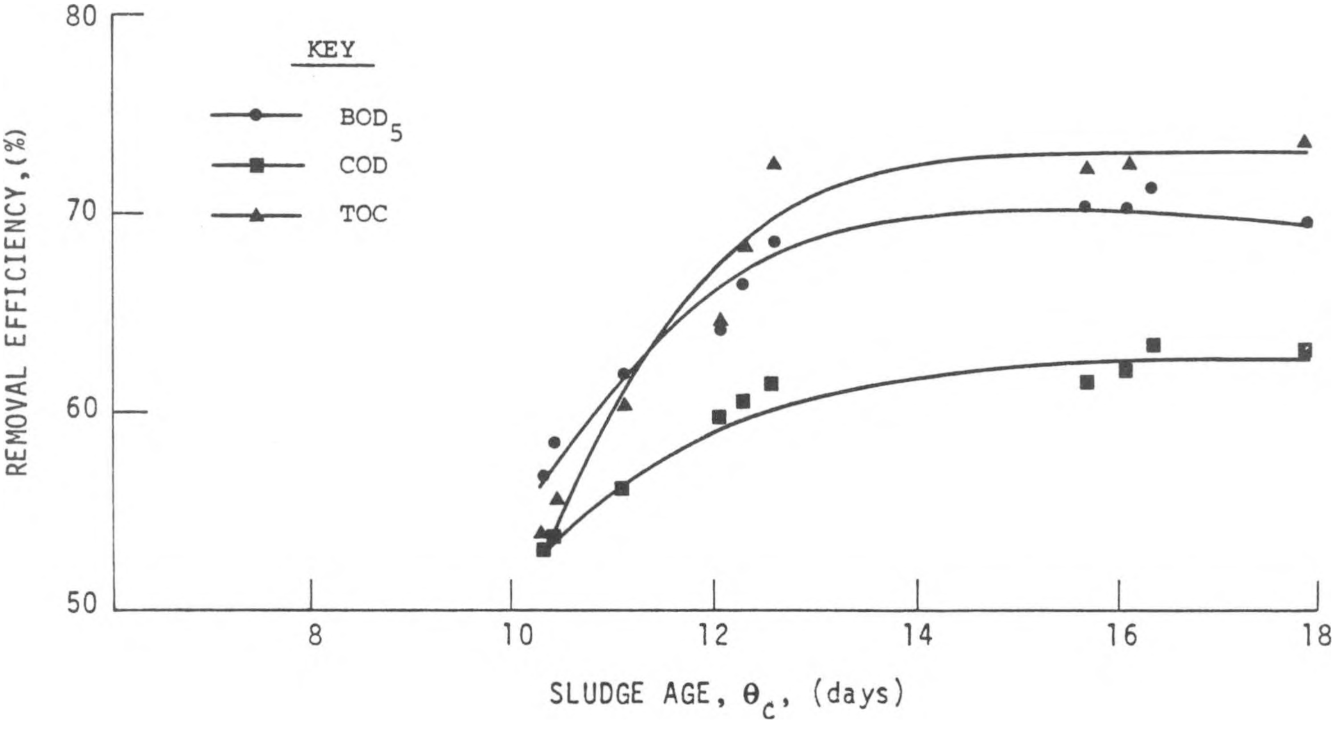


Figure 4-43.

Effect of sludge age on removal efficiency in the RBC-PAC-AS system

TABLE 4.37

SUMMARY OF SLUDGE AGE AND EFFICIENCY IN THE AS SYSTEM

DATE	θ_c days	E_{BOD}, %	E_{COD}, %	E_{TOC}, %
4/6	6.11	52.3	18.3	15.6
4/12	7.51	56.3	22.0	19.0
4/19	7.11	54.0	20.4	16.9
4/21	7.69	55.7	20.0	17.5
5/ 3	7.15	55.3	20.8	16.7
5/10	6.74	54.9	21.4	17.5
6/16	8.35	63.0	25.4	21.8
6/19	8.62	64.7	26.1	22.7
6/23	8.82	64.2	27.2	23.7
6/26	8.90	62.2	26.8	23.8
6/30	9.56	64.4	25.6	23.4
7/ 3	9.26	65.0	25.8	23.5
7/ 7	10.41	67.5	27.8	24.9
7/10	10.93	67.4	28.7	24.8
7/15	10.06	66.4	26.7	23.9
7/18	9.88	64.9	27.0	23.0

TABLE 4.38

SUMMARY OF SLUDGE AGE AND EFFICIENCY IN THE PAC-AS SYSTEM

DATE	θ_c days	E_{BOD}, %	E_{COD}, %	E_{TOC}, %
4/ 6	17.37	68.0	55.0	50.0
4/12	30.69	71.1	58.3	55.2
4/19	26.75	71.4	58.4	54.2
4/21	29.13	72.1	59.3	54.4
5/ 3	17.52	69.9	56.8	51.7
5/10	16.92	68.2	54.0	50.0
6/16	18.17	79.6	68.8	69.8
6/19	17.53	79.8	67.5	68.2
6/23	17.14	80.9	67.6	70.1
6/26	16.95	80.1	68.4	69.5
6/30	16.77	79.7	67.6	71.1
7/ 3	17.73	80.1	68.8	72.5
7/ 7	23.10	80.9	70.2	73.5
7/10	25.12	81.8	71.3	75.9
7/15	25.49	82.7	70.4	75.6
7/18	26.00	82.0	70.1	74.8

TABLE 4.39

SUMMARY OF SLUDGE AGE AND EFFICIENCY IN THE RBC-PAC-AS SYSTEM

DATE	θ_c days	E_{BOD}, %	E_{COD}, %	E_{TOC}, %
6/16	10.34	56.9	53.4	53.8
6/19	10.34	58.5	53.8	55.6
6/23	11.10	62.0	56.0	60.2
6/26	12.02	64.1	59.1	64.5
6/30	12.24	66.7	60.7	68.6
7/ 3	12.59	68.6	61.4	72.4
7/ 7	17.82	69.6	63.0	73.7
7/10	16.36	71.4	63.3	71.8
7/15	16.05	70.0	62.2	72.5
7/18	15.67	70.4	61.5	72.2

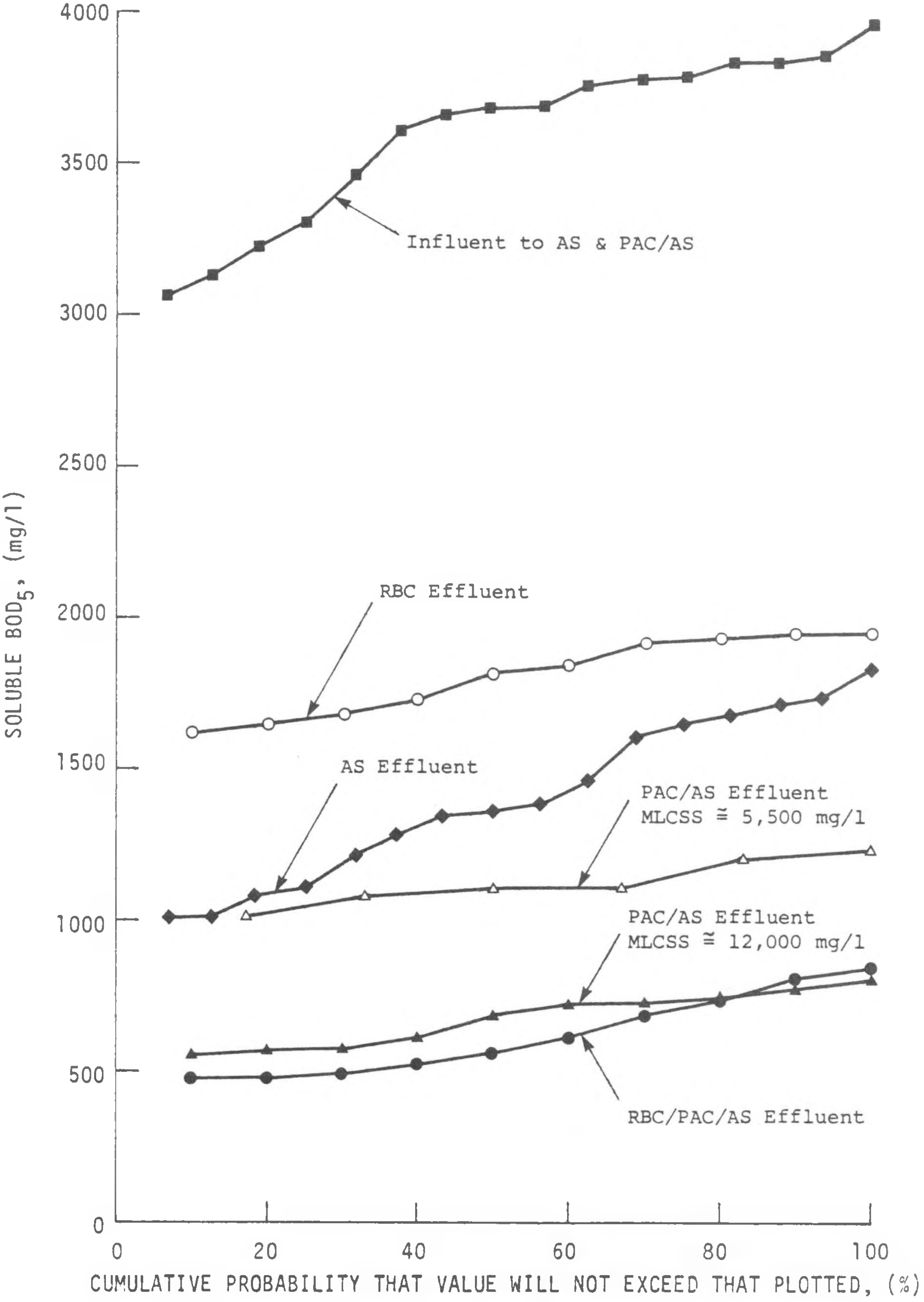


Figure 4-44. Variability of influent and effluent BOD_5.

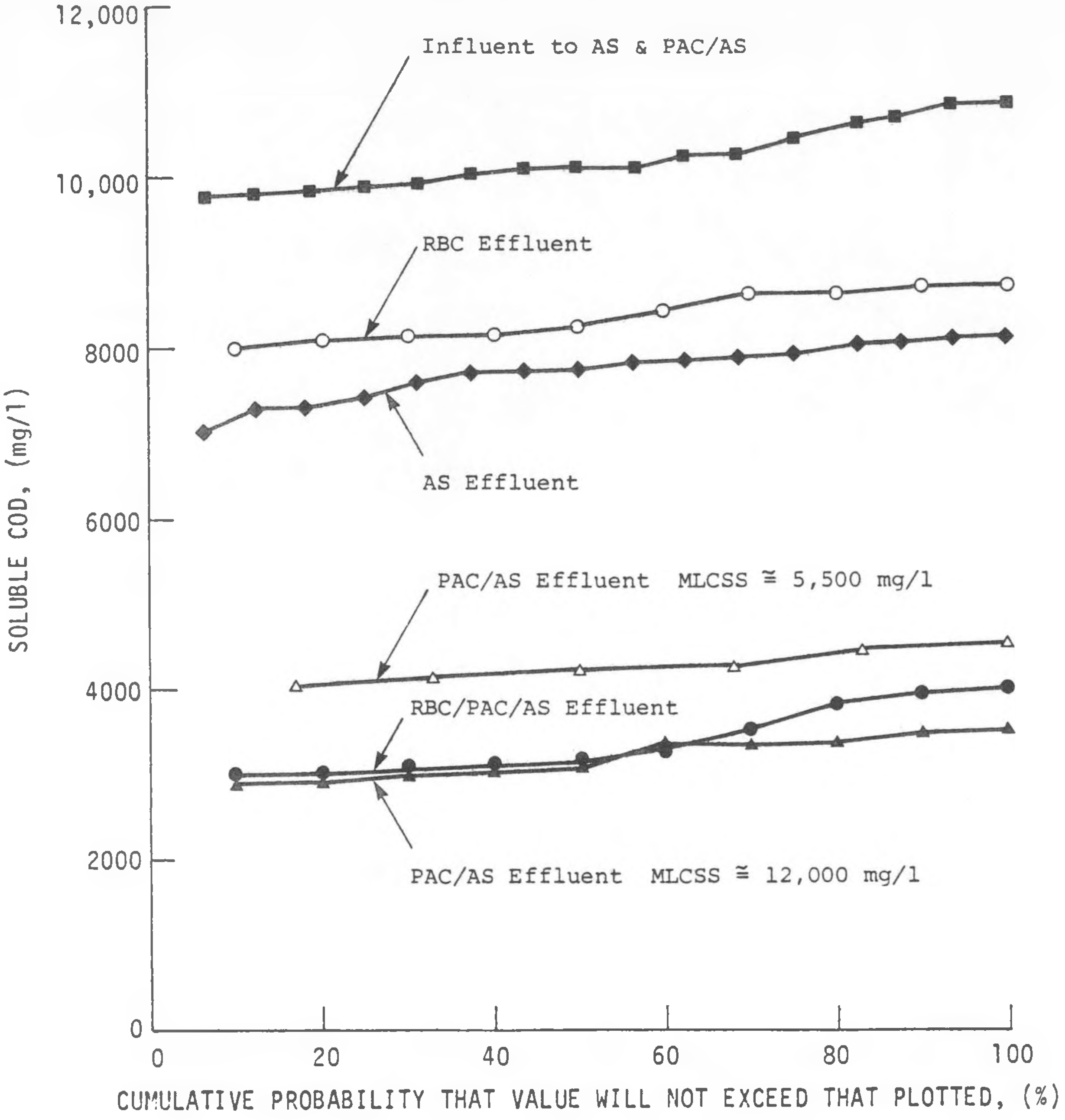


Figure 4-45. Variability of influent and effluent COD.

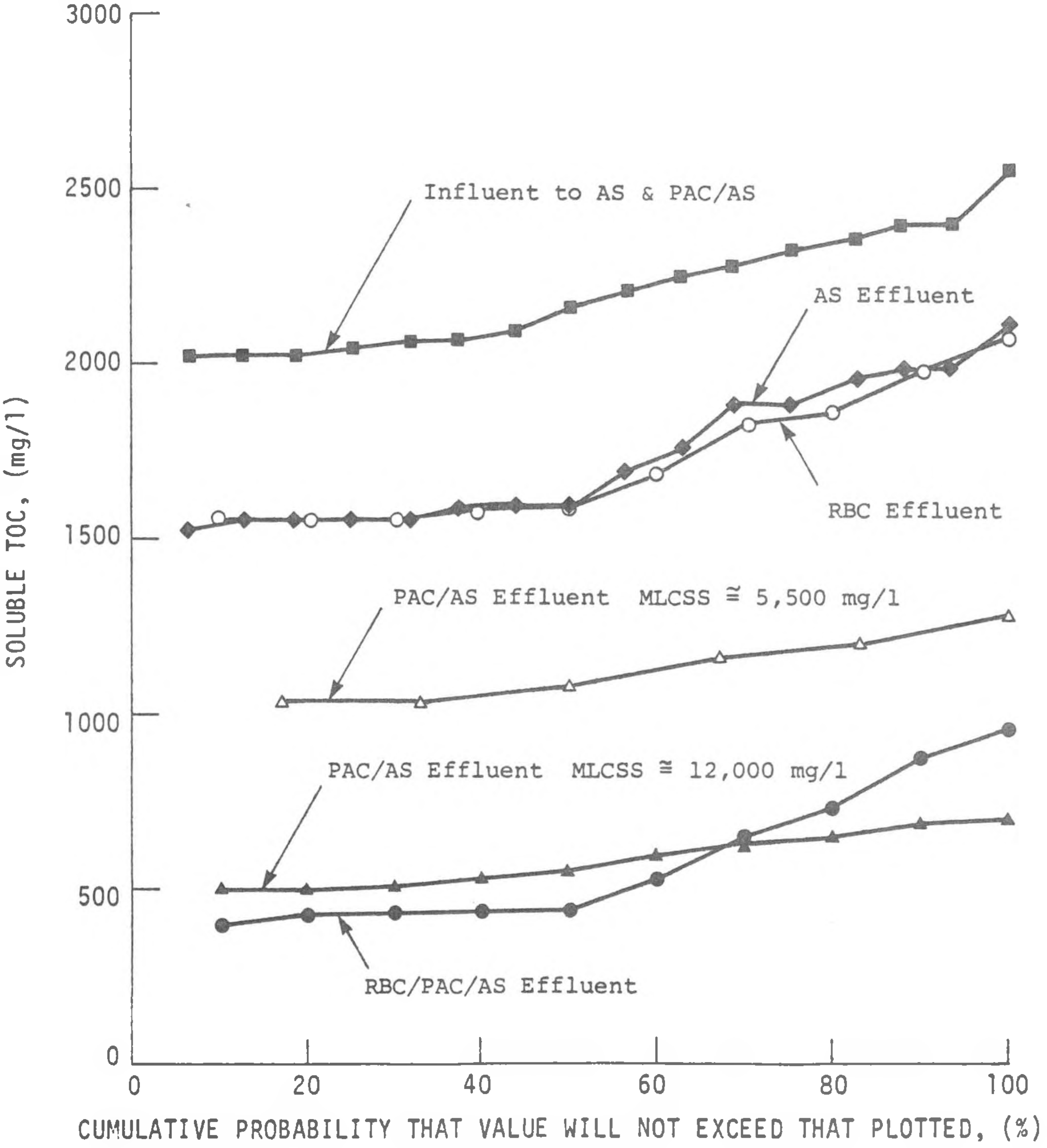


Figure 4-46. Variability of influent and effluent TOC.

system did. This might be due to the use of different types of PAC in the PAC-AS and RBC-PAC-AS systems.

(3) The three systems demonstrated a more consistent performance in COD than in BOD_5 and TOC. This could be due in part to a rather stable influent COD.

(4) The AS system seemed to perform better in degrading BOD_5 and COD than the RBC did, and both systems had essentially the same removal of TOC.

4.5.7 Sludge Dewatering

The Buchner-funnel test was employed to assess the dewatering characteristics of the sludges from the three systems. The results are shown in Table 4.40. It may be seen that the sludge from the PAC-AS system had the lowest specific resistance and was thus more easily filtered. However these specific resistance values are close to those for ordinary activated sludge in sewage treatment plants, and thus no special difficulty is expected in filtering these sludges if the sludges can be effectively separated from the effluent. Consequently the most important consideration in treating retort water biologically is the solid separation process following the bioreactor. The addition of PAC is definitely helpful in this regard, but a multi-media filtration process downstream might be necessary. This was beyond the scope of this study and was not investigated.

TABLE 4.40

AVERAGE SPECIFIC RESISTANCE OF THE SLUDGES

SLUDGE FROM	AVERAGE SPECIFIC RESISTANCE, sec^2/gm
AS	1.53×10^8
PAC-AS	1.05×10^8
RBC-PAC-AS	6.92×10^8

4.5.8 Summary and Conclusions

Oil shale retort water, after proper pretreatment, was found treatable by the activated sludge process supplemented by PAC Type PX-21. Initially, in the period 4/6/80 to 5/10/80 when PAC dosage was about 570 mg/l of influent, with carbon concentration in the mixed liquor (MLCSS) averaging 5,470 mg/l, the system which was maintained at a sludge age (θ_c) of 17 to 31 days was able to remove 70% of BOD_5, 57% of COD and 53% of TOC. In the second period (6/16/80 to 7/18/80) the PAC dosage was increased to 2090 mg/l, thus bringing MLCSS up to about 12,000 mg/l. The system was operated in the same θ_c range, and the efficiency was significantly increased to 81% removal of BOD_5, 69% of COD and 72% of TOC. Carbon concentration at this level sometimes caused clogging in the gravity tubing between the reactor and the settling unit, but foaming and odor, especially odor, which were experienced previously, were altogether eliminated.

The combined operation——RBC effluent being fed to PAC-added activated sludge unit——was initiated later. Using a PAC commercially available but less adsorptive than PX-21, the bioreactor and clarifier never experienced any foaming or odor nuisance, even though the PAC dosage was averaging 1,620 mg/l and MLCSS about 5860 mg/l. The combined operation was able to remove about 66% of BOD_5, 59% of COD and 66% of TOC. This brings the overall efficiency of the RBC-PAC-AS sequence to roughly 82% of BOD_5, 67% of COD and 74% of TOC.

In general, a comparison among the three treatment systems discussed, i.e., AS, PAC-AS and RBC-PAC-AS, showed that

(1) PAC addition increased the removal efficiency in BOD_5, COD, and TOC. The increase in BOD_5 removal efficiency was, however, less than those in COD and TOC.

(2) An increase in PAC dosage increased the removal efficiency in BOD_5, COD, and TOC. The increase in TOC removal efficiency was, however, larger than those in BOD_5 and COD.

(3) PAC addition improved the stability of treatment performance.

(4) In terms of treatment performance, the use of RBC as a roughing unit ahead of PAC-AS would have effects similar to an increase in PAC dosage in the PAC-AS system.

The sludge from the three systems had specific resistance values similar to those for the activated sludge in sewage treatment plants. The results also showed that the PAC-AS sludge had the lowest specific resistance and combined operation sludge the highest. The PAC addition improve the settability of sludge, but the separation of sludge from effluent remained the key for the success of biotreatment of retort water.

4.6 SUMMARY OF THE RESULTS OF EXPERIMENTS ON BIOLOGICAL TREATMENT

On Table 4.41 are shown the percentage removals for the various tests made. BOD removals in excess of 80% could be obtained with oxygen activated sludge or the combination RBC-AAS-PAC (rotating biological disc followed by air activated sludge containing powdered activated carbon). The RBC alone gave high removals when the water was diluted 20:1. However, our dilution water was tap water, not recycled water, this is not practical.

COD removals were always poor. When a sample was aerated for 4.5 months and 95% of the BOD was oxidized, only 28% of the COD was removed. The weight of COD removed equalled the weight of BOD removed and was not more (see Table 4.17). There is a high biorefractory content to the retort water and carbon was required to remove it as shown by the PAC results on Table 4.41.

TABLE 4.41

REMOVAL PERCENTAGES ACHIEVED

	% BOD REMOVAL	% COD REMOVAL	COMMENT
RBC undiluted single stage	53	25	Hydraulic Residence: 3 hrs. Organic Loading: 5.6 lb BOD/(1000 ft^2)(day)
RBC undiluted 4 stages	57	29	Hydraulic Residence: 12 hrs. Organic Loading: 5.6 lb BOD/(1000 ft^2)(day)
RBC 20:1 dilution with fresh water 3 stages	94	43	Hydraulic Residence: 2.6 hrs. Organic Loading: 1.4 lb BOD/(1000 ft^2)(day)
Air activated sludge	60 - 80%		F/M = 1 to 2
Oxygen activated sludge	60 - 90%		F/M = 0.6 to 2
AAS and powdered activated carbon	70 - 81	57 - 69	MLCSS = 5,500 to 12,000 mg/l AMOCO-PX21 carbon
RBC followed by AAC-PAC	82	67	MLCSS = 5,500 mg/l Calgon NAP carbon

5. DESIGN OF BIOLOGICAL TREATMENT SYSTEMS

Using the experimental results of the foregoing section the following biological treatment systems have been sized:

Rotating biological contactor
Oxygen activated sludge
Air activated sludge with powdered activated carbon addition
Rotating biological contactor followed by air activated
sludge with powdered activated carbon addition

The treatments have been approximately sized and costed for a flow of 10^6 gal/day (about 700 gal/min) having an influent BOD_5 of 4,000 mg/l. Where appropriate the probable effluent BOD has been estimated and the effect on cost and size of trying to obtain a lower effluent BOD is also mentioned. When carbon is not added the COD removal is approximately the same as the BOD removal found in the experiments. When carbon is added the effluent and influent COD are also given.

