

Wastewater Engineering

Treatment and Reuse

Fourth Edition

Metcalf & Eddy, Inc.

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Contents

<i>Preface</i>	xxi	2-2	Sampling and Analytical Procedures	29
<i>Acknowledgments</i>	xxv		<i>Sampling</i>	29
<i>Foreword</i>	xxvii		<i>Methods of Analysis</i>	34
			<i>Units of Measurement for Physical and Chemical Parameters</i>	35
1 Wastewater Engineering: An Overview	1		<i>Useful Chemical Relationships</i>	35
1-1 Terminology	3	2-3	Physical Characteristics	42
1-2 Impact of Regulations on Wastewater Engineering	3		<i>Solids</i>	42
1-3 Health and Environmental Concerns in Wastewater Management	7		<i>Particle Size Distribution</i>	48
1-4 Wastewater Characteristics	9		<i>Turbidity</i>	51
<i>Improved Analytical Techniques</i>	10		<i>Color</i>	52
<i>Importance of Improved Wastewater Characterization</i>	10		<i>Absorption/Transmittance</i>	52
1-5 Wastewater Treatment	10		<i>Temperature</i>	54
<i>Treatment Methods</i>	11		<i>Conductivity</i>	56
<i>Current Status</i>	12		<i>Density, Specific Gravity, and Specific Weight</i>	56
<i>New Directions and Concerns</i>	15	2-4	Inorganic Nonmetallic Constituents	57
<i>Future Trends in Wastewater Treatment</i>	20		<i>pH</i>	57
1-6 Wastewater Reclamation and Reuse	20		<i>Chlorides</i>	59
<i>Current Status</i>	21		<i>Alkalinity</i>	59
<i>New Directions and Concerns</i>	21		<i>Nitrogen</i>	60
<i>Future Trends in Technology</i>	21		<i>Phosphorus</i>	63
1-7 Biosolids and Residuals Management	22		<i>Sulfur</i>	64
<i>Current Status</i>	22		<i>Gases</i>	64
<i>New Directions and Concerns</i>	23		<i>Odors</i>	70
<i>Future Trends in Biosolids Processing</i>	23	2-5	Metallic Constituents	77
			<i>Importance of Metals</i>	77
2 Constituents in Wastewater	27		<i>Sources of Metals</i>	77
2-1 Wastewater Constituents	29		<i>Sampling and Methods of Analysis</i>	77
<i>Constituents Found in Wastewater</i>	29		<i>Typical Effluent Discharge Limits for Metals</i>	78
<i>Constituents of Concern in Wastewater Treatment</i>	29	2-6	Aggregate Organic Constituents	80
			<i>Measurement of Organic Content</i>	81
			<i>Biochemical Oxygen Demand (BOD)</i>	81
			<i>Total and Soluble Chemical Oxygen Demand (COD and SCOD)</i>	93
			<i>Total and Dissolved Organic Carbon (TOC and DTOC)</i>	94
			<i>UV-Absorbing Organic Constituents</i>	95