5.1 Conclusions

The calculated results are shown on Table 5.1. An oxygen activated sludge plant, while more expensive than a RBC gives so much better a removal of BOD that OAS is preferred.

Removal of COD is poor without carbon. Carbon was found to halve the COD in the effluent. The cheapest sequence including carbon is RBC-PAC-AS.

High COD's remained whatever treatment was tested and alternatives to biological treatment should be investigated.

5.2 Rotating Biological Contactor (RBC)

The optimum 4-stage reactor was found, in Section 4.3.5, to have a loading of 5.6 lb BOD/(1000 ft^2)(day) and to give a removal of 57% of the BOD and 29% of the COD with the weight of COD removed being very close to the weight of BOD removed (see Table 4.9). However, 53% of the total removal of BOD occured in the first stage. We have, therefore, sized and costed a four stage reactor loaded at 5.6 lb BOD/(1,000 ft^2)(day) and a one-stage reactor loaded at 21 lb BOD/(1,000 ft^2)(day). The difference in cost between the one-stage and 4-stage reactors does not merit trying to obtain the extra 4% BOD removal (extra 145 mg/l BOD removed).

Performance differences have been reported between pilot and full-scale RBC units[4]. As the disc diameter is increased removal efficiency decreases. In a study using parallel flows into different size units scale-up factors were developed for sizing commercial units from pilot study units. The study

TABLE 5.1

COST AND EFFLUENT OF BIOLOGICAL TREATMENTS

	Capital (10^6)	Operating		Effluent (1)	
		($/$10^3$ gal)	($/lb BOD Removed)	BOD (mg/l)	COD (mg/l)
Rotating Biological Contactor (RBC)					
4-stage (5.6 lb BOD/(10^3 ft^3)(day)	3.75	3.4	0.18	1,720	7,100
one-stage (21 lb BOD/(10^3 ft^3)(day)	0.9	1.6	0.009	1,880	7,500
Oxygen Activated Sludge (OAS)					
one-stage	2.81	3.0	0.14	330	6,330 (2)
2-stage (5)	3.43	3.4	0.15	98	6,098 (2)
Air Activated sludge with PAC					
5,500 mg/l PAC	4.6	8.9 (3)	(4)	1,200	4,300
12,000 mg/l PAC	5.0	21.6 (3)	(4)	760	3,100
RBC-PAC-AS					
5,900 mg/l PAC	4.0	16.8 (3)	(4)	600	3,400

(1) Influent 10^6 gal/day (700 gal/min) with 4,000 mg/l BOD and 10,000 mg/l COD

(2) Assuming COD removed equals only BOD removed

(3) Without carbon recovery

(4) Not applicable because more COD is removed than in non-carbon systems

(5) Based on calculations; experiments not made.

recommended using a 25% increase in disc area when a 0.5 meter diameter pilot unit is used and a 10% increase when using a 2.0 meter RBC unit. The bench scale units used in this study have 0.2 meter diameter discs and a scale-up factor of 25% was chosen to be used in sizing the full-scale units. This factor may be optimistic because the bench scale units were so small.

<u>Specification for 4-stage reactor</u>

Plant Size = 10^6 gal/day

Influent BOD_5 = 4,000 mg/l

Cost of Disc media = 45¢/ft^2

BOD_5 Loading Rate = 5.6 lb/(1,000 ft^2)(day)

Scale-up factor = 1.25

Design BOD loading = 10^6 gal/day x 8.34 x 4,000 mg/l = 33,360 lb/day

RBC Area = (33,360 lb/day)/(5.6 lb/(1,000 ft^2)(day)

= 5,957,200 ft^2

5,957,200 x Scale-up Factor (1.25) = 7,450,000 ft^2

Cost = 7.5 x 10^6 ft^2 x \$0.45/ft^2 = \$3.75 x 10^6

(see Note 3)

Number of Shafts $= \dfrac{7{,}500{,}00\ ft^2}{100{,}000\ ft^2/shaft}$ = 75 shafts (see Note 1)

Power Consumption = 75 shafts x 3 HP/shaft = 225 HP

or 75 shafts x 7 HP/shaft = 525 HP (see Note 2)

<u>Notes</u>

(1) Assuming discs are Autotrol 12 foot diameter by 25 foot long assemblies containing 100,000 ft^2 of standard media.[1]

(2) Power requirements vary greatly depending on rotational speed and thickness of biological growth. Power requirements increase with increasing disc velocity and increased slime thickness. The horsepower required should fall somewhere within the range given.

(3) Cost includes concrete tanks, fiber glass covers, and installation[1]. 1978 dollars were used.

The approximate operating cost is

	10^3\$/yr	\$/10^3 gals	\$/lb BOD
Maintenance at 4% of capital	150		
Amortization at 15%/yr	563		
Phosphorus at 52¢/lb	38		
Electricity at 3.5¢/kw-hr	83		
Labor with overhead	300		
	1134	3.4	0.175

Alternative Specification for Stage Reactor

BOD_5 Loading Rate = 21 lb/(1,000 ft^2)(day)

So

RBC area required = 1.99×10^6 ft^2

Approximate capital cost = \$0.9 x 10^6

No. of shafts = 20

Power = 40 H_p

Approximate operating cost = \$520 x 10^3/yr

= \$1.56/10^3 gallons

= \$0.088/lb BOD removed

Clarifiers and filters for sludge removal and dewatering, if the RBC is not followed by AAS-PAC, will cost about \$0.42 x 10^6.

5.3 Design of an Oxygen Activated Sludge Plant

Because, in the experiments the oxygen activated sludge gave settleable sludge and much smoother operation than air activated sludge we will design the plant which does not use powdered activated carbon to use oxygen rather than air. The calculations, which follow, show that a plant can reasonably be designed for an effluent of 300 mg/l BOD (90% removal) in one stage, with a further reduction to 100 mg/l BOD in a second stage.

5.3.1 Design Equations

Details will be found in Metcalf and Eddy[15]. A brief summary of the theory follows.

The Biokinetic Model

The biokinetic model developed by Lawrence and McCarty will be used here. It is primarily based on a relationship between substrate utilization and microbial growth, which can be formulated in two basic equations. The first equation is an empirically developed relationship between the net growth rate of microbes and the rate of substrate utilization:

$$\frac{dX}{dt} = Y \frac{dS}{dt} - k_d X \qquad (5\text{-}1)$$

where X = concentration of microorganisms

t = time

Y = growth yield coefficient; weight of microorganisms produced per weight of substrate removed

S = concentration of substrate or degradable contaminant

k_d = microorganism decay coefficient, time^{-1}

If equation (5-1) is divided by X, we obtain:

$$\frac{1}{X}\frac{dX}{dt} = \frac{Y}{X}\frac{dS}{dt} - k_d \qquad (5\text{-}2)$$

In Equation (5-2) each term has the dimension (time^{-1}) and compatible units must be used. The lefthand side of Equation (5-2), which is the rate of increase of concentration of microorganisms per unit concentration, may also be written $1/\Theta_c$, where Θ_c is called the mean cell residence time, or sludge age. The first term on the righthand side of Equation (5-2) includes the quantity $\frac{1}{X}\frac{dS}{dt}$, which is the rate of decrease of concentration of substrate per unit concentration of microorganisms, often described as F/M ratio.

The quantity $\frac{1}{X}\frac{dS}{dt}$ = F/M is a function of the concentration of substrate and the second equation of the Lawrence and McCarty model assumes the function:

$$\frac{1}{X}\frac{dS}{dt} = \frac{kS}{K_s + S} \qquad (5\text{-}3)$$

The coefficients k, K_s, y and k_d are listed on Table 4.27.

The Flow Scheme

Activated sludge processes include the two major components shown in Figure 5-1, the bioreactor followed by the solids separator. These components should be considered an integral system in terms of treatment performance, design and operation of the system.

Relationships for the Mean Cell Residence Time

The best parameter for the design and operation of an activated sludge process is probably the mean cell residence time θ_c, which is defined as:

$$\theta_c = \frac{X_T}{(\Delta X/\Delta t)_T} \tag{5-4}$$

in which X_T = total active microbial mass in the treatment system, mass; and $(\Delta X/\Delta t)_T$ = total quantity of active microbial mass withdrawn daily, including those solids purposely wasted as well as those lost in the effluent, mass/time. In essence, θ_c is a measure of the average retention time of active microorganisms in the treatment system, and we will show that a desired treatment efficiency, E, can be obtained by controlling θ_c. Furthermore, θ_c is readily measurable and easily controlled in the operation of an activated sludge process.

For the flow scheme in Figure 5-1, θ_c, as defined in Equation (5-4) is:

$$\theta_c = \frac{VX}{wX_r + QX_e} \tag{5-5}$$

in which the various symbols are defined in Figure 5-1. Usually the value of X_e may be assumed to be negligible, and Equation (5-5) then leads to:

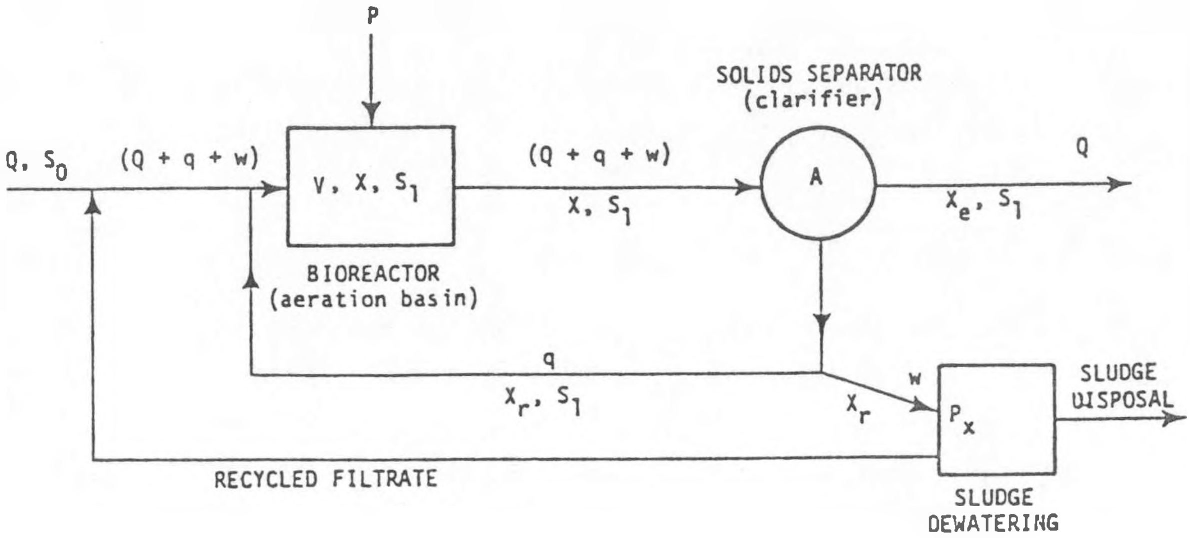
$$\theta_c = \frac{V}{w}\frac{X}{X_r} \tag{5-6}$$

A material balance for microbial mass around the entire AAS system gives:

(net rate of change of microbial mass) = (growth rate)
- (washout rate)

that is,

$$\left(\frac{dx}{dt}\right) (V) = \left[Y \left(\frac{dS}{dt}\right) - k_d X\right] V - (wX_r + QX_e) \tag{5-7}$$



Q = flow rate of liquid waste to be treated biologically, volume/time;

q = flow rate of recycled sludge, volume/time;

w = flow rate of wasted sludge, volume/time;

S_0 = influent substrate concentration, mass/volume;

S_1 = effluent substrate concentration, mass/volume;

X = microbial mass concentration, mass/volume;

X_e = microbial mass concentration in the clarified overflow from the solids separator, mass/volume;

X_r = microbial mass concentration in the underflow from the solids separator, mass/volume;

P = power requirement for aeration, energy/time;

P_x = excess microorganisms production rate, mass/time.

V = volume of aeration basin

Figure 5-1. Activated sludge material balance

Under steady state, $(\frac{dx}{dt})$ will be equal to zero, and substituting for $(wX_r + QX_e)$ from Equation (5-5) will lead to a relationship between θ_c and substrate utilization rate:

$$\frac{1}{\theta_c} = \frac{Y\,(\frac{ds}{dt})}{X} - k_d \qquad (5\text{-}8)$$

Substituting for $\frac{dS}{dt}$ from Equation (5-3) results in a relationship between θ_c and effluent substrate concentration S_1:

$$\frac{1}{\theta_c} = \frac{YkS_1}{K_s + S_1} - k_d \qquad (5\text{-}9)$$

or

$$S_1 = \frac{K_s(k_d + 1/\theta_c)}{Yk - k_d - 1/\theta_c} = \frac{K_s(1 + k_d\theta_c)}{\theta_c(Yk - k_d) - 1} \qquad (5\text{-}10)$$

Equation (5-8) may also be written as:

$$\frac{1}{\theta_c} = Y\ (F/M) - k_d \qquad (5\text{-}11)$$

in which F/M is food to microorganism ratio usually in lbs substrate per lb biological solids per day.

Equation (5-10) shows how control of θ_c controls the effluent concentration S_1 and that as θ_c is reduced, S_1 increases, and if θ_c is made small enough, then S_1 will equal S_o and the process will fail.

Sludge Recycle

A material balance for microbial mass around the solids separator gives:

$$(Q + q + w)X = (q + w)X_r + QX_e \qquad (5\text{-}12)$$

Assuming X_e to be negligible, that is, perfect solids capture by the separator, and letting $\frac{q}{Q} = r$, the recycle ratio, Equation (5-12) gives:

$$X = X_r\ (\frac{r + w/Q}{1 + r + w/Q}) \qquad (5\text{-}13)$$

or,

$$r = \frac{1 - \frac{w}{Q} \; \frac{X_r}{X} - 1}{\frac{X_r}{X} - 1} \quad = \text{(using Equation (5-6)}$$

$$\frac{1 - \frac{V}{Q\theta_c}\left(1 - \frac{X}{X_r}\right)}{\frac{X_r}{X} - 1} \tag{5-14}$$

Equations (5-13) and (5-14) can also be derived by a material balance for microbial mass around the bioractor alone.

Aeration Basin Volume

Under steady state conditions the rate of substrate utilization by microorganisms, $\frac{dS}{dt}$, may be related to the actual substrate removal as follows:

$$\frac{dS}{dt} = \frac{Q(S_o - S_1)}{V} \tag{5-15}$$

Incorporating Equation (5-15) into Equation (5-8) leads to:

$$\frac{1}{\theta_c} + k_d = \frac{1 + k_d\theta_c}{\theta_c} = \frac{Y}{X} \frac{Q(S_o - S_1)}{V}$$

and

$$XV = \frac{YQ\theta_c(S_o - S_1)}{1 + k_d\theta_c} \tag{5-16}$$

In an operating system, Equation (5-16) is a relationship between θ_c and X. For the designer, Equation (5-16) allows determination of the aeration basin volume if X is chosen.

5.3.2 Summary of the design Equations

For this design we have used the coefficients given for oxygen activated sludge on Table 4.27 and have taken the MLVSS, X, to be 3,000 mg/l, which is highest achieved in our experiments. The higher the MLVSS the smaller the aeration basin need be.

For any chosen value of mean cell residence time, θ_c, we can calculate the effluent BOD, S_1, from Equation (5-10),

$$S_1 = \frac{370 + 11.4\Theta_c}{0.211\Theta_c - 1}$$

and the aeration basin volume, V, from Equation (5-10)

$$V = \frac{5.33\text{-}110^{-5}\ Q\Theta_c(S_o - S_1)}{1 + 0.0307\Theta_c}$$

To calculate the recycle ration, r, we need a value for the sludge concentration in the recycle, X_r. Laboratory measurement does not give reliable information and we have assumed the reasonable value $X_r/X = 3.5$. Equation (5-14) thus gives

$$r = (1 - 0.714\ V/Q\Theta_c)/2.5$$

From equation (5-6) the flow rate of waste sludge, w, is

$$w = 0.286\ V/\Theta_c$$

Finally, the hydraulic residence time is

$$V/(Q + w + q) = V/(Q(1 + r) + w)$$

5.3.3 Calculations to Relate Effluent Concentration to Aeration Basin Volume

For a feed flow, Q, of 10^6 gallons some calculations are presented on Table 5.2. The influent BOD is 4,000 mg/l. The sludge production rate, Y, is low and not enough sludge is made to keep the system running unless the sludge age is greater than 4.74 days. Useful removals of BOD require a sludge age over 8 to 10 days.

To obtain effluent BOD's below about 300 mg/l requires very large aeration basins. This is most clearly shown on Figure 5-2 where it can be seen that the size of aeration basin increases rapidly when effluent concentrations below 300 mg/l are required. In the laboratory tests the best removal was 90% corresponding to an effluent of 400 mg/l. The reason for this is that K_s has the high value of 370 mg/l.

TABLE 5.2

CALCULATIONS FOR AN OXYGEN ACTIVATED SLUDGE PLANT

Feed = 10^6 gallons/day at So = 3,000 mg/l

Sludge Age, θ_c, (days)	Effluent, S_1, (mg/l)	Aeration Basin Volume, V. (10^6 gallons)	(10^3 ft^3)	Recycle ratio r	Sludge waste rate, W, (10^6 gal/day)	Hydraulic Residence Time (days)
less than 4.74	negative					
6	1,648	0.64	84	0.37	0.031	0.5
7	943	0.94	126	0.36	0.038	0.7
8	670	1.14	152	0.36	0.041	0.8
9	526	1.31	175	0.36	0.042	0.9
10	430	1.46	194	0.36	0.042	1.0
12	330	1.72	229	0.36	0.041	1.2
15	250	2.05	274	0.36	0.039	1.5
20	180	2.52	337	0.36	0.036	1.8
50	98	4.10	548	0.38	0.023	2.9
100	75	5.14	687	0.39	0.015	3.7

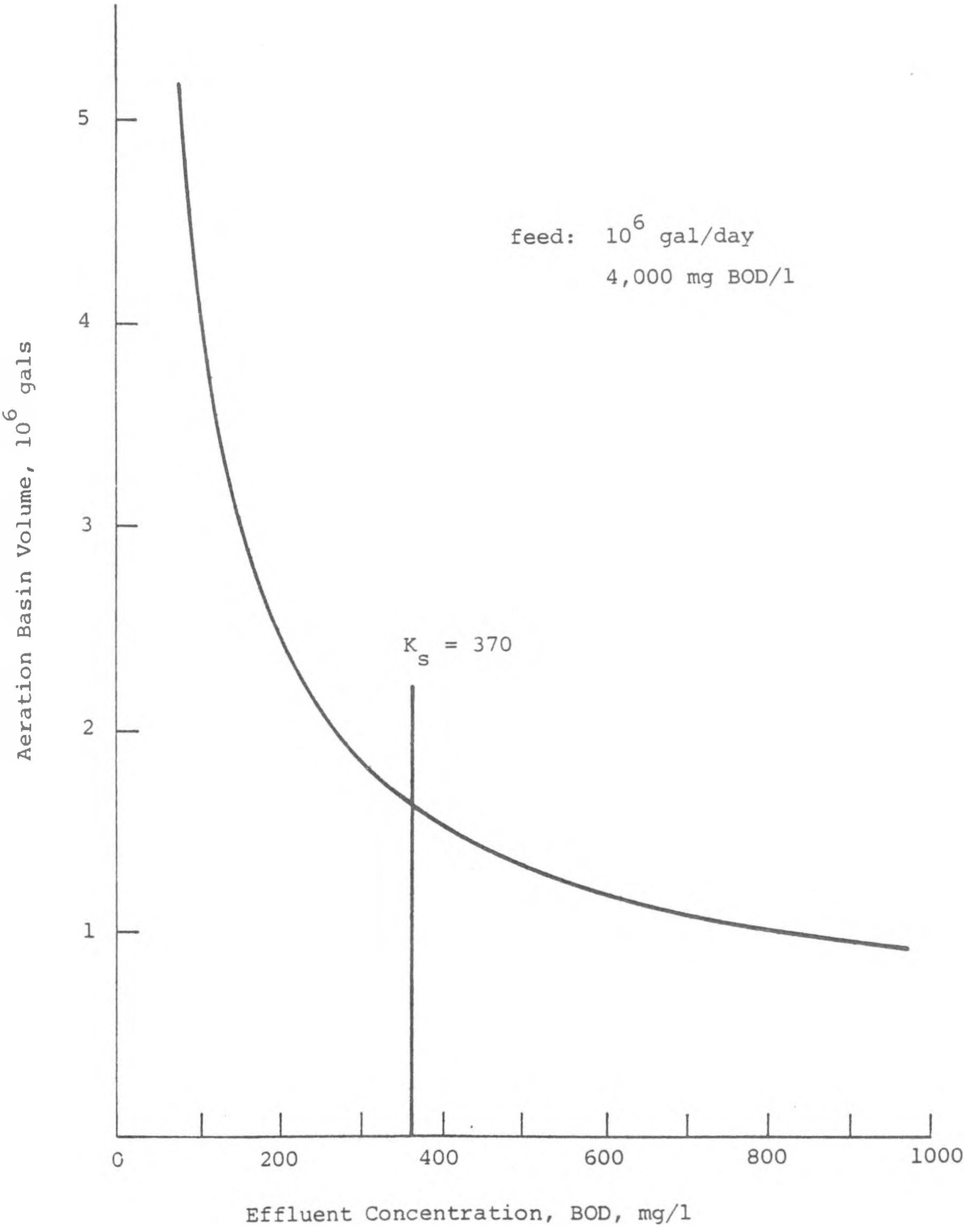


Figure 5-2

THE EFFECT OF INCREASING AERATION BASIN VOLUME ON EFFLUENT BOD

From equation (5-3) it can be seen that

$$\text{for } S \gg K_s, \frac{1}{X}\frac{dS}{dt} = R$$

which is a zero order reaction in which the rate of oxidation of BOD is independent of the concentration, and

$$\text{for } S \ll K_s, \frac{1}{X}\frac{dS}{dt} = \frac{k}{K_s} S$$

which is a first order reaction in which the rate of oxidation of BOD is' directly proportional to the concentration of BOD. This means that K_s is a measure of the concentration at which the reaction changes from zero order to first order. It is impractical to run a system in which all the BOD is oxidized at a slow, first order rate. It is impractical to reduce the effluent BOD much below K_s in a single stage.

We have, therefore chosen as a first stage

1.72×10^6 gallons
θ_c = 12 days
effluent = 330 mg/l

From the first stage the effluent can pass to a second stage for which calculations are shown on Table 5.3. In the second stage the oxidation rate is first order and slow because we want a low concentration. However, the quantity of BOD to be oxidized is low.

The sludge age must be high. For a 50 day sludge age which as high as can reasonably be expected the concentration can be reduced from 330 to 98 mg/l in an aeration basin of $0.2. \times 10^6$ gallons. We think it impractical to design for below 98 mg/l in the effluent. The sum of the volumes of the first plus second stages is 1.93×10^6 gallons. To obtain the same effluent in a single stage would require 4.1×10^6 gallons (Table 5.2). The saving in total volume will more than pay for the complication of two stages. The recycle ratios are on the high side, but reasonable (0.36 to 0.4 in both stages). The waste rate is 41,000 gallons/day in stage 1 and only 1,000 galllons/day in stage 2.

TABLE 5.3

SECOND STAGE CALCULATIONS FOR AN OXYGEN ACTIVATED SLUDGE PLANT

Feed = 10^6 gal/day at 330 mg BOD/l

θ_c (days)	Effluent S_1 (mg/l)	Basin Volume (10^6 gals)	Basin Volume (10^3 ft^3)	Recycle r	Waste Rate (10^6 gal/day)	Hydraulic Residence (days)
20	180	0.10	13	0.40	0.0014	0.07
50	98	0.21	28	0.40	0.001	0.15
100	75	0.33	45	0.40	0.0001	0.24

5.3.4 Other Design Factors

We will use two stages, the first being 1.72 x 10^6 gallons (225,000 ft^3) and the second being 0.21 x 10^6 gallons (28,000 ft^3). For a complete design we need to determine the clarifier sizes, the oxygen requirement, the phosphorus requirement, and the sludge dewatering equipment.

Note that a recycle cooler is not required. In oxygen activated sludge oxidation of high strength wastewaters overheating can occur because the heat generated by oxidation of BOD is not carried away by a sponge of nitrogen. The approximate temperature rise is 1^oF of each 165 mg BOD/l oxidized[42]. In our system the temperature rise is expected to be about 16^oF and a cooler is not needed.

Clarifiers

Because settling in the laboratory tests was so difficult we have sized the clarifiers for a very conservative 300 gal/(day)(ft^2). Each stage, therefore, requires 3,333 ft^2 or two, parallel, 46 ft diameter clarifiers. If the clarifiers are 15 ft deep the hydraulic residence time per stage is 0.37 days.

Oxygen Requirement

The oxygen requirement was measured, with the same removals and MLVSS concentration as in the design, to be 1.1 lb oz/lb BOD removed. About 75% of the oxygen supplied will be utilized[42,43] so the requirements are

Stage 1	44,800 lb O_2/day
Stage 2	2,800 lb O_2/day

Phosphorous Requirement

The requirement of phosphorous (as P) is 1 lb/100 lb BOD removed. The requirement is, therefore

Stage 1	300 lb P/day
Stage 2	19 lb P/day

Sludge Production Rate and Sludge Dewatering

From Table 5.2 the sludge production rate in Stage 1 is 41,000 gallons/day. From Table 5.3 the sludge production rate in stage 2 is 1,000 gallons/day. From both stages the concentration is taken to be 3.5 x 4,000 = 14,000 mg/l.

The dry sludge production rate for the total plant is 4,900 lb/day. The dewatering equipment can be a rotary vacuum filter sized for 72 lb dry weight/ (ft^2)(day) (Reference 42). The minimum required active area is 68 ft^2. A modestly sized filter 6 ft long x 6 ft diameter will have about 100 ft^2 and need be operated only half time. The clarifiers have enough holding capacity so that additional sludge storage is not needed.

5.3.5 Summary and Cost for Oxygen Activated Sludge

The summary and cost is shown on Table 5.4. Unit costs are largely drawn from Seufert et al[43]. The oxygen is made on site. The operating cost for oxygen is the air compressor power at 0.17 kw-hrs/lb oz and 3.5¢/kw-hr. The rest of the electricity is for the mixer/aerators. The labor cost is quite high and may be reduced if operators can be assigned part time. The overall cost of 15¢/lb BOD removed is higher than that found before[42].

TABLE 5.4

COST OF OXYGEN ACTIVATED SLUDGE PLANT

Capital Cost

Stage 1	10^6\$
Covered oxygenation basin, 229,000 ft^3 @ \$8.20/ft^3	1.88
Mixers/Aerators at 120 lb O_2/(hp)(day) and \$600/hp; 273 hp	0.22
Clarifiers, 2 x 46 ft diam at \$0.1 12 x 10^6	0.22
Vacuum filter, 100 ft^2 active area	0.20
Oxygen plant and contigency	0.29
	2.81

Stage 2	
Covered oxygenation basin; 28,000 ft^3 @ \$10.80/ft^3	0.301
Mixers Aerators, 18 hp at \$700/hp	0.013
Clarifiers	0.225
Vacuum filter (use stage 1)	-
Oxygen plant and contingency	0.08
	0.619

Operating Cost (8,000 hrs/yr)

Stage 1	10^3\$/yr	\$/10^3 gals	\$/lb BOD
Maintenance at 4% of capital	112	0.336	0.0151
Amortization at 15%/yr	422	1.266	0.0569
Oxygen at 0.6¢/lb	70	0.21	0.0094
Phosphorus at 52¢/lb	52	0.157	0.0070
Electricity at 3.5¢/kw-hr	56	0.168	0.0068
Labor with overhead	300	0.900	0.0404
	1,012	3.04	0.136
Stage 2			
Maintenance at 4% of capital	25		
Amortization at 15%/yr	93		
Oxygen at 0.6¢/lb	6		
Phosphorus at 52¢/lb	3		
Electricity at 3.50/kw-hr	4		
Labor included in stage 1	-	-	-
	131	0.39	0.20
Total Plant	1,143	3.43	0.15

Note that stage 1 reduces BOD from 3,000 to 330 mg/l
stage 2 further reduces BOD to 98 mg/l

5.4 Activated Sludge with Powdered Activated Carbon (PAC-AAS)

In comparison with the oxygen activated sludge process, the PAC-AS process is mechansitically more complex and our experimental data are limited to two sets of operating conditions, distinguished primarily by the level of the PAC concentration in the aeration unit (MLCSS). These two MLCSS levels are approximately 5,500 and 12,000 mg/l, using AMOCO PX-21 PAC. As shown in Table 4.35 the removals are about 70% in BOD_5, 57% in COD, and 52% in TOC for the lower MLCSS of 5,500 mg/l; the removals are about 81% in BOD_5, 69% in COD, and 72% in TOC for the higher MLCSS of 12,000 mg/l. Two sets of design calculations are done in the following sections on the basis of the experimental data available. However, these designs are preliminary and no optimization is possible.

5.4.1 Design Basis and Equations

Reactor Volume

Since the Monod-type biochemical model, which was used in the design of the oxygen activated sludge process, can not be used for the PAC-AS system without substantial modifications, the following designs are based on the two operating conditions in our experiments, as summarized in Table 5.5. The F/M ratios calculated are 0.3 and 0.1 for the corresponding MLCSS of 5,500 mg/l and 12,000 mg/l, respectively. The higher level of MLCSS apparently led to a larger biomass in the reactor and resulted in a lower F/M ratio. Both F/M ratios are within the common range of biotreatment practice.

Knowing the F/M ratio, the feed BOD_5 and the MLBSS in the reactor, the hydraulic residence time, Θ, can be calculated as:

$$\Theta(\text{hrs.}) = \frac{\text{Feed BOD}_5\ (\text{mg/l}) \times 24\ \text{hrs/day}}{\text{MLBSS}\ (\text{mg/l}) \times \text{F/M} \left(\dfrac{\text{mg BOD}_5}{\text{mg MLBSS}\quad \text{day}} \right)} \qquad (5\text{-}17)$$

The reactor volume, V, can then be calculated as the product of Θ and volumetric feed rate, Q.

Oxygen Requirement

The oxygen requirement is calculated by using the following equation:

$$O_2 \text{ required in kg/d} = \text{Total Mass of BOD}_1 \text{ Utilized in kg/d)}$$
$$1.42\ \text{(Mass of Organisms Lost in kg/d)} \qquad (5\text{-}18)$$

which is based on an oxygen demand balance on the reactor-clarifier system.

TABLE 5.5

TWO OPERATING CONDITIONS OF PAC-AS SYSTEM

PAC-AS

	1st Period	2nd Period	Combined Unit
MLCSS, mg/l	5,500	12,000	5,900
Reactor Volume, V, liter	6.67	6.67	3.17
Volumetric Feed Rate, Q, ml/day	1,875	1,880	1,340
Influent BOD_5, mg/l	3,767	3,512	1,800
MLBSS, X, mg/l	3,560	10,120	5,450
F/M, $\frac{\text{mg } BOD_5 \text{ Applied}}{\text{mg MLBSS x day}}$	0.30	0.10	0.14

Sludge Production

The production rate, in kg/d of the biological cells may be calculated as:

$$\frac{dX}{dt} = \frac{XV}{\theta_c} \tag{5-19}$$

where X = MLBSS

V = reactor volume

θ_c = mean cell residence time or sludge age

To calculate the PAC portion of the volatile sludge, the ratios of MLCSS to MLBSS are used as an estimate. These were 1.54 for the first period, 1.19 for the second period, and 1.08 for the combined RBC-PAC-AS system. Since the sludge was wasted directly from the reactor in our experiments, the PAC portion of the volatile sludge may be estimated by the product of this ratio and $\frac{dX}{dt}$.

The volatile fraction of the sludge ranges from 85% to 94%. Assuming 85% as volatile, the production rate of total sludge can then be calculated by dividing the production rate of volatile sludge by 0.85.

5.4.2 Summary of Design Calculations

Reactor Volume

The calculation is shown in Table 5.6. Corresponding to a MLCSS of 5,500 mg/l and 12,000 mg/l the reactor volumes are 4.95×10^5 and 5.35×10^5 cubic

TABLE 5.6

EVALUATION OF REACTOR VOLUME AND OXYGEN REQUIREMENT

Design:	PAC-AS		RBC-PAC-AS
Influent BOD_5, mg/l	4,000		1,800
Volumetric Feed Rate, Q, (10^6 gal/day)	1	1	1
MLBSS, X, mg/l	3,600	10,000	5,450
Estimated MLCSS, mg/l	5,500	12,000	5,900
F/M	0.3	0.1	0.14
Calculated θ, hours (days)	88.9(3.7)	96.0(4.0)	56.6 (2.4)
Calculated Reactor Volume, V, ft^3	$4.95x10^5$	$5.35x10^5$	$3.15x10^5$
BOD_5 removal %	70	80	66
BOD_5 removed, mg/l	2,800	3,200	1,188
BOD rate coefficient, base e	0.207	0.207	0.207
BOD_1 removed, mg/l	4,350	5,000	1,840
kg/d	16,456	18,915	6,970
XV, kg	50,466	151,512	48,618
θ_c, day	23	20	13.5
Cell Growth Rate, $\frac{dX}{dt}$, kg/d	2,194	7,576	3,600
1.42 $(\frac{dX}{dt})$, VSS kg/d	3,115	10,757	5,114
O_2 Requirement, kg/d	13,340	8,158	1,856
O_2 to be supplied, kg/d, (kg/hr)	17,787(741)	10,877(453)	2,475(103)
Estimated Aerator Power Required, hp, (kw)	765(570)	468(349)	106(79)
PAC Dosage, mg/l	570^a	$2,090^a$	$1,620^b$

a Amoco PX-21

b Calgon NAP

feet respectively, and the hydraulic residence times are 3.7 and 4.0 days.

Oxygen Requirement

Also shown in Table 5.6 the oxygen requirements are calculated from Equations (5-18) and (5-19). Assuming that 75% of the oxygen supplied will be utilized, the amount of O_2 to be supplied can be calculated. To estimate the energy required for oxygen transfer we assume that 0.35 kw-hr will be required per pound of oxygen supplied, i.e. 0.77 kw-hr/kg O_2. The required aerator powers are also shown in Table 5.6. No data is available to evaluate the mixing requirement. So we assume that the aeration for oxygen requirement is sufficient for the mixing.

Sludge Production and Dewatering

The various forms of sludge are calculated in Table 5.7, including biological cells, PAC sludge, volatile sludge, and total sludge. If rotary vacuum filters are used for dewatering and are sized for 72 lb dry sludge/(ft^2)(day), the required active areas are also shown in Table 5.7.

TABLE 5.7

SLUDGE PRODUCTION

	PAC-AAS		RBC-PAC-AAS
MLCSS, mg/l	5,500	12,000	5,900
Cell Growth Rate, $\frac{dX}{dt}$, kg/d	2,194	7,576	3,600
Cell Growth/PAC	1.54	1.19	1.08
PAC Sludge Production, kg/d	3,379	9,015	3,888
Volatile Sludge Production, kg/d	5,573	16,591	7,488
Total Sludge Production, kg/d	6,556	19,519	8,809
lb/d	14,423	42,942	19,380
Vacuum Filter Surface Area Required, ft^2	200	596	269

Phosphorous Requirement

The requirement of phosphorous (as P) is 1 lb/100 lb BOD_5 removed. The requirements are, therefore,

PAC-AS	P required, lb/d
MLCSS = 5,500	235
= 12,000	267

Clarifiers

The settling characteristic of the PAC-AS sludge was not evaluated in this study. So we assume a very conservative overflow rate, 300 gal/(day)(ft^2), as used in the oxygen activated sludge design. The required surface area, 3,333 ft^2, may be provided by using two 46 ft diameter clarifiers in parallel. If the clarifiers are 15 ft deep, the hydraulic residence time will be 0.37 days.

Carbon Requirement

In determing cost the carbon requirement has been taken to be the quantity to produce the concentrations in the feed stream shown on the bottom line of Table 5.6. These are the values used in the laboratory experiments. The PAC sludge production shown on Table 5.7 should be equal to or less than the carbon input to the system. (The sludge will be less than the input if carbon is lost in the clarifier effluent). In fact, the PAC sludge production is 1.5 times the input for the first PAC-AS test, 1.1 times the input for the second PAC-AS Test, and 0.6 times the input for the RBC-PAC-AS test. The calculated PAC sludge production is based on the analysis of MLCSS done as described in Appendix 5. This is the best procedure known to us but we have made no independent check on the analysis.

Carbon has proved to be the controling cost and it is preferable to lower the requirement. The way to lower the carbon requirement is to lower the wastage by lowering the sludge wasting rate. This is done by increasing the mean cell residence time (θ_c). Our experiment covered a range of θ_c from 16 to 30 days and we have designed within this range at θ_c = 23 days. The PAC sludge production is inversely proportional to θ_c. To reduce the carbon requirement to, for example, one-third, θ_c must be increased to 69 days. We think it unsafe to base a design on θ_c = 69 without prior laboratory tests.

5.4.3 Costs

Both capital and operating costs are summarized in Table 5.8. The price of PAC has been quoted as $1/lb by a major manufacturer, and appears to be the most significant cost item. It should also be pointed out that any cost comparison with Table 5.8 should be carefully done. This is because no optimization in PAC-AS system was possible and the PAC-AS system achieved better COD removal, i.e., the removal of refractory substances.

The cost of carbon is high as previously stated. It may be possible and economic to recover carbon by, for example, wet air oxidation. We have not determined this.

TABLE 5.8

COSTS OF PAC-AS (ACTIVATED SLUDGE WITH POWDERED ACTIVATED CARBON ADDITION) PLANT

Capital Cost		10^6\$		10^6\$
MLCSS, mg/l	5,500		12,000	
Aeration Basin Volume, 10^5 ft^3	4.95		5.35	
Aeration Basin Cost at \$7.20/ft^3		3.56		3.85
Mixers/Aerators, hp.	765		468	
at \$600/hp		0.46		0.28
Clarifiers, 2 x 46 ft diam at \$0.112 x 10^6		0.224		0.224
Vacuum Filter Area, ft^2	200		600	
at \$0.2 x 10^6/100 ft^2		0.40		0.60
		4.644		4.954

Operating Cost (8000 hrs/yr)	10^3\$/yr	
Maintenance at 4% of Capital	186	198
Amortization at 15%/yr	698	742
Phosphorous at 52¢/lb	41	46
Electricity at 3.5¢/kw-hr	160	98
Labor with Overhead	300	300
Powdered Carbon at 1\$/lb[a]	1,584	5,810
	2,969	7,194

a. A quotation from Calgon, October 1980

5.5 Rotating Biological Contactor followed by Air Activated Sludge with Powdered Activated Carbon Addition (RBC-PAC-AAS)

Our experimental data on RBC and PAC-AS processes have indicated that a combination of these processes, i.e., RBC followed with PAC-AS, may be a potential alternative treatment scheme. The effluent from a four-stage RBC unit with a hydraulic residence time of 12 to 18 hours was fed into a PAC-AAS unit, and the experimental results have been presented in the preceding PAC-AAS section. The data obtained from such a combined units were used here as the design basis. It should be pointed out that in view of the commercial availability of PAC, the Amoco PX-21 was replaced with Calgon NAP, and the MLCSS was about 5,900 mg/l.

5.5.1 RBC Design

For a four-stage RBC unit, the hydraulic residence time is selected to be 12 hours and the BOD_5 loading rate 5.6 lb/(1000 ft^2)(day), and these are the same as those used for the RBC design in section 5.2. The design and costing for RBC in Section 5.2 may be used here. Furthermore, as discussed in section 5.2, a single stage RBC unit will suffice even though this was not the system used for experiments.

The characteristics of the feed to the PAC-AS portion of the combined units are, as shown in Table 4.35, about 1,800 mg/l in BOD_5, 8,400 mg/l in COD, and 1,700 in TOC. The effluent is expected to be about 600 mg/l in BOD_5, 3,400 mg/l in COD, and 600 mg/l in TOC.

5.5.2 PAC-AAS Design

The design approach is exactly the same as in Section 5.4.1. Calculations have been included in Tables 5.5 through 5.7. Key design parameters will be summarized in the following paragraphs.

Reactor Volume

If MLCSS is maintained at 5,900 mg/l with the PAC from Calgon NAP, the hydraulic residence time is about 2.4 days and the reactor volume is 3.15×10^5 ft^3.

Oxygen Requirement

The amount of oxygen to be supplied will be about 2,475 kg/d, and the required aerator power will be 106 hp (79 kw).

Sludge Production and Dewatering

The rate of total sludge production is calculated in Table 5.7, and is estimated to be about 19,380 lb/d. The vacuum filter surface area required would be about 269 ft^2.

Phosphorous Requirement

Based on 1 lb P required per 100 lbs of $BOD_{\%}$ removed, the phosphorous requirement is about 100 lb/d.

Clarifiers

Same clarifiers as in Section 5.4.2 will be used.

5.5.3 Costs

Both capital and operating costs for the RBC-PAC-AAS system are summarized in Table 5.9. The capital costs for both single-stage and four-stage RBC are shown. However the operating cost was calculated only for the system utilizing the single-stage RBC.

The system gives the same performance as the PAC-AS system loaded at 12,000 mg/l PAC with a considerable reduction in cost.

TABLE 5.9

COSTS OF RBC-PAC-AAS PLANT

Capital Cost	10^6 \$	
	Single Stage	Four Stage
RBC	0.9	3.38
Aeration Basin at \$7.20/ft^3	2.27	
Mixers/Aerators at \$600/hp	0.064	
Clarifiers, 2 x 46 ft diam at \$0.112 x 10^6	0.224	
Vacuum Filters at \$0.2 x 10^6/100 ft^2	0.538	
	4.0	6.5

Operating Cost (8000 hrs/yr)	10^3 \$/yr
Maintenance at 4% of Capital	160
Amortization at 15%/yr	600
Phosphorous at 52¢/lb	17
Electricity at 3.5¢/kw-hr	22
Labor with Overhead	300
Powdered Carbon at 1 \$/lb	4,504
	5,603

6. PRE-, POST- AND ALTERNATIVE TREATMENTS

Biological treatment has not proved to be uniquely useful as a treatment for MIS retort water. If used it must be preceded by some other treatments and, because of the high level of refractory COD, followed by additional treatment. To define a full treatment sequence we decided it necessary to consider the following:

Pretreatments	oil/water separation
	ammonia stripping
Major treatments (may use two in sequence)	biological oxidation
	solvent extraction
	resin adsorbtion
	carbon adsorbtion
	reverse osmosis
Alternative	production of dirty stream oxidation

Experiments were not conducted on oil-water separators; designs have been made and costs given on the assumption that standard API separators will suffice. We recommend that oil-water separation be given, at least, a brief experimental study.

Experiments are not usually required for stripping. Designs and costs have been given based on a calculational procedure which is described in detail below.

Tests on solvent extraction and resin adsorption showed that these treatments were not satisfactory.

Activated carbon seemed to be a functional treatment as a follow-up to biological oxidation.

Reverse osmosis proved to be so useful a procedure that the tests were expanded and a separate report is being issued.

It is most probable that wet air oxidation will suffice as an alternative clean-up treatment. However, the procedure requires pressures up to 1,000 psi for times of up to one hour and the equipment is very expensive. There is an untried process recently described which uses oxygen and ozone as the oxidant at pressures below 60 psi. This process should be tried on retort water.

Since an MIS retort probably requires more steam influent than the quantity of retort water produced, the raising of dirty steam from dirty water is an alternative treatment which we strongly recommend be tested. Equipment exists which is expected to work.

6.1 Oil-Water Separation

Oil-water separation of oil shale wastewaters has not been studied in detail. Available samples of retort waters often show oil in water emulsions that appear stable and suggest that separation by conventional means may not prove adequate. It is, however, necessary to remove most of the oil present to prevent interference, fouling and foaming in downstream treatment units, and to provide a water more acceptable for recycle and reuse.

A detailed study of the oil-water separation problem is being considered by LETC. Until the results of this study are available, it will be necessary to base our designs on conventional systems, and to discuss some of the methods available for the control of emulsions.

The principal function of an oil-water separation is to effect the separation and removal of free oil from oil contaminated water by the action of gravity. Consequently, oil-water separations will not separate dissolved substances nor will they break emulsions. The American Petroleum Institute has conducted an intensive investigation of the principle governing the design and operation of oil-water separations. Their findings[44] are summarized here.

6.1.1 Design Procedure

Rate of Rise of Oil Globules

As a result of an intensive investigation including both experimental and plant operating data, the design of oil-water separators should be based on the rise rate of oil globules having a diameter of 0.015 cm. This globule size has been adopted as the design standard because plant designs based on it have achieved satisfactory removal. It has not been shown that this value is applicable to oil shale wastewaters. The rate of rise of oil globules having a diameter of 0.015 cm in wastewater can be expressed in feet per minute as:

$$v_t = 0.0241 \frac{S_w - S_o}{\mu} \qquad (6\text{-}1)$$

Where:

v_t = rate of rise of oil globule (0.015 cm in diamter) in wastewater, in feet per minute.

S_w = specific gravity of wastewater at design temperature of flow.

S_o = specific gravity of oil in wastewater at design temperature of flow.

μ = absolute viscosity of the wastewater at design temperature, in poise.

The required physical properties should be determined by actual measurement whenever possible, but for purposes of developing order of magnitude cost estimates the values given on Figures 6-1 and 6-2 may be used.

Following the concept of rising oil globules as expressed by equation (1), the design of an API oil-water separator is based on the following three relationships:

(1) Minimum horizontal area, A_H

$$A_H = \frac{F\,Q_m}{V_t} \tag{6-2}$$

Where:

F = design factor from turbulence, F_t, and short-circuiting, F_s factors. $(F = (F_s)\ (F_t))$

Q_m = wastewater flow, in cubic feet per minute

(2) Minimum vertical cross-sectional area, A_c

$$A_c = \frac{Q_m}{V_H} \tag{6-3}$$

Where:

V_H = horizontal flow velocity, in feet per minute, not to exceed 15 v_t or 3 fpm.