	<i>Theoretical Oxygen Demand (ThOD)</i>	96		<i>Sources and Rates of Industrial</i>	
	<i>Interrelationships between BOD, COD,</i>			<i>(Nondomestic) Wastewater Flows</i>	162
	<i>and TOC</i>	96		<i>Infiltration/Inflow</i>	163
	<i>Oil and Grease</i>	98		<i>Exfiltration from Collection Systems</i>	167
	<i>Surfactants</i>	98		<i>Combined System Flowrates</i>	168
2-7	<i>Individual Organic Compounds</i>	99	3-3	<i>Statistical Analysis of Flowrates,</i>	
	<i>Priority Pollutants</i>	99		<i>Constituent Concentrations, and</i>	
	<i>Analysis of Individual</i>			<i>Mass Loadings</i>	170
	<i>Organic Compounds</i>	100		<i>Common Statistical Parameters</i>	170
	<i>Volatile Organic Compounds (VOCs)</i>	100		<i>Graphical Analysis of Data</i>	171
	<i>Disinfection Byproducts</i>	102	3-4	<i>Analysis of Wastewater Flowrate Data</i>	178
	<i>Pesticides and Agricultural Chemicals</i>	102		<i>Definition of Terms</i>	178
	<i>Emerging Organic Compounds</i>	102		<i>Variations in Wastewater Flowrates</i>	179
2-8	<i>Biological Characteristics</i>	104		<i>Wastewater Flowrate Factors</i>	180
	<i>Microorganisms Found in Surface</i>		3-5	<i>Analysis of Constituent Mass</i>	
	<i>Waters and Wastewater</i>	104		<i>Loading Data</i>	181
	<i>Pathogenic Organisms</i>	109		<i>Wastewater Constituent Concentrations</i>	181
	<i>Use of Indicator Organisms</i>	115		<i>Variations in Constituent Concentrations</i>	185
	<i>Enumeration and Identification</i>			<i>Flow-Weighted Constituent</i>	
	<i>of Bacteria</i>	118		<i>Concentrations</i>	192
	<i>Enumeration and Identification</i>			<i>Calculation of Mass Loadings</i>	194
	<i>of Viruses</i>	126		<i>Effect of Mass Loading Variability</i>	
	<i>Polymerase Chain Reaction (PCR)</i>	129		<i>on Treatment Plant Performance</i>	197
	<i>Development of Microorganisms</i>		3-6	<i>Selection of Design Flowrates and</i>	
	<i>Typing Techniques</i>	130		<i>Mass Loadings</i>	197
	<i>New and Reemerging Microorganisms</i>	130		<i>Design Flowrates</i>	199
2-9	<i>Toxicity Tests</i>	130		<i>Design Mass Loadings</i>	205
	<i>Toxicity Terminology</i>	131			
	<i>Toxicity Testing</i>	133			
	<i>Analysis of Toxicity Test Results</i>	134	4	Introduction to Process	
	<i>Application of Toxicity Test Results</i>	136		Analysis and Selection	215
	<i>Identification of Toxicity Components</i>	137	4-1	<i>Reactors Used for the Treatment</i>	
3	Analysis and Selection			<i>of Wastewater</i>	218
	of Wastewater			<i>Types of Reactors</i>	218
	Flowrates and			<i>Application of Reactors</i>	220
	Constituent Loadings	153		<i>Hydraulic Characteristics of Reactors</i>	220
3-1	<i>Components of Wastewater Flows</i>	154	4-2	<i>Mass-Balance Analysis</i>	222
3-2	<i>Wastewater Sources and Flowrates</i>	154		<i>The Mass-Balance Principle</i>	222
	<i>Domestic Wastewater Sources</i>			<i>Preparation of Mass Balances</i>	224
	<i>and Flowrates</i>	155		<i>Application of the Mass-Balance</i>	
	<i>Strategies for Reducing Interior Water</i>			<i>Analysis</i>	224
	<i>Use and Wastewater Flowrates</i>	158		<i>Steady-State Simplification</i>	225
	<i>Water Use in Developing Countries</i>	162	4-3	<i>Modeling Ideal Flow in Reactors</i>	226
				<i>Ideal Flow in Complete-Mix Reactor</i>	226
				<i>Ideal Flow in Plug-Flow Reactor</i>	227