(3) Minimum depth to width ratio of 0.3.

$$\frac{d}{B} = 0.3 \tag{6-4}$$

Where:

d = depth of wastewater in separator, in feet

B = width of separator chamber, in feet

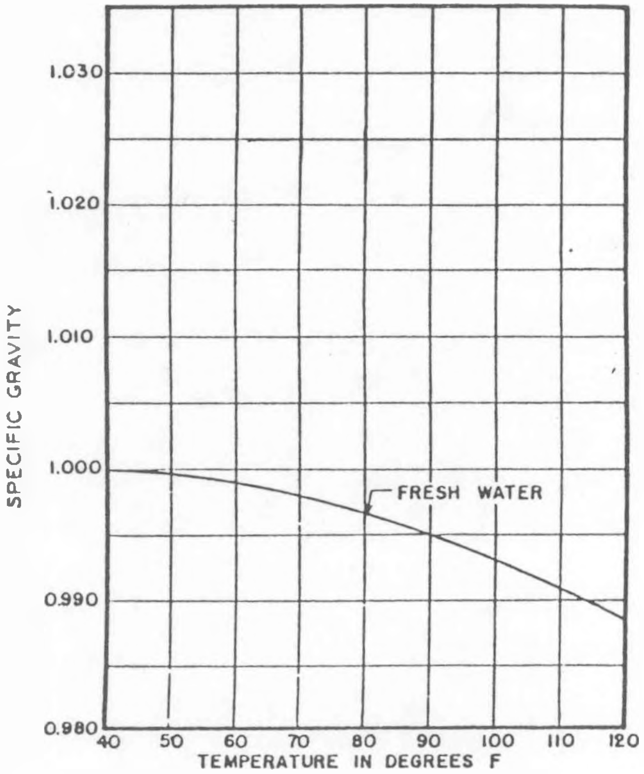


Figure 6-1. Specific gravity of clear water for temperatures between 40° F and 120° F. (Reference 44)

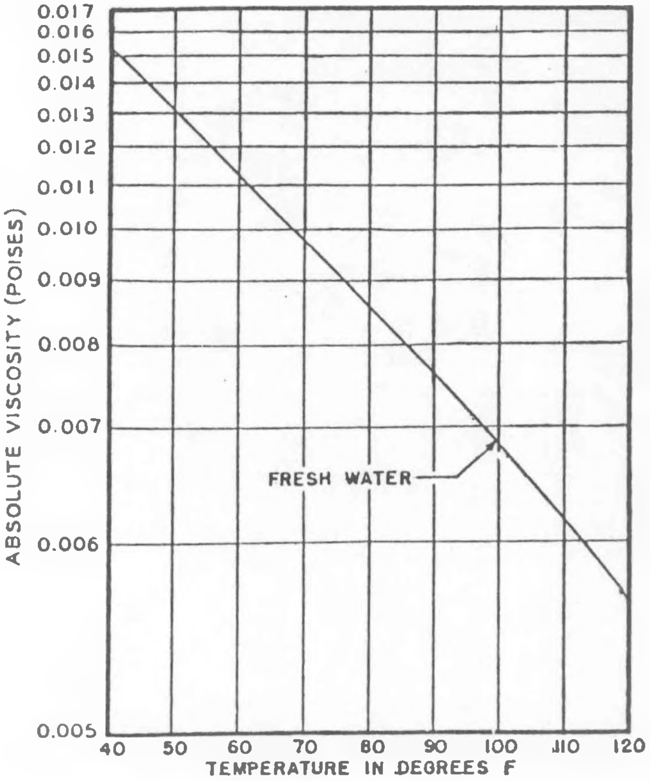


Figure 6-2. Absolute viscosity of clear water for temperatures between 40° F and 120° F. (Reference 44)

Minimum Horizontal Area of Separator

A number of studies have been undertaken to determine the effects of short-circuiting and turbulence on the minimum horizontal area of the separator. As a result of these studies, the design factor, as shown in equation (3), was found to be a function of both short-circuiting and turbulence. The short-circuiting factor, F_s, was found to be a constant and a value of 1.2 is recommended. The turbulence factor, F_z, was found to be a function of the ratio of mean horizontal velocity, V_H, to the rate of rise of the oil globule, v_t. A tabulation of turbulence factors is presented in Table 6.1.

Table 6.1 Recommended Values of Turbulence Factors

V_H/v_t	Turbulence Factor, F_t
20	1.45
15	1.37
10	1.27
6	1.14
3	1.07

The design factor, F, used in equation (6-2) is the product of the short-circuiting factor, $F_s = 1.2$ and the turbulence factor, F_z. The curve in Figure 6-3 can be used to obtain the design factor F.

In the recommended design method which follows, the value of the horizontal area, A_H, is not determined directly. Acceptable values of width and depth are established first using equations (6-3) and (6-4). The separator length is then calculated from the following formula derived from equations (6-2) and (6-3).

$$L = F\frac{V_H}{v_t} d \qquad (6\text{-}5)$$

where:

L = length of separator chamber, in feet.

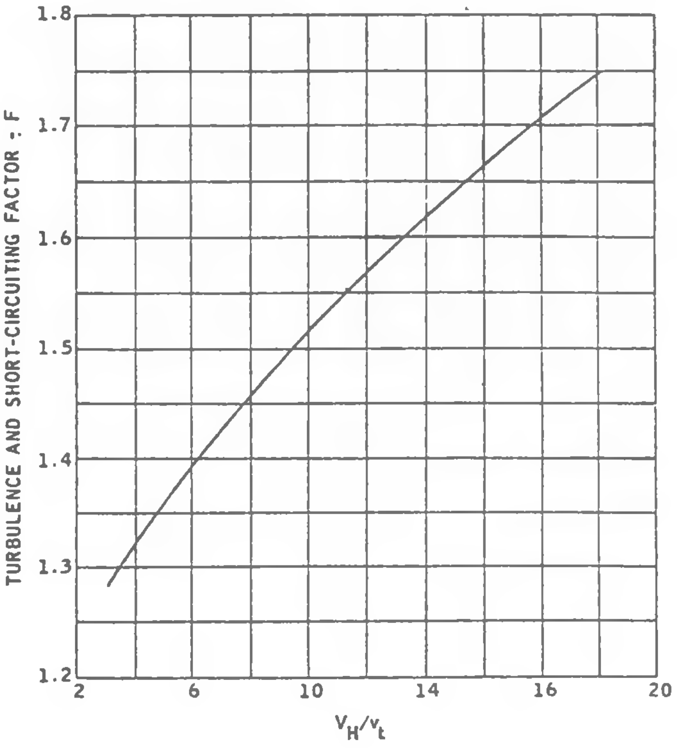


Figure 6-3. Recommended values for F for various values of $\frac{V_H}{V_t}$.

Minimum Cross-Sectional Area of Separator

The purpose of this specification is to limit the influence of turbulence on the operation of the separator. A maximum velocity ratio, V_H/v_t, of 15 and a maximum value of 3 fpm for V_H have been selected. There is no theory to define a maximum value of the mean horizontal velocity; the value of 3 fpm has been determined by operating experience.

Minimum Depth-to-Width-Ratio

Tests conducted on experimental separators indicate that, for chambers with the same surface area, the influence of depth on oil retention is not significant until the depth-to-width ratio becomes less than 0.3. The maximum recommended is 0.5.

Number and Dimensions of Separator Channels

Due to practical limitations on the size of separator channels, it may be necessary to use two or more parallel channels. These limitations are:

a. Separator channels equipped with flight scrapers normally are limited to a width of 20 ft. (Greater widths may be used if necessary to meet unusual conditions.)

b. The disturbing effect of operating flight scrapers in shallow water has led to the recommendation that the minimum depth of water shall be 3 ft.

c. It is recommended that a minimum of two parallel channels be provided so that one is available for use when it becomes necessary for the other to be removed from service for repair or cleaning.

In summary, a separator should be designed within the following limits:

a. Horizontal velocity, V_H, maximum = 3 fpm or 15 v_t, whichever is smaller.

b. Depth, d = 3 ft. minimum to 8 ft. maximum.

c. Depth-to-width ratio, d/B = 0.3 minimum to 0.5 maximum.

d. Width, B = 6 ft. minimum to 20 ft. maximum.

In general, the most economical design will be one with the minimum number of channels obtained by selecting the maximum cross-sectional area for the individual channels.

6.1.2 Example of Oil-Water Separator Design

The equations presented are used here to design an API oil-water gravity separator for a liquid flow of 6,200 pgm. This flow is three times the expected gas condensate flow rate and should be an upper limit for wastewater flows in a commercial oil shale plant.

Condition Assumed for Wastewater and Oil

a. Wastewater:

Maximum flow, Q_m = 830 cfm (6,200 gpm)
Temperature = 105°F
Specific gravity, SW = 0.992.
Absolute viscosity, μ = 0.0065
Maximum allowable mean horizontal velocity,
$V_H = 15\ v_t$, not to exceed 3 fpm

b. Shale Oil Globules in Water

Diameter of globule (estimated), D = 0.015 in.
Specific gravity, S_o 0.92
Rate of rise in wastewater Equation (6-1)

$$v_t = \frac{0.0241\ (0.992 - 0.920)}{0.0065} = 0.267 \text{ fpm}$$

Maximum allowable mean horizontal velocity:

$$V_H = (15)\ (0.267) = 4 \text{ fpm}$$

This exceeds 3 fpm; therefore, use limiting value of $V_H = 3$.

Design Factor

From Figure 6-3, F = 1.55 for $\frac{V_H}{v_t} = \frac{3.0}{0.267} = 11.2$

Minimum Areas and Dimensions

a. Minimum cross-sectional area:

$$A_c = \frac{Q_m}{V_H}$$

$$= \frac{830}{3} = 276.67 \text{ sq. ft.}$$

b. Number of channels: the largest practical channel is 20 ft wide and 8 ft deep. The number of channels is the ratio of the total cross-sectional area required to that of the largest practical channel.

$$n = \frac{276.67}{160.0} = 1.73$$

thus, two channels will be required.

c. Dimensions of acceptable separator channel, assuming the channel will be 20 ft wide:

$$d = \frac{A_c}{B_n}$$

$$= \frac{276.67}{(20)\ (2)} = 6.9 \text{ ft}$$

The width and depth will be 20 ft and 6.9 ft, so d/B = 0.345 which is acceptable. The length can be computed from Equation (6-5):

$$L = F\frac{V_H}{V_t}\ d = 1.55 \times 11.2 \times 6.9 = 120 \text{ ft}$$

Final Design

Number of channels, n = 2
Width, B = 20 ft
Depth, d = 6.9 ft
Length, L = 120 ft

The above example is based on flow condition which requires at least 240 sq ft of cross-sectional area. Frequently, a smaller or cross-sectional area will be required, and it will be necessary to modify the design calculation in two respects:

a. Good practice recommends that even for small flows one channel always should be available while another is being cleaned or repaired. Therefore, a minimum of two channels should be constructed, even though the calculations may indicate that one will suffice.

b. For smaller flows, the required cross-sectional area may be such that use of a 20-ft width results in a depth less than the recommended minimum 0.3 depth-to-width ratio.

6.1.3 Cost

We have designed and costed separators for handling flows from 700 to 6,000 gpm which should cover the range of condensate flows at a commercial scale oil plant. Costs were based on the cost of concrete and estimated construction/installation charges. The results are shown in Figure 6-4 which may be represented by

$$\text{Capital cost, API separator} = 478.5\ (Q,\ \text{cfm})^{1.067} \quad \text{(1979\$)}$$

The costs presented are for unenclosed separators. As many of the oil shale condensates are characterized by a foul odor, it may be necessary to enclose the separation tanks, and this would significantly increase their capital costs. If, however, oil-water separation can occur after the stripping process, then enclosure should not be necessary. It is not known whether this sequence of treatment would cause uncontrollable foaming or fouling in the stripping column.

6.1.4 Emulsions

The separation of oil from water using differential gravity-type separators is standard practice in the chemical process industry. However, gravity-type separators alone may be unable to effect adequate separation of the oil-water mixtures associated with oil shale processing, due to the formation of stable emulsions. Some form of additional "emulsion breaking treatment" may therefore be required.

An emulsion is defined as an intimate, two-phase mixture of oil and water with one phase dispersed as very small globules in the other phase. The globules are stablized by an interfacial film or stabilizing agent that inhibits coalescence and gravity settling.

Emulsion breaking technology is only quasi-scientific with a lot of trial-and-error experimentation required before an optimum treatment scheme can be specified. Specification of generalized treatment schemes is risky and it is normally recommended that a thorough experimental investigation be carried out to determine optimum treatment methods. As experimental data on the nature of

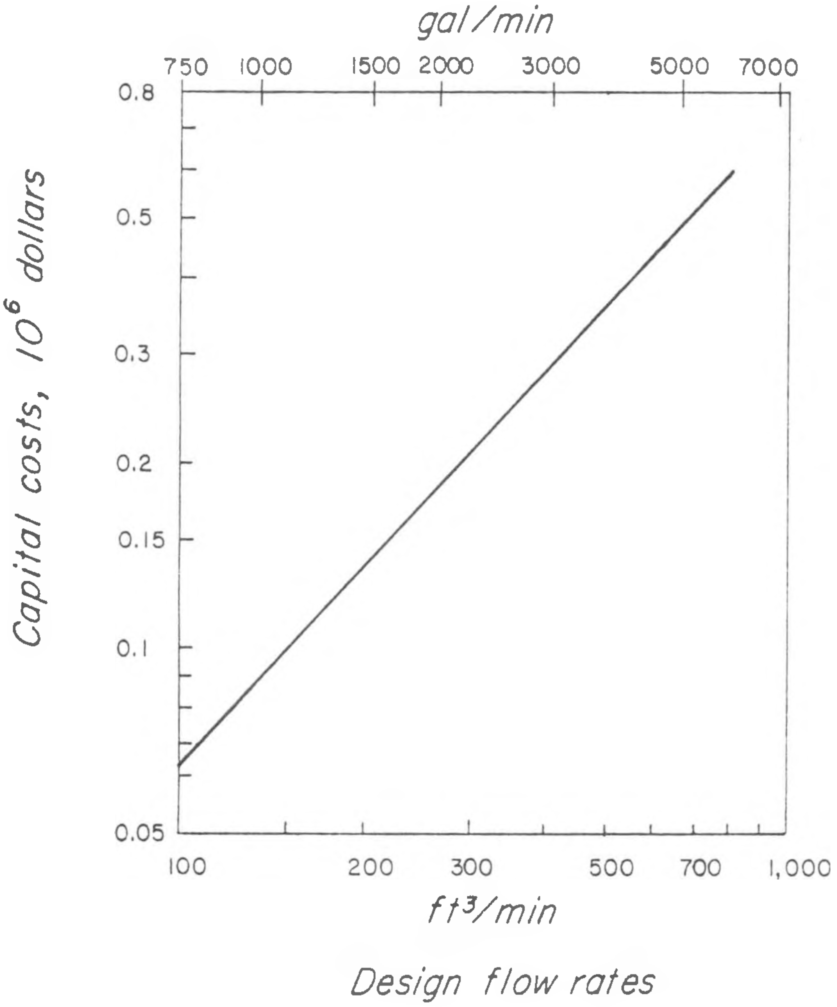


Figure 6-4. Order of magnitude capital cost estimate for API gravity oil-water separators.

the emulsions associated with oil shale processing is not available, it would not be proper to propose a specific treatment method. Instead, a discussion on emulsion breaking methods taken from an American Petroleum Institute's publication[44] is presented.

Methods of Emulsion Breaking

Chemical, electrical and physical methods are used to break emulsions. A physical method that may be of use for oil shale wastewaters is "filter coalescence" of the small oil droplets to a size sufficient for gravity separation. When a dispersion of micron-sized droplets of one liquid (oil) in another (water) is caused to flow through an appropriate porous solid, coalescence of the dispersed phase is induced and separation of the liquids results. The dispersed phase may be allowed to accumulate without leaving the porous medium, with periodic regeneration to remove accumulated oil (intermittent filtration) or a steady state may be reached where effluent oil flow rate equals influent oil flow rate, but where the effluent oil has been coalesced into globules (millimeters or larger) which are much more readily separated by gravity than the smaller droplets in the influent (continuous coalescence). In continuous coalescence, the filter augments gravity separation, reducing the cost of the separator.

Filter media are usually either the packed fibrous type (e.g. fiber glass, steel wool, spun synthetics) or unconsolidated granular materials (e.g. sand, gravel, crushed coal). Process arrangements often provide sequential media. Because of their large specific surfaces and high voids, fibrous media are usually more efficient in removing droplets for a given bed depth than are granular media, but fibrous media are also more susceptible to blockage by suspended solids and are more difficult to regenerate, besides being more costly than most granular media. Thus, granular media seem better suited to oily wastewater treatment than fibrous media because the former are less expensive and more readily regenerated by backwashing or steam cleaning.

Electrial methods are frequently used to break water in oil emulsions; however, a combination of electrical and chemical methods is sometimes used where neither method alone is successful.

Emulsions can be broken by the use of chemicals which balance or reverse the interfacial surface tension on each side of the interfacial film, neutralize the stabilizing electrical charges, or precipitate the emulsifying agents. Reactive cations, such as H^+, Al^{+++}, and Fe^{+++} are effective in breaking oil in water emulsions. The "converting capacity" of other reactive cations is in the order of:

$$\begin{array}{l} \mathrm{Cr} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Ba} > \mathrm{Sr} \\ \phantom{\mathrm{Cr} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Ba} > {}}\mathrm{Ca} \\ \phantom{\mathrm{Cr} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Ba} > {}}\mathrm{Fe}^{++} \\ \phantom{\mathrm{Cr} > \mathrm{Ni} > \mathrm{Pb} > \mathrm{Ba} > {}}\mathrm{Mg} \end{array}$$

The effectiveness of the various chemical methods can be determined quickly and easily by a microscopic technique followed by larger scale examination in test tubes.

6.2 Ammonia and Acid Gas Stripping

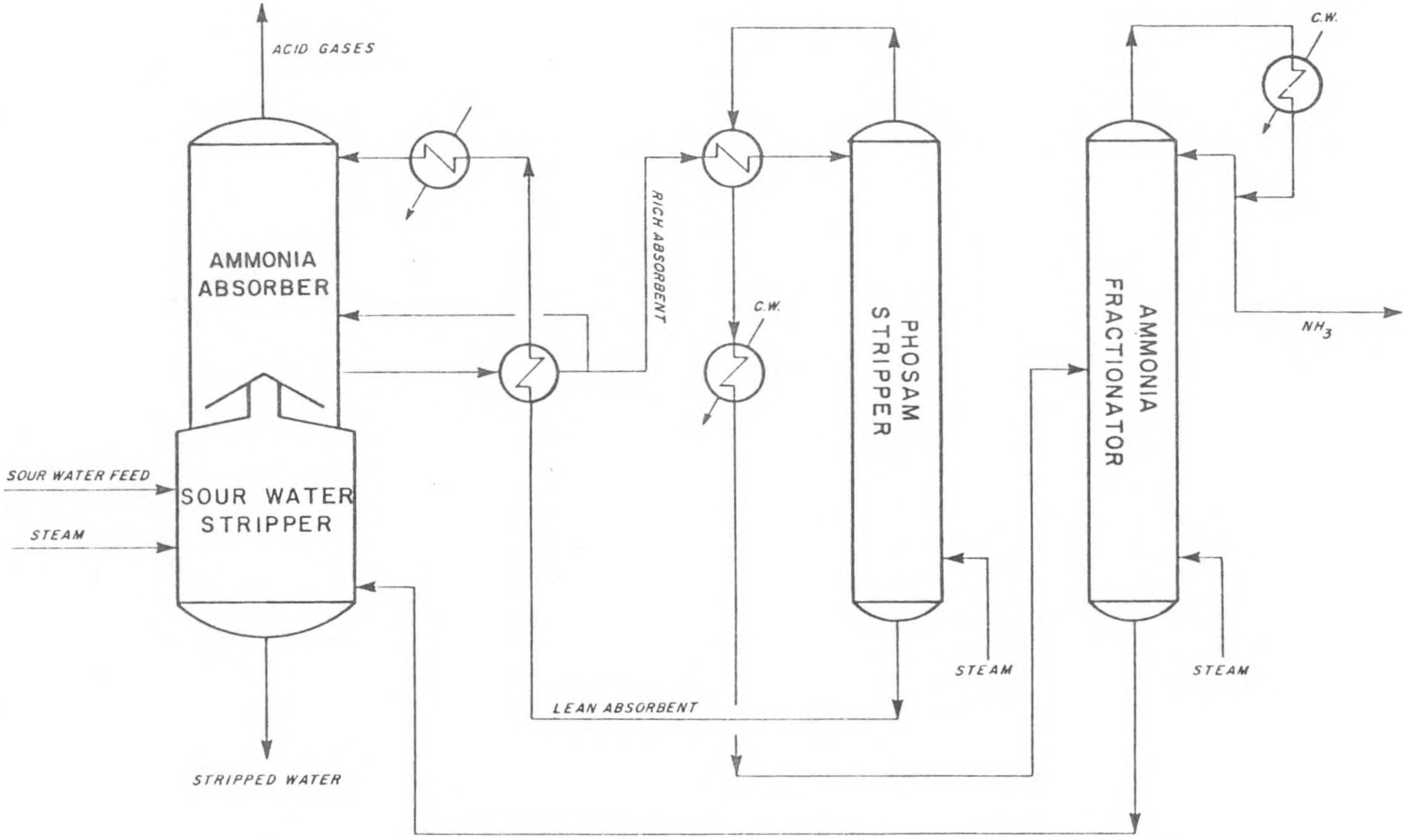
Stripping is a well established process for removal of ammonia, carbon dioxide and hydrogen sulfide from sour water streams. It has been practiced in refineries and steel plants (coke oven liquor) as well as in coal gasification plants (e.g. within the Lurgi phenolsolvan plant at SASOL), on waters similar in many respects to the oil shale process condensates. Some differences in water quality that may lead to stripping difficulties are the very high CO_2 concentrations, and, in particular, the high TDS levels in retort waters. Foaming and fouling are ever-present problems in stripping columns, and may require special purpose trays, increased diameters, and proprietary antifoam agents appropriate to the characteristics of the wastewaters[45].

More important than the stripping is the separation of the stripped gases and the production of marketable byproducts. Washing the stripped gases with sulfuric acid to produce fertilizer grade ammonium sulfate is not profitable unless sulfuric acid is available on site as a very low cost byproduct. Even then, the fertilizer market is, and may remain, depressed, so that anhydrous ammonia appears to be more suitable than sulfate when considering market value, storage and transport costs, and demand. Two of the commercially available processes for separating stripped gases and production of anhydrous ammonia are the U.S.S. Engineers and Consultants' (UEC) Phosam-W process[46] and Chevron's Wastewater Treatment process[47]. The Chevron process is not directly applicable to wastewaters containing significant CO_2 levels but might find application in stripping the NH_3-H_2S sour waters from shale oil upgrading plants.

The UEC Phosam-W process is shown in Figure 6-5. The steam stripped gases are washed with an ammonium phosphate solution which absorbs the ammonia, leaving an H_2S and CO_2 stream which may be taken to a sulfur recovery unit. The rich ammonium phosphate solution is stripped to produce an aqua ammonia stream and a lean absorbent solution for recycle. The aqua ammonia is fed to the ammonia still for production of anhydrous ammonia. Sodium hydroxide and proprietary agents are used to control organics in the ammonia column. The organics are returned to the water stripper and exit with the stripped water. More detailed descriptions of the process are available[34,46].

6.2.1 Free Ammonia Stripping

The gas condensate contains mainly ammonium bicarbonate with only small quantities of other inorganic salts. Ammonia fixation by acid anions should therefore not be a problem, and pH adjustment will probably not be required.



SIMPLIFIED FLOW SHEET FOR AMMONIA RECOVERY (U.E.C. PHOSAM-W PROCESS)

Figure 6-5. Stripping and ammonia recovery by the U.E.C. Phosam-W process.

The van Krevelen vapor-liquid equilibrium data are suitable for the stripping column design[33,34] and have been used to size and cost units for the gas condensate stream having a composition as shown in Table 3.6. The results are summarized in Figures 6-6 and 6-7.

6.2.2 The Effect of Fixed Ammonia

Stripping the retort condensate will require pH adjustment to release fixed ammonia. This has been described in section 4.2.1. The van Krevelen vapor-liquid data as used for the gas condensate stripping calculations are not directly applicable to retort water/fixed ammonia calculations. We have reviewed several vapor-liquid calculational procedures for sour water systems[48,49] and selected the method published by the American Petroleum Institute[32] as a basis for our calculations. The API sour water equilibrium model is suitable for handling the effects of carboxylic and other acids on ammonia fixation and its release by caustic addition. However, the model does not have facilities for the required additional acidic and basic components. We have expanded the model and, because the expansion has not been published, it is presented here in detail.

Henry's Law

Henry's law states that the mass of gas dissolved by a given volume of solvent, at constant temperature, is proportional to the pressure of the gas with which it is in equilibrium. In a gas mixture it is the partial pressure of the gas that must be used. Henry's law may be written

$$\text{gas partial pressure} = H \times \text{dissolved gas concentration}$$

where H is Henry's law constant.

Values of H for the three gases under consideration, ammonia, carbon dioxide, and hydrogen sulfied are listed in Table 6.2. The higher the value of H the less soluble the gas, and the more easily it is stripped. According to the values in the table, carbon dioxide and hydrogen sulfide strip significantly faster than ammonia, although increasing the temperature does improve the volatility of ammonia relative to the other two gases.

Unfortunately the application of Henry's law is not as straightforward as suggested in the preceeding paragraph. This is because Henry's law is applicable to the concentration of unionized dissolved gas in solution, whereas in practice it is the total species concentration (ionized plus unionized forms)

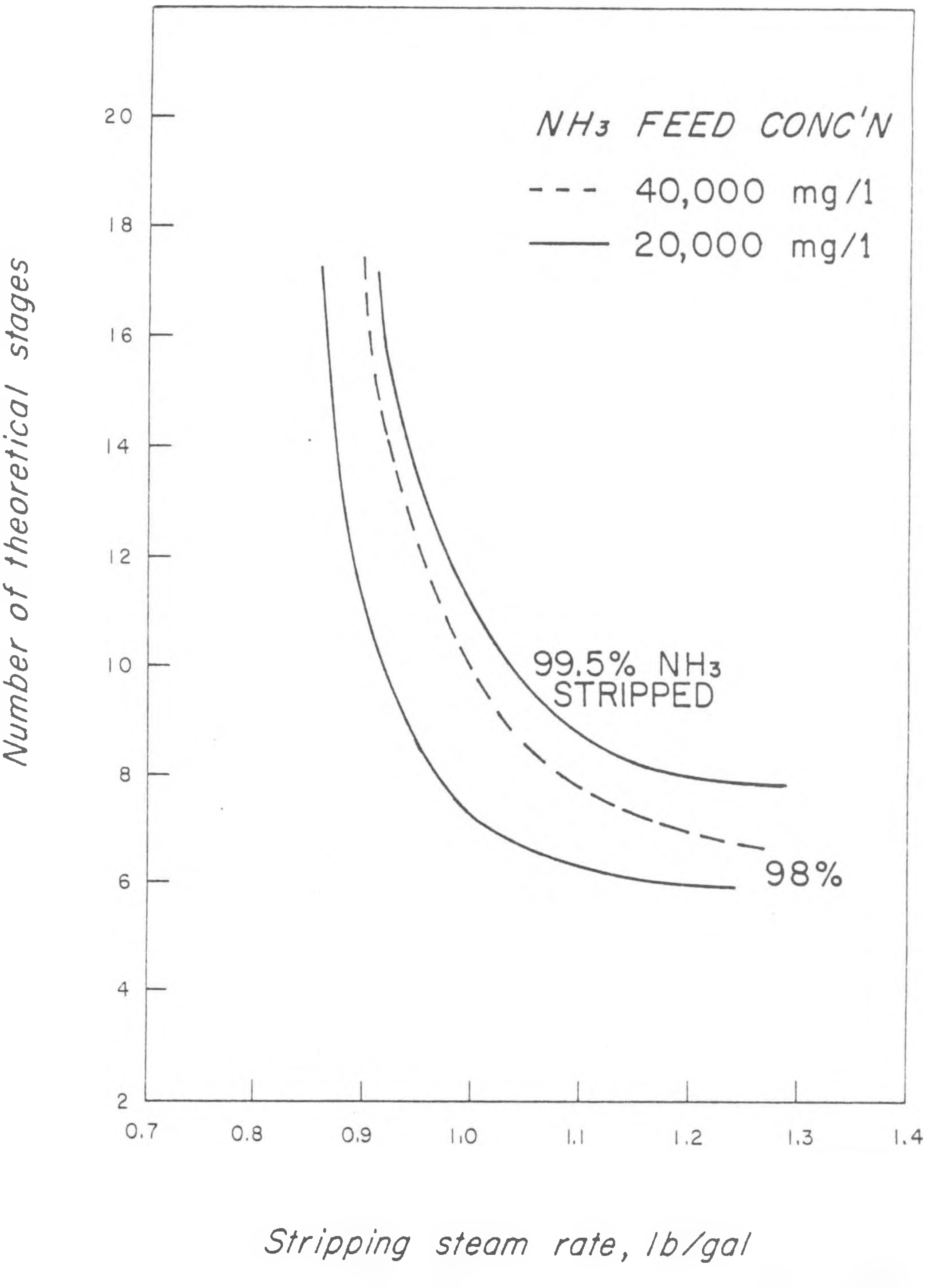


Figure 6-6. Dependence of stripping column height on steam rate, ammonia removal efficiency and ammonia concentration in feed.

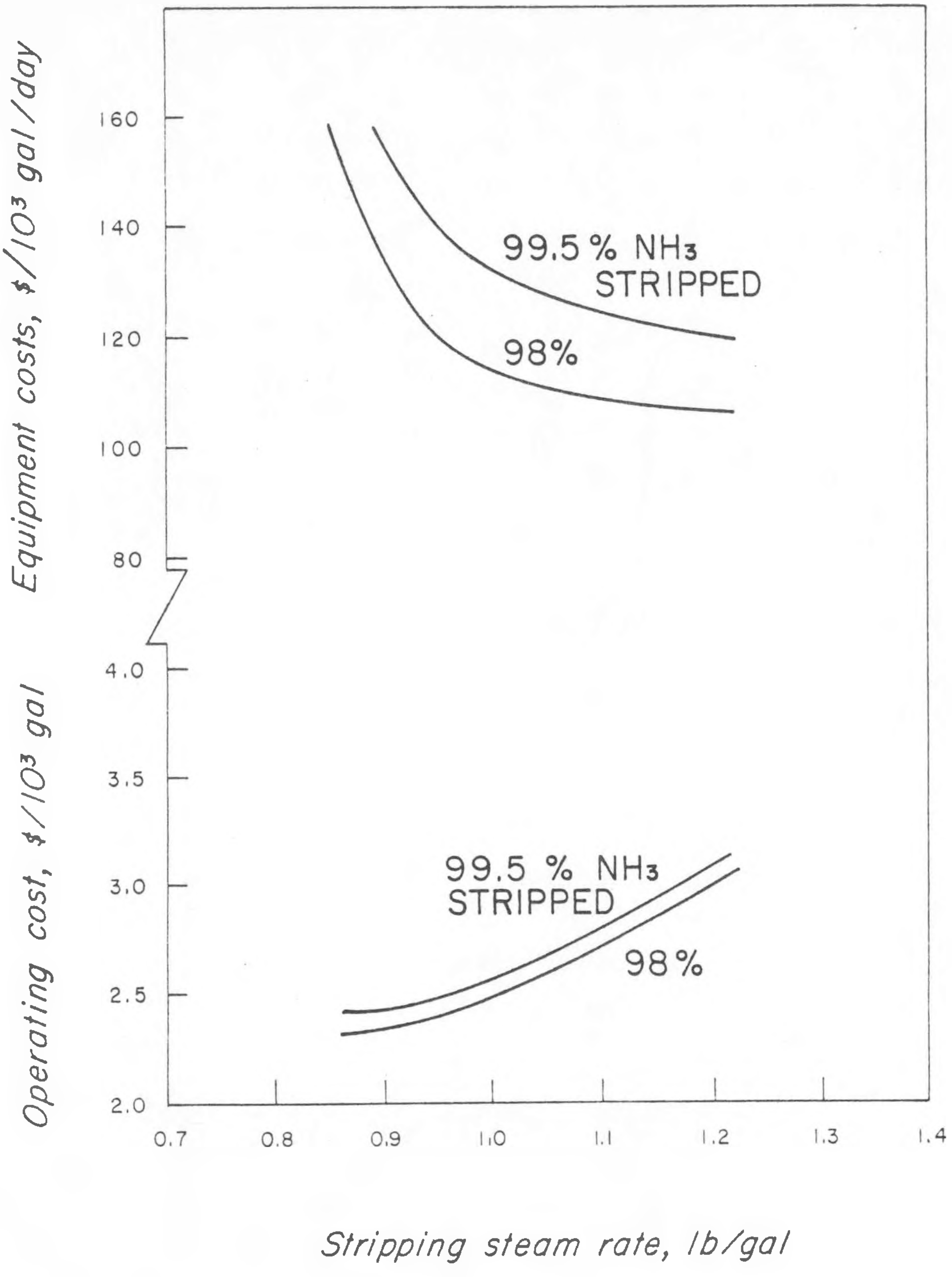


Figure 6-7. Capital and operating costs for ammonia stripping from a 20,000 mg/l gas condensate stream. Equipment costs for tower and reboiler. Operating costs based on 15% capital amortization, maintenance at 4% of installed costs, and 50 psig steam at $\$2.5/10^6$ Btu. Installed cost assumed to be four times equipment cost. Flow rates in range 1,000 - 3,000 pgm. Steam cost is from 80% to 90% of total operating cost.

TABLE 6.2. HENRY'S LAW CONSTANTS (H) FOR AMMONIA, CARBON DIOXIDE AND HYDROGEN SULFIDE AT INFINITE DILUTION*

H = Gas Partial Pressure, psia/(Concentration of Unionized Dissolved Gas, Gram Moles/Kg soln.)

Gas	25°C	100°C
Ammonia (NH_3)	0.25	3.66
Carbon Dioxide (CO_2)	441	1,218
Hydrogen Sulfide (H_2S)	158	440

Ratio of Henry Constants (Relative Volatilities)

Gas Pair	25°C	100°C
CO_2/NH_3	1,764	333
H_2S/NH_3	632	120
CO_2/H_2S	2.8	2.8

---

*Calculated from analytical expressions in Reference 32.

that is normally known. To apply Henry's law, the fraction of ionized and unionized forms must be determined from the solution pH as discussed below. In addition, the Henry's law constants must be adjusted for the effect of temperature and composition. Analytical equations for these adjustments are available for the ammonia, carbon dioxide, hydrogen sulfide system.[32]

Ammonia/Acid Gas Chemistry

The form of the equations, some of the nomenclature and the values of variables used here are based on those in the API publication for the ammonia/acid gas system.[32] This format was selected because the API vapor liquid equilibrium calculation procedure was extended to include ammonia fixation effects and to allow for the presence of volatile organics. The modified procedure was then used for designing stripping columns for oil shale retort waters.

Ammonia in aqueous solution will react with hydrogen ions to form ammonium ions according to the equation

$$H^+ + NH_3 \rightleftarrows NH_4^+ \qquad (6\text{-}6)$$

The ratio of ammonium to ammonia is determined by the hydrogen ion concentration (pH) and may be calculated from the equilibrium equation

$$(NH_4^+)(NH_3) = K_A(H^+) \qquad (6\text{-}7)$$

where K_A is the equilibrium constant for ammonia dissociation and (H^+) is the hydrogen ion concentration. Values of the equilibrium constant are temperature and composition dependent; and may be calculated using expressions given in Reference[32]. Equation (6-7) was used to calculate the amount of dissolved ammonia gas (NH_3) as a percentage of the total ammonia ($NH_3 + NH_4^+$) concentration. The results, shown in Figure 6-8(a), show that the fraction of unionized gas in solution increases with both pH and temperature. As it is the unionized species that strips, we can conclude on the basis of the ionization data that ammonia stripping can be accelerated by increasing the pH and/or temperature of the wastewater.

Dissociation of carbon dioxide and hydrogen sulfied is slightly more complicated as these compounds have second ionization reactions. Using hydrogen sulfide as an example we can write:

$$H_2S \rightleftharpoons HS^- + H^+ \qquad (6\text{-}8)$$

$$HS^- \rightleftharpoons S^= + H^+ \qquad (6\text{-}9)$$

As before the fraction of each species present is a function of a dissociation constant and the solution pH:

$$(HS^-)/(H_2S) = K_B/(H^+) \qquad (6\text{-}10)$$

and

$$(S^=)/(HS) = K_C/(H^+) \qquad (6\text{-}11)$$

Here K_B and K_C are the first and second dissociation constants respectively.

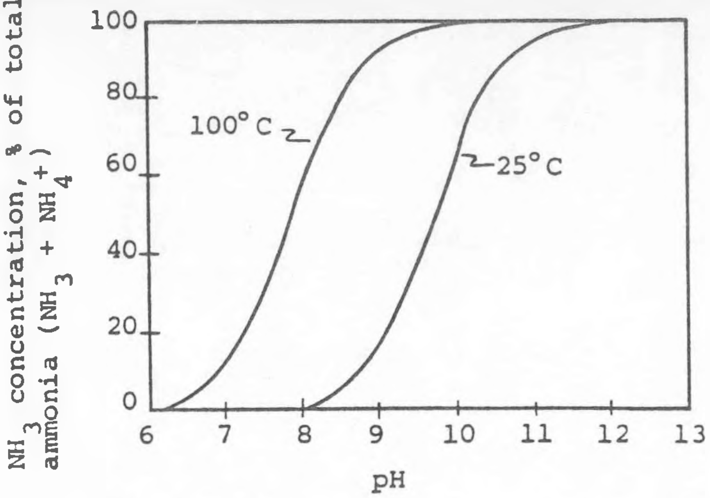
Similar equations can be written for carbon dioxide which in solution forms carbonic acid, H_2CO_3, and this in turn dissociates to form HCO_3^- and $CO_3^=$. The equations are represented in Figure 6-8 which shows the concentration of each species as a function of pH. Contrary to the results for ammonia, Figure 6-8 shows that the acid gases are ionized at high pH so that they are more readily stripped from acidic (low pH) solutions.

The foregoing results were for single components in aqueous solution. If in addition to pure ammonia in solution there are inorganic anions and cations present then we require an additional equation to determine the degree of ammonia dissociation. We therefore introduce the constraint of electroneutrality which states that the sum of positive charges in solution must equal the sum of negative charges. This may be written:

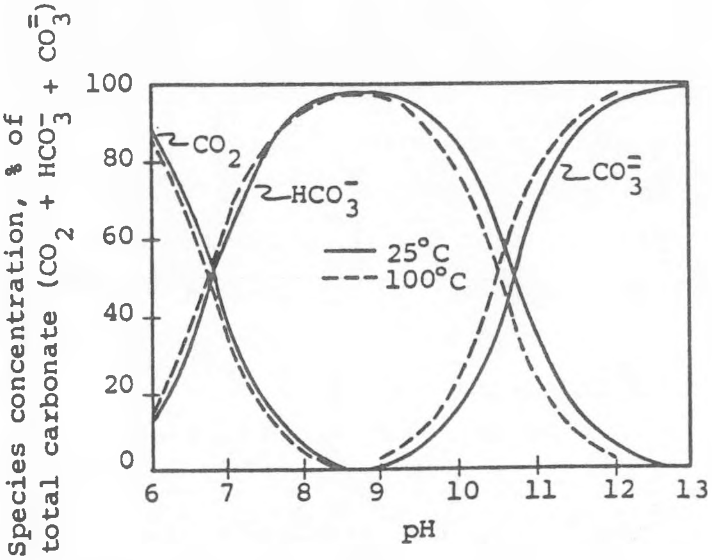
$$(NH_4^+) + (Y^+) + (H^+) = (Z^-) + (OH^-) \qquad (6\text{-}12)$$

Here (Y^+) and (Z^-) are the equivalent (monovalent) concentrations of all cations and anions (other than ammonium, hydrogen and hydroxyl) present in solution. Equation (6-12) may be used together with Equations (6-6) and (6-7) to get

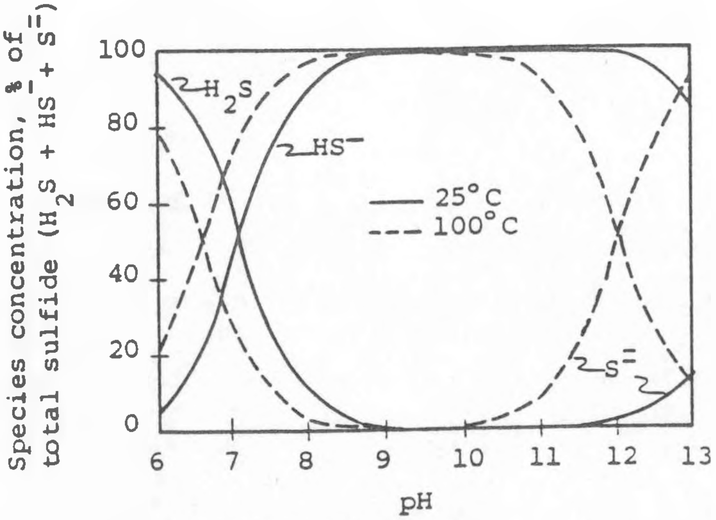
$$(H^+)^3 K_A/A + (H^+)^2 (K_A + XK_A/A + 1/A) + (H^+)(X/A - K_W K_A/A) - K_W/A = 0 \qquad (6\text{-}13)$$



(a) Ammonia



(b) Carbon Dioxide



(c) Hydrogen Sulfide

Figure 6-8. Dissociation of dissolved gases in water as a function of pH and temperature. (a) Ammonia, (b) Carbon Dioxide, (c) Hydrogen sulfide.

where $K_W = (H^+)(OH^-)$

A = total ammonia concentration, $(NH_3) + (NH_4^+)$

and X = excess ion concentration, $(Y^+) - (Z^-)$

Equation (6-12) is represented graphically in Figure 6-9, which shows the effect of fixed anions on ammonia stripping. If the concentration of anions in association with ammonia is nearly equal to the ammonia concentration, then the solution pH falls below 8 and virtually all the ammonia is present as ammonium ion and cannot be stripped. If now cations are added to the solution, say as caustic soda or lime, the solution pH increases as does the concentration of strippable unionized ammonia. The higher the total ammonia concentration the less the relative (Y^+/A) amount of cation required to free the ammonia. This is because ammonia itself elevates the pH.

The analytical solution can be extended to the case where ammonia, inorganic ions, and hydrogen sulfide are present in solution. The electroneutrality equation now becomes

$$(NH_4^+) + (Y^+) + (H^+) = (HS^-) + 2(S^=) + (Z^-) + (OH^-) \qquad (6\text{-}14)$$

In combination with Equations (6-6) - (6-11), Equation (6-13) can be reduced to

$$\begin{aligned}
&(H^+)^5 K_A/A + (H^+)^4 (K_A K_B/A + K_A X/A + K_A + 1/A) + \\
&(H^+)^3 (K_A K_B K_C/A + K_B/A + K_A K_B X/A + K_A K_B + X/A - K_A K_B S/A - K_W K_A/A) + \\
&(H^+)^2 (K_B K_C/A + K_A K_B K_C X/A + K_B X/A + K_A K_B K_C - K_B S/A - 2K_A K_B K_C S/A \\
&\qquad\qquad - K_W K_A K_B/A - K_W/A) + \\
&H^+ (K_B K_C X/A - 2K_B K_C S/A - K_W K_A K_B K_C/A - K_W K_B/A) - K_W K_B K_C/A = 0 \qquad (6\text{-}15)
\end{aligned}$$

where S is the total hydrogen sulfide concentration, $(H_2S) + (HS^-) + (S^=)$.

Equation (6-15) is represented in Figure 6-10 which shows that the effect of H_2S addition is to lower the pH or to increase the amount of cation necessary to free the fixed ammonia. In fact, if excess anions are present in solution it is good practice to first strip the hydrogen sulfide at low pH, and then add alkali to free the ammonia.

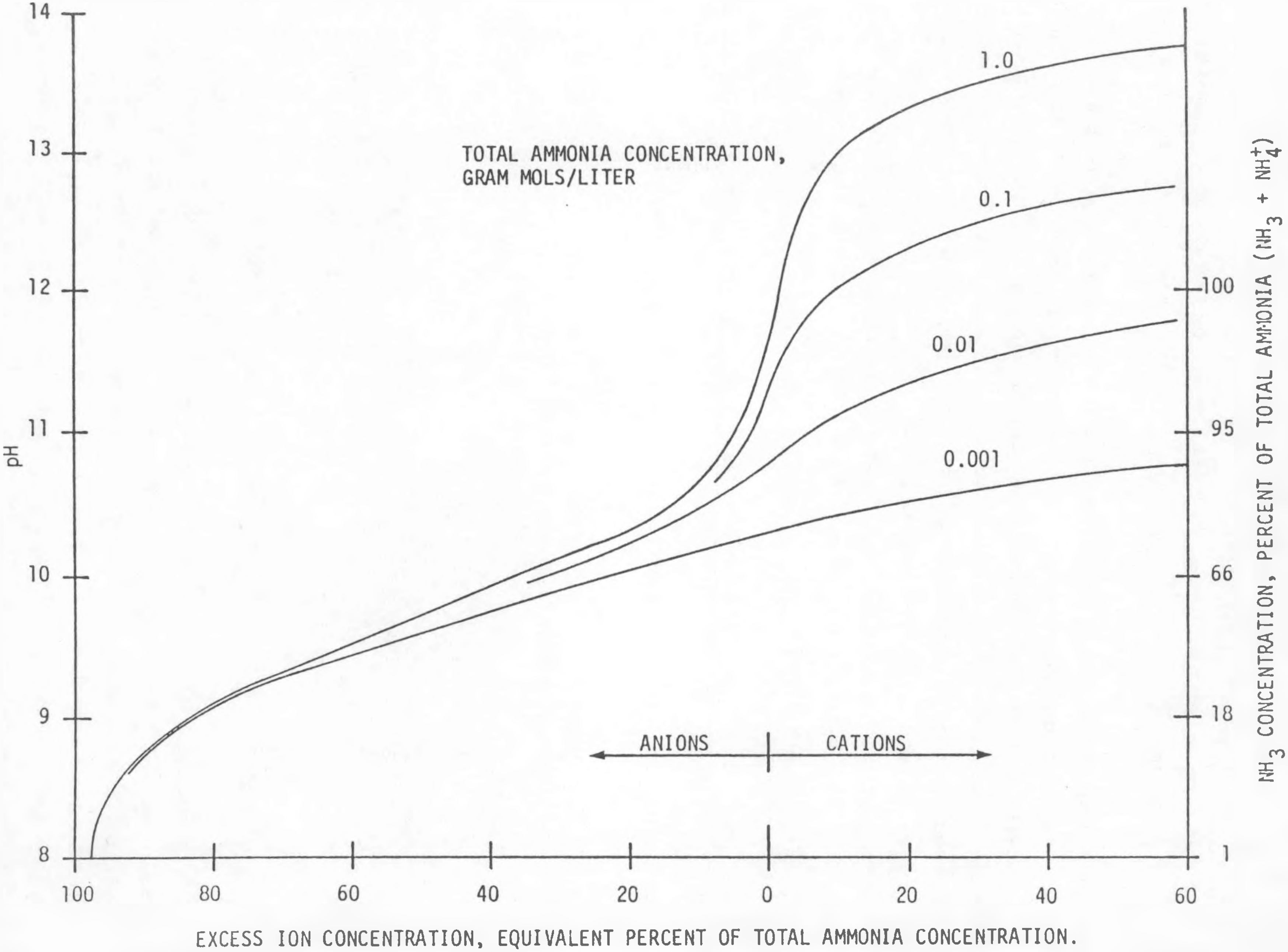


Figure 6-9. Effect of the presence of excess anions or cations (e.g. Cl^- or Na^+) on the pH of ammonia solutions, and hence on the concentration of unionized ammonia. Calculated for 25°C.

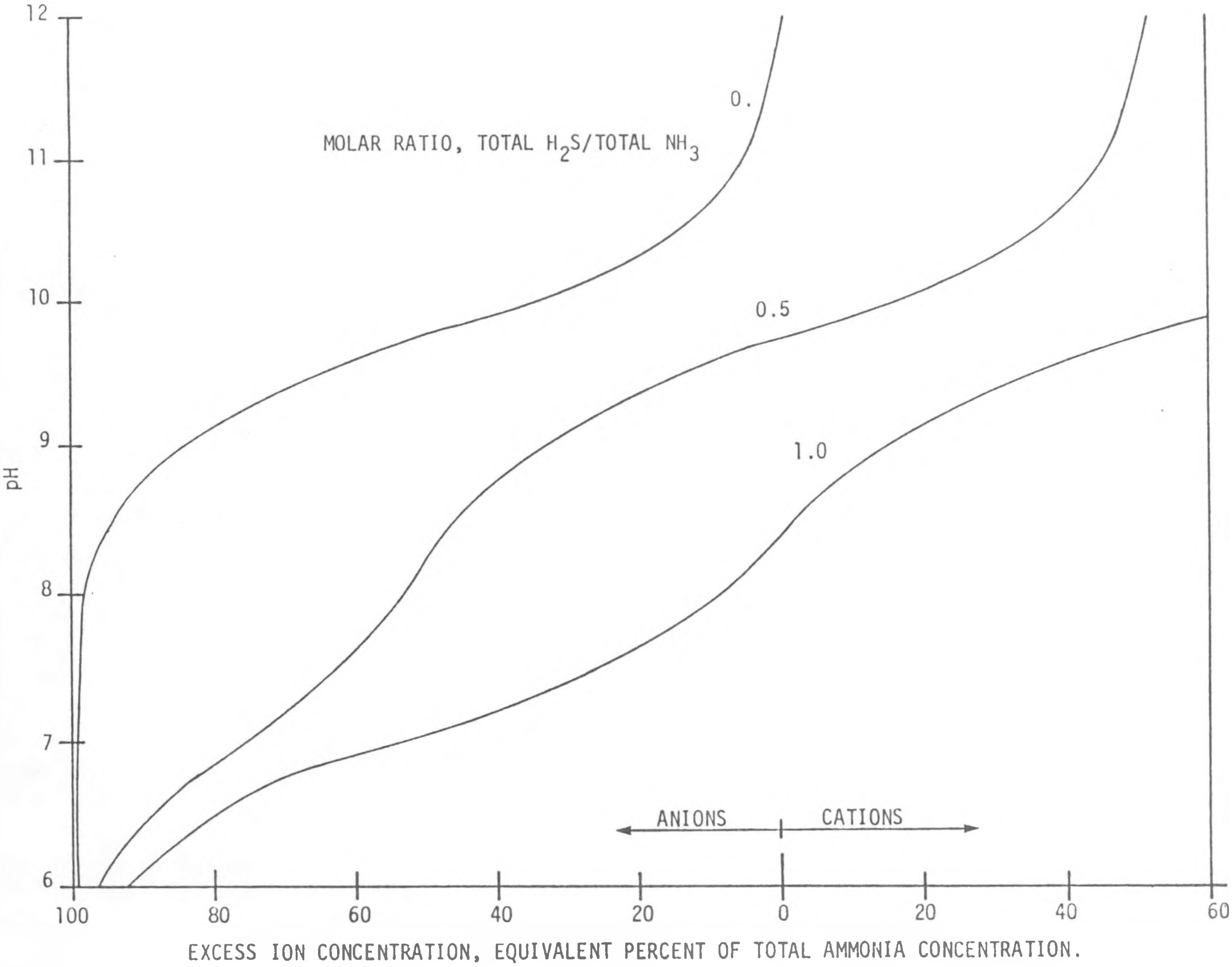


Figure 6-10. Effect of the presence of excess anions or cations (e.g. Cl^- or Na^+) on the pH of 1.0 molar ammonia solutions containing dissolved hydrogen sulfide. Calculated for 25°C.

Equation (6-14) is useful for stripping calculations for wastewaters containing ammonia, hydrogen sulfide and inorganic salts. It can be solved using the "zeros of functions" routine available with many programmable pocket calculators. Once the pH is known the concentration of unionized gas can be calculated from Equations (6-6) - (6-11) or read from Figure 6-8. Henry's law may then be applied to determine the vapor composition in equilibrium with the specified liquid. This completes the calculation around an equilibrium stripping stage, and together with material balance calculations can be used to design a stripping column[34].

If carbon dioxide is additionally present, it combines in part with ammonia to form the complex carbonate anion NH_2COO^-, in addition to the carbonate and bicarbonate ions considered previously for pure carbon dioxide in solution. An analytical solution for this system could not be obtained and an iterative solution requiring computation facilities had to be used. The procedure was based on that presented in Reference 32, but extended to include the effects of fixing inorganic salts as well as volatile organics. The equation for electroneutraility now becomes

$$(NH_4^+)+(H^+)+(Y^+) = (HS^-)+(S^=)+(HCO_3^-)+(CO_3^=)+(Z^-)+(V^-)+(OH^-) \qquad (6\text{-}16)$$

Here (V^-) is the concentration of dissociated organic present. For the initial designs the organics were assumed to dissociate collectively as acetic acid, and to have a volatility similar to phenol. These assumptions can be improved upon when more information on the organics present in retort waters becomes available.

The calculational procedure is basically similar to the analytical method described for ammonia and hydrogen sulfide systems. However when carbon dioxide is present the pH cannot be directly calculated but is assumed. The assumed pH is used to calculate the concentrations of all species present (Figure 6-8), and these concentrations are then substituted in the electroneutrality equation (Equation 6-16). If the equation does not balance, a new pH must be assumed and the calculations repeated. The procedure is complicated and tedious because the Henry law and dissociation constants are dependent on solution composition and must be recalculated for each iteration.

Results

A retort water containing 17,000 mg/l total ammonia was used to test the computation. The concentration of fixing anions was varied between zero and 80% of the ammonia on a molar basis, and the concentration of CO_2 was adjusted between 8,000 and 44,000 mg/l to achieve ionic balance. The results are summarized in Table 6-3, which shows that the number of theoretical stages required for stripping doubles when the fraction of fixed ammonia increases from zero to 80%. The fixed ammonia was stripped by adjusting the pH to 9.0 using caustic soda once the CO_2 had been removed. Increasing the pH to 10.00 or above required additional caustic soda, but did not significantly decrease the number of stages. The effect of pH on the stripping rate is further shown in Figure 6-11.

The effect of reducing the steam rate on tower height and on costs is shown in Figure 6-12 and 6-13 respectively. These data are for a retort water in which 40% of the ammonia is fixed, and 95% of the total ammonia is to be stripped.

TABLE 6.3. EFFECT OF PERCENTAGE FIXED AMMONIA ON STRIPPING

% Fixed Ammonia	Total Theoretical Stages*	Lime Required to Adjust to pH9. lb/100 lb Feed	Relative Costs Installed Equipment	Relative Costs Total**
0 (All Free)	4	0	1***	1***
20	5	.38	1.08	1.21
40	6	.58	1.11	1.29
60	7	.79	1.17	1.44
80	8	.99	1.25	1.68

---

*Steam rate = 15 lb/100 lb feed, 95% ammonia stripped.

**Capital amortized at 15% p.a., maintenance at 4% p.a., steam at \$2.5/10^6 Btu, lime at 2.5¢/lb.

***See Figure 6-7.

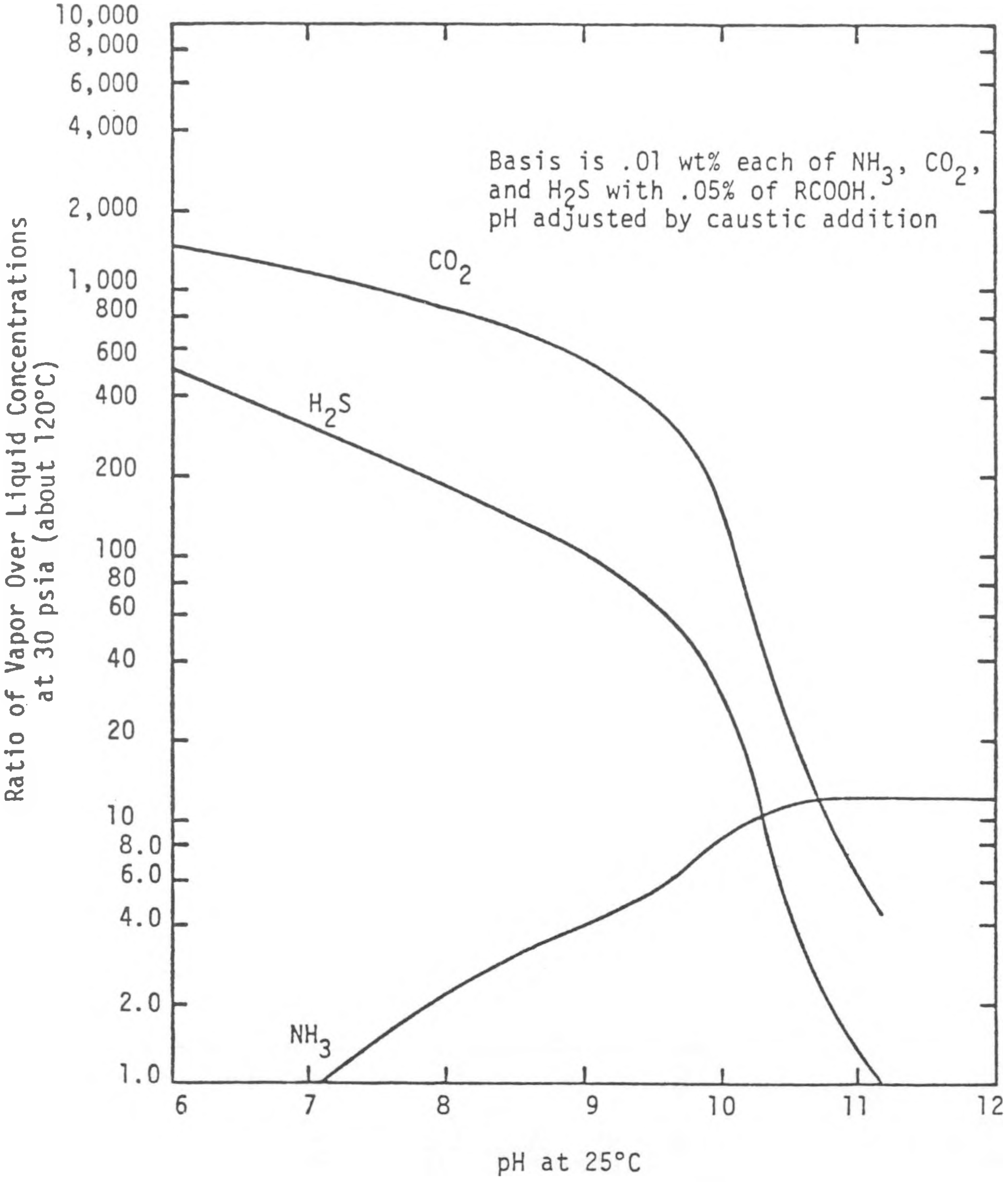


Figure 6-11. Volatility of NH_3, CO_2, and H_2S as a function of pH.[32]

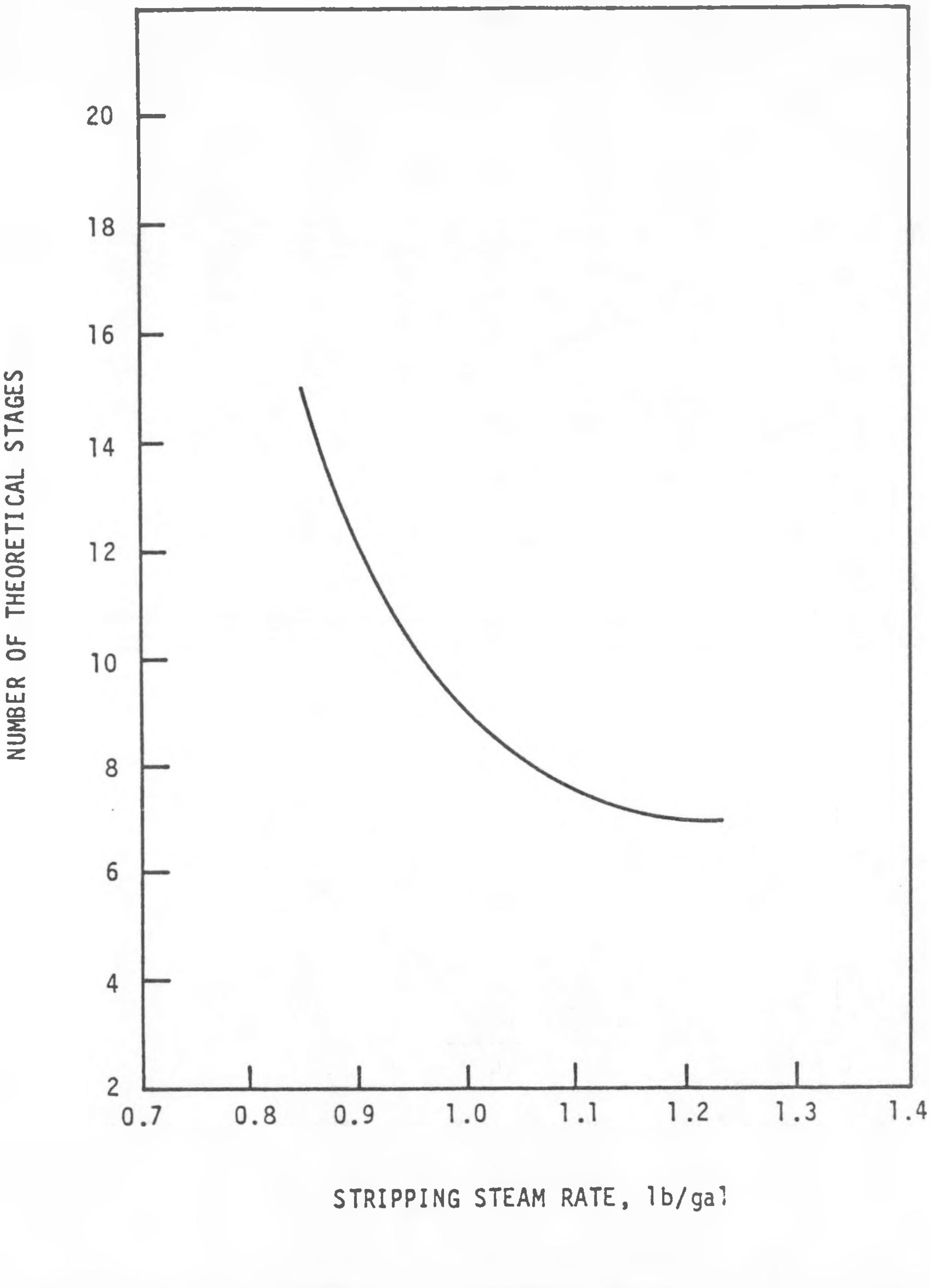


Figure 6-12. **Dependence of stripping column height on steam rate for 95% ammonia removal efficiency and 17,000 mg/l ammonia concentration in feed.**

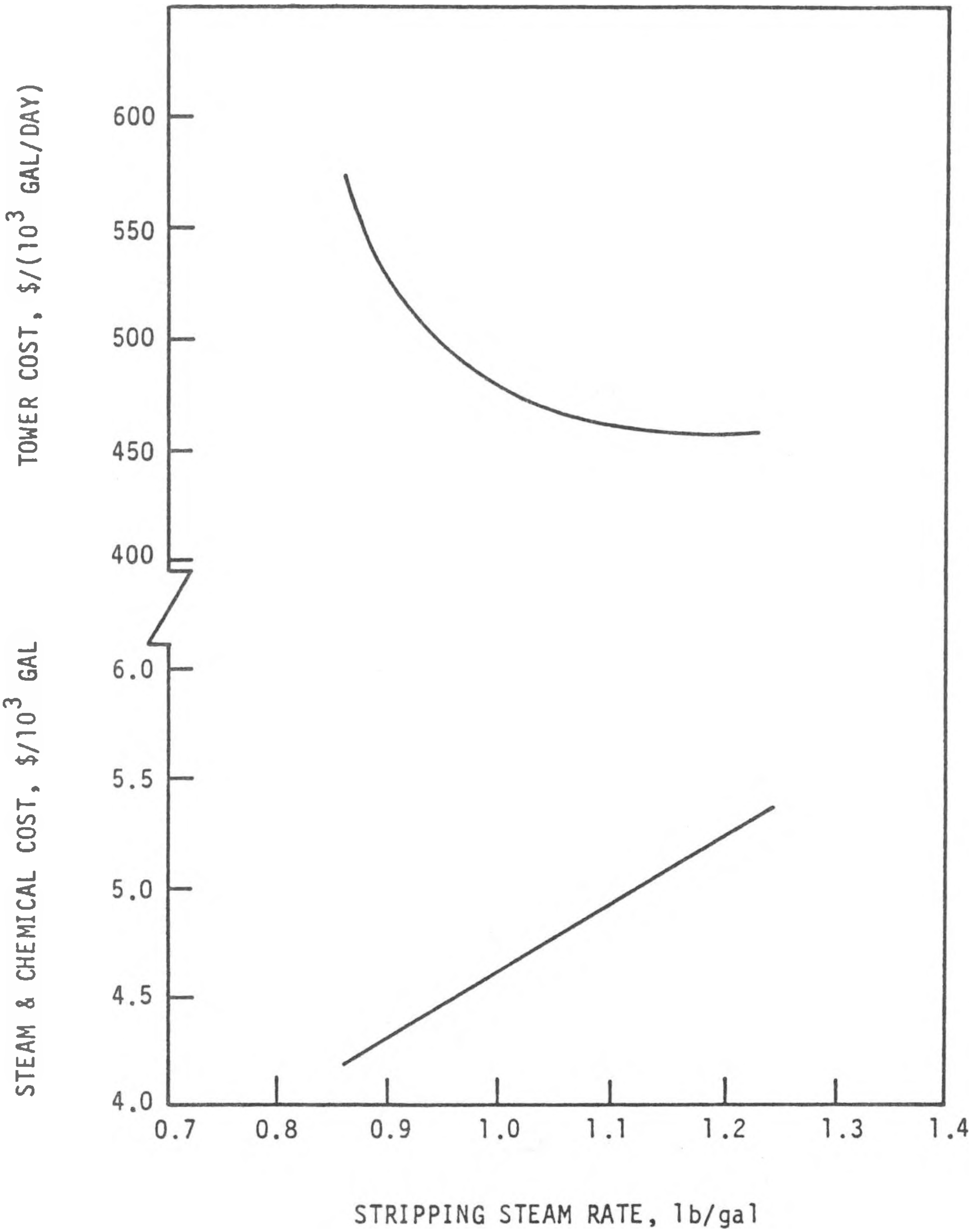


Figure 6-13. Installed tower and steam and chemical costs for ammonia stripping from a 17,000 mg/l gas condensate stream at 60 psig with $\$2.5/10^6$ BTU and lime ¢2.5/lb.

6.3 Solvent Extraction

Three solvents, methylene chloride, n-butyl acetate and isopropylether, were tested by performing batch solvent extraction tests in separatory funnels. Two hundred milliliters of stripped R17 retort water were extracted with 10 ml solvent by agitating for 1 minute and allowing the mixture to stand for 5 minutes. The solvent was separated and 10 ml of fresh solvent were added and the procedure repeated. In all, three extractions were made using 10 ml of fresh solvent each time for a total of 30 ml of solvent.

The results are shown on Table 6.4. The COD removals were unsatisfactory and the tests were not continued.

TABLE 6.4 RESULTS OF SOLVENT EXTRACTION TESTS

FEED: R-17 stripped retort water, COD = 10,500 mg/l

	COD in Extracted Water		
Solvent	As Measured (mg/l)	After Subtracting Calculated COD of Dissolved Solvent (mg/l)	% COD Removal
Butylacetate	24,365	9,058	13.7
Isopropylether	10,820	6,734	35.9
Methylene chloride	9,250	9,250	11.9

6.4 Resin Adsorption

Adsorption tests were made on resins kindly supplied by the Rohm and Haas Company. The results are shown on Table 6.5. Although high removals were obtained initially in some cases, removals were generally below 60% of the influent COD on all waters tested after five bed volumes. Frequent regeneration of the resins would be required and therefore resin adsorption appears not to be a useful treatment.

TABLE 6.5

TEST WITH RESIN ADSORPTION

Tests with R-17 Retort Water

(Bed volume was 100 ml and the bed was full of clean water when the test began. We assume that the results for the first three bed volumes of effluent were due to dilution, not adsorption).

Pretreatment Resin Influent COD (mg/l)	Stripped XAD-2 10,396		Bio(AAS) XAD-4E 9,393		Bio(AAS) XAD-2 9,393		Bio(AAS) XAD-7 9,393			Bio(PAC-AAS) XAD-4 5,031	
Bed volumes of Effluent	Effluent COD	% Removal	Effluent COD	% Removal	Effluent COD	% Removal	Effluent COD	% Removal	Bed Volumes of Effluent	Effluent COD	% Removal
1	1,676	84	155	98	3,373	64	3,834	59	1.5	2,340	53
2	3,794	64	1,240	87	1,961	79	5,269	44	3	4,434	12
3	4,308	59	3,101	67	4,118	56	4,885	48	4.5	3,849	23
4	4,901	53	3,876	59	4,667	50	5,385	43	6	3,736	26
5	5,296	49	4,263	55	5,020	47	5,615	40	7.5	3,792	25
6	5,692	45	4,031	57	5,333	43	5,923	37	9	3,698	26

Tests with Other Waters

(In these tests mixing did not cause dilution during the first bed volumes)

Water Resin Influent COD (mg/l)	Oxy-gas condensate stripped and filtered XAD-4 1,069			R17 retort water RO permeate XAD-4 346		
	Bed Volumes	Effluent COD	% Removal	Bed Volumes	Effluent COD	% Removal
	5	382	64.3	1	197	43.1
	19	465	56.4	4	186	46.2
				8	197	43.1

6.5 Carbon Adsorption

Battelle Pacific Northwest Laboratory[56] tested activated carbon adsorption on steam stripped retort water and on the same water after biological treatment. COD removal was quite inadequate on the stripped water, but the combination of biological oxidation followed by carbon adsorption gave an effluent COD of about 100 mg/l from a system influent of 5,500 mg/l and a biological treatment effluent 1,700 mg/l. The carbon gave about 94% removal of the COD in its influent.

We tested activated carbon adsorption on an Oxy gas condensate water and obtained 75 to 86% removal of the COD remaining after stripping and filtering. We also tested the RO permeate from R17 retort water and obtained 65% removal of the COD remaining after RO treatment.

Activated carbon may be useful as a polishing treatment for some applications.

6.6 Reverse Osmosis

Although reverse osmosis has in the past been applied mainly to inorganics control, the development of modern composite membranes has led to its increasing application for organics control as well. Several membranes were screened in a batch test cell, using a retort water from the LETC 10-ton simulated in-situ retort. Some of the results are summarized in Table 6.6. At high pH some 95% rejection of organics was obtained along with about 98% rejection of inorganics. Stripping to reduce alkalinity and ammonia was always used as a pretreatment, and in some cases ultrafiltration, chemical coagulation and even treatment in a rotating biological system were used as well. These pretreatments did not significantly affect the degree of removal of the organics in the reverse osmosis step. More importantly, they did not affect the flux through the membrane which were about one tenth of those obtained with the mine drainage water. The Filmtec membrane was further tested in a flow system using a 6 gal/day spiral wound module. The only pretreatments used were stripping at elevated pH and filtration through a 25 μm cartridge filter. Fluxes decreased in proportion to the increase in osmotic pressure obtained with increasing recovery. No permanent fouling was detected, and on reconstituting the feed the original flux was recovered.

Reverse osmosis was such a promising treatment that it was made the subject of a separate study being simultaneously reported (Contract DE AC20-79LC10089, DOE, LETC, Laramie).

TABLE 6.7. PERFORMANCE OF REVERSE OSMOSIS FLOW UNIT USING LETC 150 TON SIMULATED IN SITU (RUN R-17) RETORT WATER

Constituent	Retort Water Composition mg/l As Received	 Stripped	Mean Rejection %[a]
Ammonia as N	3,275	270	29.5
Alkalinity as $CaCO_3$	6,500	3,400	80.8
TDS at 105°C	62,600	23,860	98.7
COD	10,840	10,730	98.5
pH (units)	8.6	11.0	10.0 in feed 10.6 in product

---

a) Up to 75% recovery, i.e., for concentrations up to four times that in the original feed.

TABLE 6.6. SUMMARY OF REVERSE OSMOSIS MEMBRANE SCREENING TESTS ON STRIPPED LETC 10 TON SIMULATED IN SITU (RUN S-47) RETORT WATER

			% Rejection by RO Membrane			
Constituent	Stripped Retort Water (mg/l)	Ultrafiltered Water (mg/l)	Osmonics Sepa 97 (CA)	Membrane Systems Blend (CA)	Filmtec Composite	Filmtec Composite
Ammonia (N)	440	440	89	96	42	31
Alkalinity	15,800	15,600	95			
Hardness	120		>85	>85	>85	>85
TDS (105C)	53,100	50,100	96	98	96	98
COD	9,700	9,200	86	82	84	97
TOC	3,800	3,600	-	-	-	96
Feed pH	8.6→11	10.3	6.8	4.5	6.8	10.3
Product pH	10.3	10.3	8.4	5.3	8.7	10.2

% Rejection = (1 - permeate concn./avg. of feed and concentrate concn.) 100.

Recoveries were from 85-90%.

6.7 Oxidation

Oxidation is a general purpose method of removing organic matter from water. The best known procedure is called wet air oxidation and the equipment is sold by Zimpro Inc. in Rothschild, Wisconsin. Organic matter dissolved or suspended in water is oxidized by air temperatures in the range 250 to 280°C (470 to 540°F). To prevent the water from boiling at these temperatures the pressure must be between 500 and 900 psig.

The nearest equivalent wastewater to retort water known to us to have been tested is a Hygas process wastewater. This water contained 13,700 mg/l COD which was 92.7% oxidized in 60 minutes at 280°C with a little catalyst added to the water[53].

We are confident that high oxidation of the COD in retort water can be obtained. Because of the long residence time of 60 minutes, a large high pressure vessel is needed and the amortization of this vessel will constitute about 2/3 of the total operating cost[54]. The cost is dependent on throughput and independent of concentration. Indeed, if the influent COD is high enough its combustion will sustain the reaction, no outside heat will be needed and steam will be obtained to drive the air compressor. A simple arrangement is shown in Figure 6-14. However, a self-sustaining reaction requires about 40,000-50,000 mg/l COD which is more than occurs in retort water. Nevertheless, wet air oxidation would take the place of biological treatment, not follow it.

An estimate of capital cost in 1974 dollars is[54]

$$\text{capital} = 650 \left[Q \text{ (gpd)} \right]^{0.7}$$

This applies for sizes up to 0.6 x 10^6 gal/day. Extrapolation to 1980 probably means a multiplier of 1.6 to 1.8. Extrapolation to larger sizes is not possible because pressure vessels cannot be enlarged indefinitely and multiple vessels must be used. A plant for 1 x 10^6 gallons/day would, today, cost about 18 to 20 x 10^6 dollars. If maintenance and amortization were charged at a total of 17%/yr these charges alone mean a cost of $9.70/1000 gallons. Wet air oxidation is probably too expensive because retort water is too dilute to merit this treatment. Treatments whose costs are more dependent on concentration than on throughput, such as biological or adsorption, are preferable if they can be made to work.

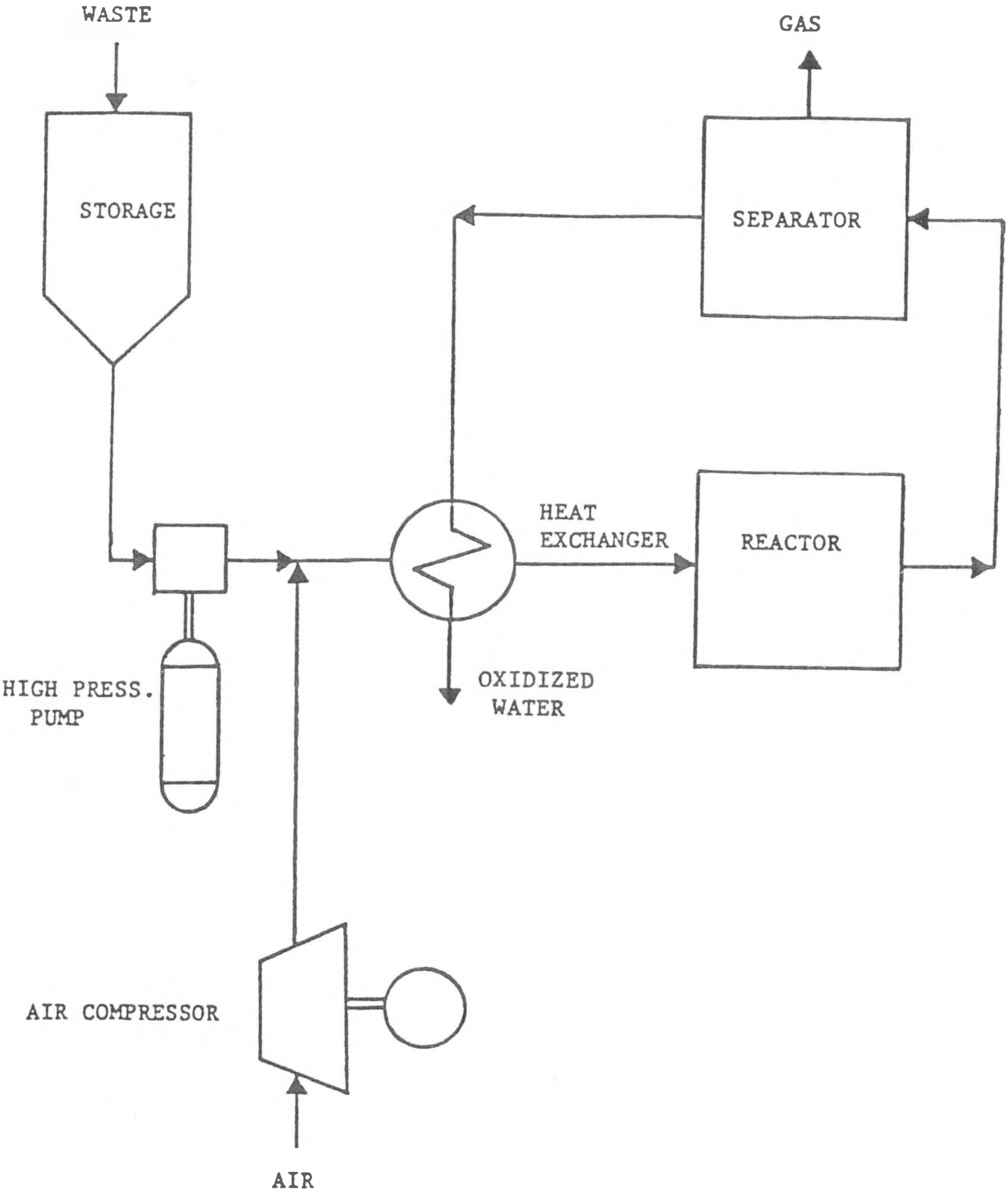


Figure 6-14. Simple arrangement for wet oxidation.

Preliminary work with a different oxidation process has been reported by Zobady and Edwards[55]. In this process pure oxygen, often with a little ozone, is used to oxidize the COD in the wastewater. The pressure is 20 to 60 psig and the temperatures are low. Residence times have been up to one hour but we are told that with equipment redesign the residence is being reduced toward 15 minutes, particularly when the COD is all soluble. There is insufficient data to determine how well different molecules are oxidized and a comparison with the cost of the high pressure process has not been made. However, with the much lower pressure and possibly shorter residence times this form of oxidation may easily prove very interesting for retort water and some preliminary tests are recommended.

6.8 Production of Dirty Steam

Since MIS retort probably requires more steam influent than the quantity of retort water produced, it is interesting to consider whether the retort water cannot be turned into dirty steam for retorting use. The dirty steam will contain the organic matter, the ammonia, the carbon dioxide and the sulfide that was in the retort water. We cannot determine whether any of these contaminants will effect the retort or alter the polluting potential of the process. However, we expect no problems and suggest that dirty steam be considered. If the volatile gases, NH_3, CO_2 and H_2S are not permitted in the steam, they can easily be stripped before steam is made. If recovery of ammonia pays for the stripping, the water might be stripped in any case. But the steam will contain organic matter if this concept is to be used.

There exists a "Thermosludge Process"[50,51] which was developed to provide steam for oil recovery in oil fields while disposing of associated brines. A modification of the process has been considered for use on coal gas condensate water[52]. Retort water, when compared to oil field waters, contains salts in the middle of the range of the oil field waters, somewhat more organic matter and a lot more strippable gases. It is quite possible that the Thermosludge Process will work well on retort water. A brief description follows.

The several elements of the patented thermosludge process are shown schematically in Figure 6-15. Various components are provided to allow the direct generation of steam from dirty condensate based on three primary principles:
1) use of a secondary liquid heat transfer medium to help control scaling;
2) provision for classical water chemical reactions preceding boiling; and
3) the provisions of sludge reaction product control throughout the boiling zone.

With reference to Figure 6-15, hot blowdown from the steam drum is flashed to preheat the feed water in the holding tank. The feedwater having been preheated then enters the top of the vertical stripping column by means of a charging pump in series with a high pressure feed water pump. A film-forming amine corrosion inhibitor and sodium sulfite for scavenging dissolved oxygen, may also be injected at the suction inlet of the charging pump.

Feedwater flows downward counter-currently interacting with the upflow of steam from the steam drum in the stripping column. Volatile materials, including oil, oxygen, carbon dioxide, hydrogen sulfide, ammonia, and other species present in the feedwater will be stripped by the steam in this counter-current

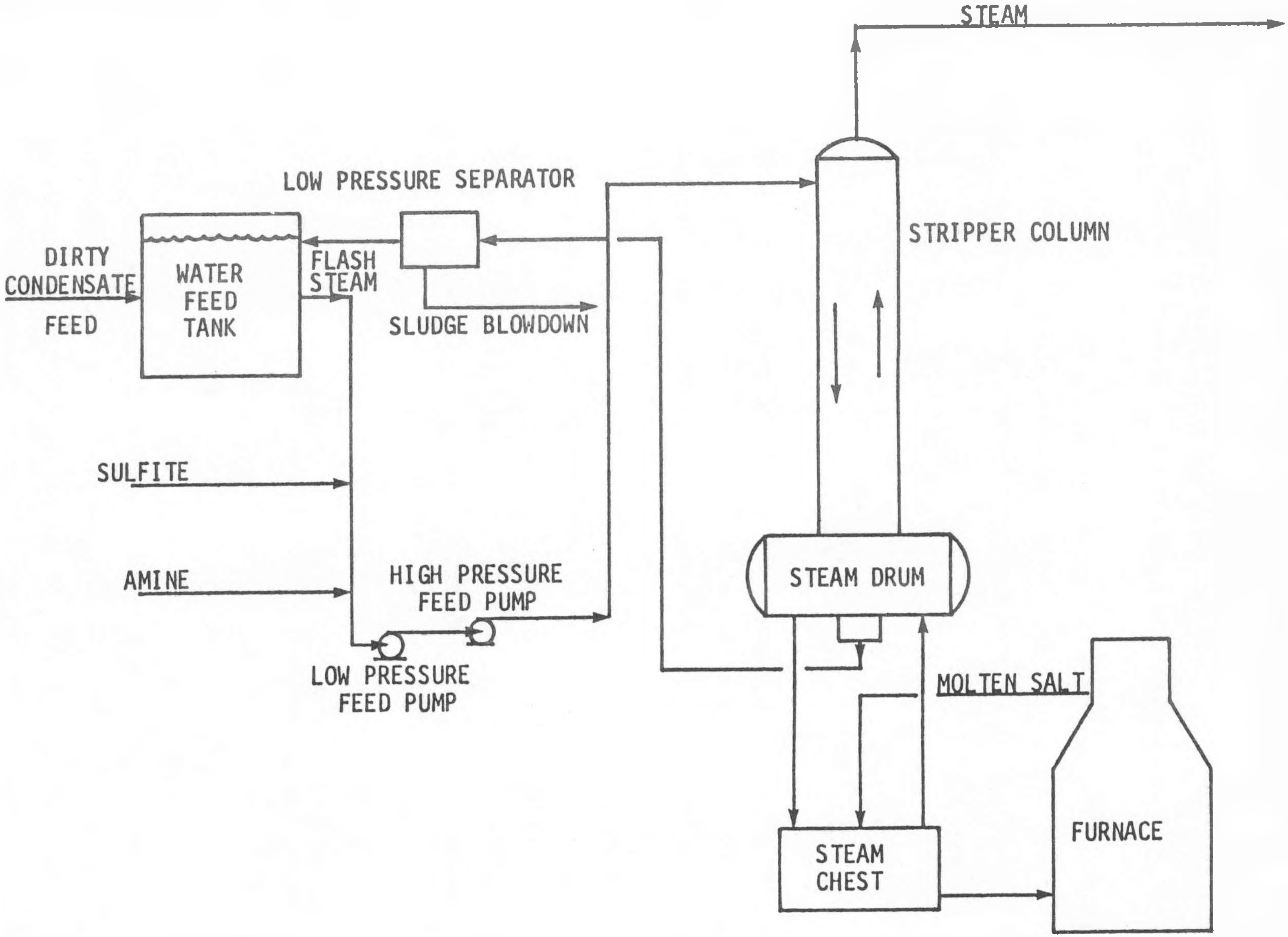


Figure 6-15. Schematic of patented Thermosludge process

action. The feedwater will be fully heated to the steam temperature as it moves counter-currently from the top of the column to the entrance of the steam drum. The classical reactions for formation of solid calcium carbonate, calcium sulfate, magnesium hydroxide, and magnesium silicate, should near completion by the time the water is ready to enter the steam drum. The feedwater pH-value will have undergone a change from pH equal to 7-8 to about 10-11 by the time it leaves the stripping column and enters the steam drum. For oil field operation, further carbon dioxide release and solids concentration occurs in the steam drum resulting in a further pH increase to 11-12.

The steam drum water passes through riser connections at the ends of the steam drum through thermosiphon action. It is passed through horizontal tubes within the steam chest where steam is produced which then passes to the stripping column. In the stripping column, this steam interacts with the downward flowing feedwater to heat it and strip out the volatiles. The steam containing the volatiles leaves the top of the stripper and is ready for use. Treatment of the sludge withdrawal stream is not shown.

In the patented Thermosludge unit, heat is provided to the steam chest by a molten transfer salt circulated through an external furnace. This feature is considered essential to control scaling during boiling by maintaining a well-controlled temperature which would not be possible by direct heating in the furnace. The basic unit can be operated with most any standard fuel with gross efficiency approach 80%.

In reference 52 it was found to be cheaper to raise dirty steam from a Lurgi process condensate than to clean up the condensate for use in a conventional boiler. Since shale retort water is at least as expensive to treat as Lurgi condensate the raising of dirty steam will be cheaper than treatment.

APPENDIX 1

TABULATED COD MEASUREMENTS FROM EXPERIMENTS ON THE ROTATING BIOLOGICAL CONTACTOR

DATE	UNIT	HYDRAULIC RESIDENCE TIME (HRS)	SAMPLE	COD*	% REMOVAL
1/29/80	A	35	Inf.	10,379	
			St 1	9,112	12
			St 2	8,512	18
			St 3	8,440	19
			St 4/Eff.	8,183	21
2/06/80	A	35	Inf.	9,866	
			St 1	7,968	19
			St 2	7,655	22
			St 3	7,677	22
			St 4/Eff.	7,423	25
2/08/80	A	35	Inf.	9,866	
			St 1	8,707	12
			St 2	8,176	17
			St 3	7,838	21
			St 4/Eff.	7,530	24
2/10/80	A	35	Inf.	9,866	
			St 1	7,680	22
			St 2	7,375	25
			St 3	7,395	25
			St 4/Eff.	6,794	31
2/12/80	A	35	Inf.	10,099	
			St 1	8,476	16
			St 2	8,493	16
			St 3	7,851	22
			St 4/Eff.	7,740	23
2/24/80	A	27	Inf.	10,260	
			St 1	8,157	21
			St 2	8,203	20
			St 3	7,918	23
			St 4/Eff.	7,737	25
2/26/80	A	27	Inf.	10,260	
			St 1	8,267	19
			St 2	8,059	21
			St 3	7,883	23
			St 4/Eff.	7,669	25

---

*All COD values given are averages of two replicates.

DATE	UNIT	HYDRAULIC RESIDENCE TIME (HRS)	SAMPLE	COD	% REMOVAL
2/29/80	A	27	Inf.	10,368	
			St 1	8,504	18
			St 2	8,217	21
			St 3	7,931	24
			St 4/Eff.	7,512	28
3/28/80	A	24	Inf.	10,108	
			St 1	8,100	20
			St 2	7,731	24
			St 3	8,056	20
			St 4/Eff.	7,904	22
3/31/80	A	24	Inf.	9,956	
			St 1	7,688	23
			St 2	7,804	22
			St 3	7,480	25
			St 4/Eff.	7,410	26
4/02/80	A	24	Inf.	9,728	
			St 1	8,024	18
			St 2	7,548	22
			St 3	7,769	20
			St 4/Eff.	7,621	22
4/04/80	A	24	Inf.	9,994	
			St 1	7,912	21
			St 2	7,475	25
			St 3	7,373	26
			St 4/Eff.	7,304	27
4/21/80	A	12	Inf.	9,906	
			St 1	7,517	24
			St 2	7,579	23
			St 3	7,426	25
			St 4/Eff.	7,702	22
4/25/80	A	12	Inf.	9,682	
			St 1	7,226	25
			St 2	7,123	26
			St 3	6,943	28
			St 4/Eff.	6,766	30
4/27/80	A	12	Inf.	9,889	
			St 1	7,379	25
			St 2	6,869	31
			St 3	6,953	30
			St 4/Eff.	6,563	34

DATE	UNIT	HYDRAULIC RESIDENCE TIME (HRS)	SAMPLE	COD	% REMOVAL
5/11/80	A	6	Inf.	9,972	
			St 1	8,497	15
			St 2	8,498	15
			St 3	8,614	14
			St 4/Eff.	8,730	12
5/13/80	A	6	Inf.	9,804	
			St 1	8,588	12
			St 2	8,778	10
			St 3	8,208	16
			St 4/Eff.	7,904	19
5/14/80	A	6	Inf.	9,943	
			St 1	8,553	14
			St 2	8,490	15
			St 3	8,454	15
			St 4/Eff.	8,356	16
6/11/80	A	9	Inf.	11,856	
			St 1	9,272	22
			St 2	9,576	19
			St 3	9,500	20
			St 4/Eff.	9,538	20
6/13/80	A	9	Inf.	11,431	
			St 1	9,362	18
			St 2	9,212	19
			St 3	9,212	19
			St 4/Eff.	9,212	19
3/04/80	D	1.1	Inf.	549	
			St 1	455	17
			St 2	470	14
			St 3/Eff.	-	-
3/05/80	D	1.1	Inf.	454	-
			St 1	445	2
			St 2	427	6
			St 3/Eff.	418	8
3/10/80	D	1.1	Inf.	530	-
			St 1	471	11
			St 2	456	13
			St 3/Eff.	460	14
4/02/80	D	1.1	Inf.	359	
			St 1	346	4
			St 2	337	6
			St 3/Eff.	331	8

DATE	UNIT	HYDRAULIC RESIDENCE TIME (HRS)	SAMPLE	COD	% REMOVAL
4/04/80	D	1.1	Inf.	382	-
			Eff.	364	5
4/25/80	C	3.5	Inf.	508	-
			St 1	314	38
			St 2	298	41
			St 3/Eff.	408	20
4/27/80	C	3.5	Inf.	444	
			St 1	275	38
			St 2	280	37
			St 3/Eff.	260	41
4/28/80	C	3.5	Inf.	535	-
			St 1	317	41
			St 2	298	44
			St 3/Eff.	297	44
5/05/80	C	3.5	Inf.	411	-
			St 1	270	34
			St 2	262	36
			St 3/Eff.	258	37
5/29/80	C	2.6	Inf.	562	-
			St 1	297	47
			St 2	293	48
			St 3/Eff.	299	47
6/22/80	C	2.6	Inf.	553	-
			St 1	372	33
			St 2	355	36
			St 3/Eff.	347	37
5/29/80	C	2.6	Inf.	430	-
			St 1	317	33
			St 2	282	40
			St 3/Eff.	257	45

APPENDIX 2

TABULATED BOD MEASUREMENTS FROM EXPERIMENTS ON THE ROTATING BIOLOGICAL CONTACTOR

DATE	UNIT	HYDRAULIC RESIDENCE TIME (HRS)	SAMPLE	BOD	% REMOVAL
1/29/80	A	35	Inf.	3,700	
			St 1	2,034	45
			St 2	1,758	52
			St 3	1,688	54
			St 4/Eff.	1,596	57
2/06/80	A	35	Inf.	3,400	
			St 1	1,346	60
			St 2	1,154	66
			St 3	1,062	69
			St 4/Eff.	974	71
2/08/80	A	35	Inf.	3,900	
			St 1	1,683	57
			St 2	1,685	57
			St 3	1,660	57
			St 4/Eff.	1,440	61
2/10/80	A	35	Inf.	3,900	
			St 1	1,803	54
			St 2	1,547	60
			St 3	1,524	61
			St 4/Eff.	1,482	62
2/21/80	A	35	Inf.	3,825	
			St 1	1,683	56
			St 2	1,708	52
			St 3	1,549	59
			St 4/Eff.	1,450	62
2/24/80	A	27	Inf.	4,150	
			St 1	1,651	60
			St 2	1,555	63
			St 3	1,508	64
			St 4/Eff.	1,571	62

DATE	UNIT	HYDRAULIC RESIDENCE TIME (Hrs)	SAMPLE	BOD	% REMOVAL
2/26/80	A	27	Inf.	4,150	
			St 1	2,210	47
			St 2	2,191	47
			St 3	2,056	50
			St 4/Eff.	1,947	53
2/29/80	A	27	Inf.	4,225	
			St 1	1,991	53
			St 2	1,956	54
			St 3	1,828	57
			St 4/Eff.	1,682	60
3/28/80	A	24	Inf.	4,000	
			St 1	1,743	56
			St 2	1,663	58
			St 3	1,608	60
			St 4/Eff.	1,671	58
3/31/80	A	24	Inf.	3,800	
			St 1	1,620	57
			St 2	1,494	61
			St 3	1,679	56
			St 4/Eff.	1,439	62
4/04/80	A	24	Inf.	4,200	
			St 1	2,038	51
			St 2	1,904	55
			St 3	1,750	58
			St 4/Eff.	1,764	58
4/21/80	A	12	Inf.	3,750	
			St 1	1,943	48
			St 2	1,964	48
			St 3	1,679	55
			St 4/Eff.	1,664	56
4/25/80	A	12	Inf.	4,200	
			St 1	1,908	55
			St 2	1,817	57
			St 3	1,703	59
			St 4/Eff.	1,832	56
4/27/80	A	12	Inf.	4,000	
			St 1	1,710	57
			St 2	1,522	62
			St 3	1,484	63
			St 4/Eff.	1,519	62

DATE	UNIT	HYDRAULIC RESIDENCE TIME (Hrs)	SAMPLE	BOD	% REMOVAL
5/11/80	A	6	Inf.	4,214	
			St 1	2,650	37
			St 2	3,000	29
			St 3	2,925	31
			St 4/Eff.	2,525	40
5/13/80	A	6	Inf.	4,000	
			St 1	2,475	38
			St 2	2,525	37
			St 3	2,400	40
			St 4/Eff.	2,450	39
5/14/80	A	6	Inf.	4,000	
			St 1	3,150	21
			St 2	2,950	26
			St 3	2,950	26
			St 4/Eff.	2,900	28
6/11/80	A	9	Inf.	4,071	
			St 1	2,375	42
			St 2	2,550	37
			St 3	2,275	44
			St 4/Eff.	2,300	44
6/13/80	A	9	Inf.	4,071	
			St 1	2,525	38
			St 2	2,300	44
			St 3	2,150	47
			St 4/Eff.	2,175	47
3/04/80	D	1.1	Inf.	153	-
			St 1	93	40
			St 2	96	38
			St 3/Eff.	-	-
3/10/80	D	1.1	Inf.	115	
			St 1	82	29
			St 2	82	29
			St 3/Eff.	74	36
4/02/80	D	1.1	Inf.	85	
			St 1	70	18
			St 2	70	18
			St 3/Eff.	64	25
4/04/80	D	1.1	Inf.	86	
			Eff.	62	28

DATE	UNIT	HYDRAULIC RESIDENCE TIME (Hrs)	SAMPLE	BOD	% REMOVAL
4/14/80	C	3.5	Inf.	240	-
			St 1	108	55
			St 2	129	46
			St 3/Eff.	129	46
4/25/80	C	3.5	Inf.	200	-
			St 1	96	52
			St 2	113	44
			St 3/Eff.	98	51
4/27/80	C	3.5	Inf.	141	-
			St 1	21	85
			St 2	24	83
			St 3/Eff.	17	88
4/28/80	C	3.5	Inf.	288	-
			St 1	37	84
			St 2	30	87
			St 3/Eff	30	87
5/5/80	C	3.5	Inf.	171	-
			St 1	13.5	92
			St 2	12.8	93
			St 3/Eff.	12	93
5/29/80	C	2.6	Inf.	210	-
			St 1	11.1	94
			St 2	5.4	97
			St 3/Eff.	17.8	94
6/22/80	C	2.6	Inf.	187	-
			St 1	13.2	93
			St 2	19.8	89
			St 3/Eff.	16.8	91
6/24/80	C	2.6	Inf.	182	-
			St 1	28.3	89
			St 2	8.4	95
			St 3/Eff		96

APPENDIX 3

TABULATED SOLIDS MEASUREMENTS FROM EXPERIMENTS ON THE ROTATING BIOLOGICAL CONTACTOR

DATE	UNIT	HYDRAULIC RESIDENCE TIME (Hrs)	SAMPLE	SS(mg/l)	VSS(mg/l)
1/29/80	A	35	Inf.	230	72
			St 1	833	561
			St 2	1,023	465
			St 3	812	534
			St 4	765	533
			Eff.	536	272
2/06/80	A	35	Inf.	130	70
			St 1	648	516
			St 2	640	420
			St 3	526	402
			St 4	588	420
			Eff.	444	310
2/08/80	A	35	Inf.	120	46
			St 1	524	398
			St 2	558	374
			St 3	518	358
			St 4	592	368
			Eff.	440	310
2/10/80	A	35	Inf.	108	56
			St 1	554	416
			St 2	530	374
			St 3	420	294
			St 4	494	374
			Eff.	504	378
2/12/80	A	35	Inf.	100	40
			St 1	596	442
			St 2	568	406
			St 3	526	388
			St 4	512	388
			Eff.	490	328
2/24/80	A	27	Inf.	91	36
			St 1	790	604
			St 2	646	532
			St 3	554	444
			St 4	546	406
			Eff.	462	326

DATE	UNIT	HYDRAULIC RESIDENCE TIME (Hrs)	SAMPLE	SS (mg/l)	VSS (mg/l)
2/26/80	A	27	Inf.	138	70
			St 1	568	462
			St 2	676	518
			St 3	500	414
			St 4	628	466
			Eff.	418	288
3/29/80	A	24	Inf.	260	116
			St 1	888	702
			St 2	840	683
			St 3	918	700
			St 4	888	607
			Eff.	410	350
3/31/80	A	24	Inf.	258	106
			St 1	1,100	826
			St 2	588	452
			St 3	846	628
			St 4	996	744
			Eff.	354	254
4/02/80	A	24	Inf.	249	126
			St 1	884	708
			St 2	854	684
			St 3	676	552
			St 4	876	602
			Eff.	380	294
4/04/80	A	24	Inf.	210	95
			St 1	736	631
			St 2	920	788
			St 3	910	778
			St 4	820	708
			Eff.	380	270
4/21/80	A	12	Inf.	214	116
			St 1	1,342	966
			St 2	876	624
			St 3	754	526
			St 4	624	418
			Eff.	378	190
4/25/80	A	12	Inf.	268	120
			St 1	1,058	841
			St 2	920	655
			St 3	854	688
			St 4	938	710
			Eff.	338	190

DATE	UNIT	HYDRAULIC RESIDENCE TIME (Hrs)	SAMPLE	SS (mg/l)	VSS (mg/l)
4/27/80	A	12	Inf.	334	229
			St 1	984	784
			St 2	975	754
			St 3	1,068	732
			St 4	824	624
			Eff.	314	224
5/11/80	A	6	Inf.	206	146
			St 1	1,116	890
			St 2	810	666
			St 3	894	700
			St 4	688	550
			Eff.	440	285
5/13/80	A	6	Inf.	240	94
			St 1	838	518
			St 2	1,324	968
			St 3	836	618
			St 4	1,140	846
			Eff.	480	310
5/14/80	A	6	Inf.	188	124
			St 1	564	314
			St 2	818	708
			St 3	558	410
			St 4	984	650
			Eff.	418	268
6/11/80	A	9	Inf.	136	108
			St 1	814	626
			St 2	1,038	834
			St 3	566	440
			St 4	540	408
			Eff.	390	314
6/13/80	A	9	Inf.	156	116
			St 1	950	724
			St 2	944	724
			St 3	840	710
			St 4	812	792
			Eff.	384	326

APPENDIX 4

NOMENCLATURE USED IN SECTION 4 FOR THE ACTIVATED SLUDGE STUDY

X_R - average concentration of the MLVSS in a reactor over time of a run when the characteristics of the infulent do not change (mg/ℓ)

X_i^R - MLVSS in reactor on day "1" (mg/ℓ)

X_{i+1}^R - MLVSS in reactor on day "i+1" (mg/ℓ)

$\mathcal{L}^R$ - average concentration of substrate in reactor for time "t" (mg/ℓ)

$\mathcal{L}_i^R$ - substrate concentration in reactor on day "i" (mg/ℓ)

$\mathcal{L}_{i+1}^R$ - substrate concentration in reactor on day "i+1" (mg/ℓ)

θ_c - sludge retention time or sludge age. This accounts for the solids in both the aerated and recycled sludge. When powdered activated carbon is present θ_c does not include the carbon. (days)

V^R - reactor volume (ℓ)

Q - daily flow of influent into reactor (ℓ/d)

X_{EF} - VSS in effluent (mg/ℓ)

X_{IN} - VSS in influent (mg/ℓ)

$V_{S.T}$ - Settling tank volume (ℓ)

$X_i^{S.T}$ - VSS in settling tank on day "i" (mg/ℓ)

$X_{i+1}^{S.T}$ - VSS in settling tank on day "i+1" (mg/ℓ)

μ - net specific sludge growth rate (day^{-1})

$\Delta x/\Delta t$ - sludge growth rate over time period "t" (mg/(ℓ)(d))

$\Delta S/\Delta t$ - substrate utilization rate over time period "t" (mg/(ℓ)(d))

$\mathcal{L}_i^{S.T}$	- BOD_5 in the settling tank on day "i"	(mg/ℓ)
$\mathcal{L}_{i+1}^{S.T}$	- BOD_5 in the settling tank on day "i+1"	(mg/ℓ)
V^{EF}	- Volume of the effluent over time period "t" which is equal to the volume of influence over the same period of time	(ℓ)
L_{IN}	- BOD_5 of the influent	(mg/ℓ)
L_{EF}	- BOD_5 of the effluent	(mg/ℓ)
U	- specific substrate utilization rate	(d^{-1})
t_1	- run time	(d)
D_{i+1}	- the date at the end of a run	(d)
D_i	- the date at the start of a run	(d)
T_{i+1}	- the hour at the end of a run	(h)
T_i	- the hour at the start of a run	(h)
θ_H	- hydraulic detention time	(d)
F/M	- food to microorganism ratio	(d^{-1})
E_N	- nominal efficiency of the treatment	(%)
E_O	- overall efficiency of the treatment	(%)
OUR'	- specific oxygen uptake rate	(d^{-1})
OC_M	- oxygen consumption per unit sludge produced	(ℓ/mg)
OC_F	- oxygen consumption per unit substrate utilized	(ℓ/mg)
Y	- growth - yield coefficient	
k_d	- microorganism - decay coefficient	(d^{-1})
K_s	- Mikhaelis - Menton constant	(mg/ℓ)
k	- max. specific substrate utilization rate	(d^{-1})

a - coefficient of oxygen consumption due to substrate utilization

C - coefficient of oxygen consumption due to endogenous respiration at the activated sludge

t/v - the ratio of filtration time to filtrate volume in the specific resistance measurement (sec/ml)

(V) - filtrate volume (ml)

$\left.\begin{matrix}c\\d\end{matrix}\right\}$ empirical coefficients

APPENDIX 5

DETERMINATION OF MLCSS AND MLBSS IN PAC-AS SYSTEMS*

Equipment: 30 ml gooch crucible fiberglass filter pad,5 or 10 ml pipet with tip cut off

I. PROCEDURE

1. Run normal suspended solids using 10 ml of sample (use 5 ml for thick samples).
2. Run nitric treated suspended solids by:
   - a. Measure 10 ml of sample into 150 ml beaker.
   - b. Add 20 ml concentrated HNO_3.
   - c. Heat sample to just under boiling (DO NOT BOIL).
   - d. Continue heating until volume is approximately 10 ml.
   - e. Cool and filter sample.
   - f. Remove all carbon from beaker into crucible with aid of rubber policeman.

II. CALCULATION

A. Normal suspended solids

B. Normal suspended ash

C. Nitric treated suspended ash

$$\frac{C - D}{0.95} = \text{g/l Carbon (MLCSS)}$$

$$A - (B + \text{Carbon}) = \text{g/l Biomass (MLBSS)}$$

Record: A

B

Carbon (MLCSS)

Biomass (MLBSS)

NOTE: Salts ppt out and are not redissolved upon filtration, i.e. wt. may be too much.

---

*From Fay, W. S., "Bio-Physical Treatment of Coal Gasification Wastewater," Master Thesis, University of West Virginia, Morgantown, West Virginia, 1978.

References

1. Antonio, R.L., Nitrogen Control with the Rotating Biological Contactor, Autotrol Corp., Milwaukee, Wisconsin, 1979.

2. Friedmann, A.A., "Effect of Disc Rotational Speed on Biological Contactor Efficiency", JWPCF, 2678, November 1979.

3. O'Shaughnessy, J.C., "Design of an RBC Unit Operation", Thomas R. Camp Lecture Series, February 19, 1980, Boston Society of Civil Engineers Section, ASCE.

4. Wilson, R.W. and Murphy, K.L., "Scale Up of Rotating Biological Contactor Design", JWPCF, 52 (3) March 1980.

5. Autotrol Corporation, Biosurf Process Information Bulletin, Autotrol Corp., Milwaukee, Wisc., 1979.

6. Blanc, F.C., O'Shaughnessy, J.C. and Miller, C.H., "Treatment of Bottling Plant Wastewater with Rotating Biological Contactors", Proceedings of 33rd Purdue Industrial Waste Conference, May 1978.

7. American Public Health Association, Standard Methods for the Examination of Water and Wastewater, 14th ed., New York, 1976.

8. Sawyer, C.N., McCarty, P.L., Chemistry for Environmental Engineers, 3rd ed., p.234-235, McGraw Hill, New York, 1978.

9. Giona, A.R. and Annesini, M.C., "Oxygen Uptake in the Activated Sludge Process", JWPCF, 51 (5) p.1009-1016, 1979.

10. Haas, C.N., "Oxygen Uptake as an Activated Sludge Control Parameter", JWPCF, 51 (5) p.938-942, 1979.

11. Benefield, L.D., et al, "Process Control by Oxygen Uptake and Solids Analysis", JWPCF, 47 (8) p.2498-2506, 1975.

12. Grieves, C.G., et al, "Powdered Carbon Enhancement Versus Granular Carbon Adsorption for Oil Refinery BATEA Wastewater Treatment", presented at 51st Annual Conference, Water Pollution Control Federation, Anaheim, Ca., October 3, 1978.

13. Crame, L.W. and Grieves, C.G., "Enhance the Activated Sludge Process with a New High-Surface-Area Activated Carbon", presented at the AIChE 87th National Meeting, Boston, Mass., August 21, 1979.

14. Hockenbury, M.E. and Grieves, C.G., "Treatment of Textile Waste with the Powdered Carbon Activated Sludge Process", presented at the 7th Annual Industrial Pollution Conference of the Waste Water Equipment Manufacturer's Association, Philadelphia, Pa., June 5, 1979.

15. Metcalf & Eddy, Inc. and Tchobanoglous, G., Wastewater Engineering: Treatment, Disposal, Reuse, McGraw-Hill Series in Water Resources & Environmental Engineering, 1979 ed.

16. Fay, W.S., "Bio-physical Treatment of Coal Gasification Wastewater", Masters Thesis, University of West Virginia, Morgantown, W.V., 1978.

17. Hicks, R.E. and Probstein, R.F., "Water Management in Surface and In-Situ Oil Shale Processing", presented at A.I.Ch.E. 87th Natl. Meeting, Boston, August 19-22, 1979.

18. Denver Research Institute/ Water Purification Associates/ Stone & Webster, "Predicted Costs of Environmental Controls for a Commercial Oil Shale Industry", U.S. D.O.E., Report COO-5107-1, July 1979.

19. Rio Blanco Oil Shale Project,"Revised Detailed Development Plan, Oil Shale Tract C-a", Vols. 1-3. Gulf Oil Corp.- Standard Oil Co. (Indiana). Submitted to Area Oil Shale Supervisor, Geological Survey, U.S. Department of the Interior, Grand Junction, Co., May 1977.

20. C-b Shale Oil Venture, "Environmental Baseline Program Final Report (Nov. 1974-Oct. 1976), V.2, Hydrology", Ashland Oil, Inc. and Occidental Oil Shale, Inc., Submitted to Area Oil Shale Supervisor, Geological Survey, U.S. D.O.I., Grand Junction, Co., May 1977.

21. C-b Shale Oil Venture, "Water Quality in Deep Aquifers under C-b Tract", Memo from N. Stellavato to G.T. Kimbrough, May 5, 1978, Personal Communication, July 1978.

22. Rio Blanco Oil Shale Co., "Materials from NPDES Permit for Disposal of Excess Upper Aquifer Groundwater", Personal Communication from K.L. Berry, July 14, 1978.

23. "Proposed NPDES Discharge Permit Limits for C-b", May 9, 1978. Personal Communication from C-b Shale Oil Venture, July 1978.

24. "Draft Copy- Summary of Rationale, Occidental Oil Shale, Inc., C-b Shale Oil Venture, Permit Number: CO-003961, Rio Blanco County", October 31, 1978. Personal communication from Colorado Department of Health, Denver, Colorado, January 17, 1979.

25. Goldstein, D.J., Gold, H. and Probstein, R.F., "Costs of Wastewater Disposal in Coal Gasification and Oil Shale Processing", Report to Department of Natural Resources, State of Colorado, January, 1979.

26. Mercer, B.W., et al, "Ammonia Removal from Secondary Effluents by Selective Ion Exchange", Journal WPCF, 42 (2), p.R95-R107, 1970.

27. Ronen, M. and Van Vuuren, L.R.J., "Ammonia Removal in a Ponds System and in a Stripping Tower", Paper presented at International Conference of Advanced Treatment and Reclamation of Wastewater, Johannesburg, July 1977.

28. Kunin, R., "A Macroreticular Boron Specific Ion Exchange Resin", in Trace Elements in the Environment, E.L. Kothay (ed.), Advances in Chemistry Series 123, American Chemical Society, 1973.

29. Burnham, A.K., "Identification and Estimation of Neutral Organic Contaminants in Potable Water", Analytical Chemistry, 44 (1), p.139-141, 1972.

30. Caracciolo, V.P., Rosenblatt, N.W., and Tomsic, V.J., "Dupont's Hollow Fiber Membranes", Chapter 16 in Reverse Osmosis and Synthetic Membranes, S. Sourirajan (ed.), Natl. Res. Council of Canada, NRCC 15627 (1977).

31. C-b Shale Oil Venture, "Oil Shale Tract C-b; Modifications to Detailed Development Plan", Ashland Oil, Inc. and Occidental Oil Inc., submitted to Area Oil Shale Supervisor, Geological Survey, U.S. D.O.I., Grand Junction, Colorado, Feb. 1977.

32. American Petroleum Institute, "A New Correlation of NH3,CO2, and H2S Volatility Data From Aqueous Sour Water Systems", API Publication 955, March 1978.

33. Van Krevelen, D.W. et al, "Composition and Vapour Pressures of Aqueous Solutions of Ammonia, Carbon Dioxide, and Hydrogen Sulfide", *Recueil Trav. Chim*., *68*, p.191-220, 1969.

34. Hicks, R.E., Goldstein, D.J., Seufert, F.B. and Wei, I.W., "Wastewater Treatment in Coal Conversion", U.S. E.P.A. Report 600/7-79/133, NTIS Catalog PB-297-587/8WE, June 1979.

35. Water Purification Associates, "A Study of Reverse Osmosis for Treating Oil Shale Process Condensates and Excess Mine Drainage Water", Quarterly Progress Report, Submitted to LETC, September 1979.

36. Fox, J.P., Farrier, D.S., Poulson, R.E., "Chemical Characterization and Analytical Considerations for an In Situ Oil Shale Process Water", Laramie Energy Technology Center, Report LETC/RI-78/7, U.S. D.O.E., Nov. 1978.

37. Fox, J.P., Mason, K.K., and Duvall, J.J., "Partitioning of Major, Minor, and Trace Elements During Simulated In Situ Oil Shale Retorting in a Controlled State Retort", 12th Oil Shale Symposium Proceedings, Colorado School of Mines, August 1979.

38. Reap, E.J., et al, "Wastewater Characteristics and Treatment Technology for the Liquifaction of Coal Using H-Coal Process", *Proceedings of the 32nd Purdue Industrial Waste Conference*, May 1977.

39. Goldstein, D.J. and Yung, D., "Water Conservation and Pollution Control in Coal Conversion Processes", U.S. E.P.A. Report 600/7-77-065, June 1977. Research Triangle Park, N.C. (NTIS Catalog PB 264-568/2WE)

40. Johnson, G.E., et al, "Treatability Studies of Condensate Water from Synthane Coal Gasification", U.S. D.O.E., Pittsburgh Energy Research Center, Report PERC/RI-77/13, November 1977.

41. Drummond, C.J., Johnson, G.E., Neufeld, R.D., and Haynes, W.P., "Biochemical Oxidation of Coal Conversion Wastewaters", A.I.Ch.E., 87th National Meeting, Wastewater from Fuel Conversion Session, Boston, Mass., August 19-22, 1979.

42. Hicks, R.E., Goldstein, D.J., Seufert, F.B. and Wei, I.W., "Wastewater Treatment in Coal Conversion", U.S. E.P.A. Report 600/7-79/133, NTIS Catalog PB-297-587/8WE, June 1979.

43. Seufert, F.B., Hicks, R.E., Wei, I.W. and Goldstein, D.J., "Conceptual Designs for Water Treatment in Demonstration Plants", U.S. D.O.E. Report FE-2635-T1, March 1979, 2 Vols.

44. American Petroleum Institute, Manual on Disposal of Refinery Wastes, Volume on Liquid Wastes, Chapter 5, "Oil-Water Separator Process Design", and Chapter 8, "Treatment of Recovered Oil Emulsions", API, 1969.

45. Dawson, G.W. and Mercer, B.W., "Analysis, Screening, and Evaluation of Control Technology for Wastewater Generated in Shale Oil Development", Quarterly Reports, January 1977- March 1979, Battelle Pacific Northwest Laboratory, Richmond, Washington 99352.

46. U.S.S. Engineers and Consultants, Inc. (UEC), "Phosam-W Process", UEC Trade Bulletin, 600 Grant Street, Pittsburgh, Pa., January 1975.

47. Klett, R.J., "Treat Sour Water for Profit", Hydrocarbon Processing, p.97, October 1972.

48. Edwards, T.J., "Thermodynamics of Aqueous Solutions Containing One or More volatile Weak Electrolytes", MS Thesis, Dept. of Chem. Engng, Univ. of California, Berkeley, 1974. See also, AIChE Journal, 21, p.248, 1975.

49. Verhoff, F.H. and Choi, M.K., "Sour Water Stripping of Coal Gasification Wastewater", METC Report CR-79/23, U.S. D.O.E., May 1979.

50. Rintoul, W., "Steam from Wastewater", Pacific Oil World, July/August 1978.

51. Hull, R.J., "Process for Treatment of Saline Waters", U.S. Patent No.3,410,796, November 12, 1968.

52. Goldstein, D.J., Seufert, F.B., van Wormer, K.A. and Gold, H., "Waste Disposal, Cooling and Related Environmental Impacts Associated with Synthetic Fuel Plant Siting and Design Criteria", W.P.A. for U.S. D.O.E. Division of Fossil Energy, Contract No. ET-78-C-01-3182, December 1979.

53. Goldstein, D.J. and Yung, D., "Water Conservation and Pollution Control in Coal Conversion Processes", U.S. E.P.A. Report 600/7-77-065, June 1977. Research Triangle Park, N.C. (NTIS Catalog PB 264-568/2WE)

54. Water Purification Associates and Process Research Inc., "Innovative Technologies for Water Pollution Abatement", NCWQ Report No. 75/13, National Commission on Water Quality, Washington, D.C. (NTIS Catalog PB-247390), December 1975.

55. International Waste Water Reclamation Technologies Inc., "Oxyozonation Process for Treatment of Municipal and Industrial Wastewaters and Sludges: Pilot Studies", presented at 52nd Annual Conference of the Water Pollution Control Association of Pennsylvania, Penn. State Univ., August 1980.

56. Mercer, B.W., "Environmental Control Technologies for Shale Oil Wastewater", in Pacific Northwest Laboratory Annual Report for 1979, Part 5, Report PNL-3300, UC-41,11, February 1980.

57. Metcalf and Eddy, "Water Pollution Potential from Surface Disposal of Processed Oil Shale from the TOSCO II Process", report prepared for Colony Development Operation, Atlantic Richfield Company, October 1975.

58. Ossio, E.A., Fox, J.P., Thomas, J.F. and Poulson, R.E., "Anaerobic Fermentation of Simulated In-Situ Oil Shale Retort Water", ACS Div. of Fuel Chem. Reprints, 23 (2) p.202-213, 1978.

59. Spencer, R.R., "Anaerobic Treatment of Wastewater Generated During Shale Oil Production", Draft Report, Battelle Pacific Northwest Laboratory, 1979.

60. Mercer, B.W., Wakamiya, W., Spencer, R.R. and Mason, M.J., "Assessment of Control Technology for Shale Oil Wastewaters", Paper presented at Environmental Control Technology Symposium, U.S. D.O.E., November 1978.

61. Ossio, E. and Fox, P., "Anaerobic Biological Treatment of In-Situ Retort Water", Report for U.S. D.O.E., LBL-10481, UC-91, Lawrence Berkeley Lab, Univ. of Calif., March 1980.

62. Cook, E.W., "Organic Acids in Process Water from Green River Oil Shale", Chemistry and Industry, p.485, May 1, 1971.

☆U.S. GOVERNMENT PRINTING OFFICE. 1982-646-069/350