4-4	Analysis of Nonideal Flow in Reactors Using Tracers	229		<i>Gas-Liquid Mass Transfer</i>	284
	<i>Factors Leading to Nonideal Flow in Reactors</i>	229		<i>Liquid-Solid Mass Transfer</i>	293
	<i>Need for Tracer Analysis</i>	231	4-9	Introduction to Process Selection	297
	<i>Types of Tracers</i>	231		<i>Important Factors in Process Selection</i>	297
	<i>Conduct of Tracer Tests</i>	231		<i>Process Selection Based on Reaction Kinetics</i>	299
	<i>Analysis of Tracer Response Curves</i>	233		<i>Process Selection Based on Mass Transfer</i>	300
	<i>Practical Interpretation of Tracer Measurements</i>	242		<i>Process Design Based on Loading Criteria</i>	301
4-5	Modeling Nonideal Flow in Reactors	245		<i>Bench Tests and Pilot-Plant Studies</i>	301
	<i>The Distinction between Molecular Diffusion, Turbulent Diffusion, and Dispersion</i>	245		<i>Reliability Considerations in Process Selection</i>	301
	<i>Plug-Flow Reactor with Axial Dispersion</i>	246	5	Physical Unit Operations	311
	<i>Complete-Mix Reactors in Series</i>	252	5-1	Screening	315
4-6	Reactions, Reaction Rates, and Reaction Rate Coefficients	257		<i>Classification of Screens</i>	315
	<i>Types of Reactions</i>	257		<i>Coarse Screens (Bar Racks)</i>	316
	<i>Rate of Reaction</i>	258		<i>Fine Screens</i>	322
	<i>Reaction Order</i>	259		<i>Microscreens</i>	326
	<i>Types of Rate Expressions</i>	260		<i>Screenings Characteristics and Quantities</i>	327
	<i>Rate Expressions Used in Environmental Modeling</i>	261	5-2	Coarse Solids Reduction	330
	<i>Effects of Temperature on Reaction Rate Coefficients</i>	261		<i>Comminutors</i>	331
	<i>Analysis of Reaction Rate Coefficients</i>	264		<i>Macerators</i>	332
4-7	Modeling Treatment Process Kinetics	269		<i>Grinders</i>	333
	<i>Batch Reactor with Reaction</i>	269		<i>Design Considerations</i>	333
	<i>Complete-Mix Reactor with Reaction</i>	270	5-3	Flow Equalization	333
	<i>Complete-Mix Reactors in Series with Reaction</i>	271		<i>Description/Application</i>	333
	<i>Ideal Plug-Flow Reactor with Reaction</i>	274		<i>Design Considerations</i>	335
	<i>Comparison of Complete-Mix and Plug-Flow Reactors with Reaction</i>	275	5-4	Mixing and Flocculation	344
	<i>Ideal Plug-Flow Reactor with Retarded Reaction</i>	277		<i>Continuous Rapid Mixing in Wastewater Treatment</i>	345
	<i>Plug-Flow Reactor with Axial Dispersion and Reaction</i>	279		<i>Continuous Mixing in Wastewater Treatment</i>	345
	<i>Other Reactor Flow Regimes and Reactor Combinations</i>	281		<i>Energy Dissipation in Mixing and Flocculation</i>	347
4-8	Treatment Processes Involving Mass Transfer	283		<i>Timescale in Mixing</i>	350
	<i>Basic Principle of Mass Transfer</i>	283		<i>Types of Mixers Used for Rapid Mixing in Wastewater Treatment</i>	350
				<i>Types of Mixers Used for Flocculation in Wastewater Treatment</i>	355
				<i>Types of Mixers Used for Continuous Mixing in Wastewater Treatment</i>	359

	<i>New Developments in Mixing Technology</i>	361		<i>Mechanical Aerators</i>	443
5-5	Gravity Separation Theory	361		<i>Energy Requirement for Mixing in Aeration Systems</i>	448
	<i>Description</i>	362		<i>Generation and Dissolution of High-Purity Oxygen</i>	448
	<i>Particle Settling Theory</i>	363		<i>Postaeration</i>	452
	<i>Discrete Particle Settling</i>	367	5-13	Removal of Volatile Organic Compounds (VOCs) by Aeration	456
	<i>Flocculent Particle Settling</i>	372		<i>Emission of VOCs</i>	456
	<i>Inclined Plate and Tube Settling</i>	374		<i>Mass Transfer Rates for VOCs</i>	457
	<i>Hindered (Zone) Settling</i>	378		<i>Mass Transfer of VOCs from Surface and Diffused-Air Aeration Processes</i>	459
	<i>Compression Settling</i>	383		<i>Control Strategies for VOCs</i>	463
	<i>Gravity Separation in an Accelerated Flow Field</i>	383	6	Chemical Unit Processes	475
5-6	Grit Removal	384	6-1	Role of Chemical Unit Processes in Wastewater Treatment	476
	<i>Types of Grit Chambers</i>	385		<i>Application of Chemical Unit Processes</i>	477
	<i>Horizontal-Flow Grit Chambers</i>	385		<i>Considerations in the Use of Chemical Unit Processes</i>	478
	<i>Aerated Grit Chambers</i>	386	6-2	Fundamentals of Chemical Coagulation	478
	<i>Vortex-Type Grit Chambers</i>	392		<i>Basic Definitions</i>	479
	<i>Solids (Sludge) Degritting</i>	392		<i>Nature of Particles in Wastewater</i>	480
	<i>Grit Characteristics, Quantities, Processing, and Disposal</i>	394		<i>Development and Measurement of Surface Charge</i>	481
5-7	Primary Sedimentation	396		<i>Particle-Particle Interactions</i>	482
	<i>Description</i>	397		<i>Particle Destabilization with Potential- Determining Ions and Electrolytes</i>	483
	<i>Sedimentation Tank Performance</i>	405		<i>Particle Destabilization and Aggregation with Polyelectrolytes</i>	485
	<i>Design Considerations</i>	406		<i>Particle Destabilization and Removal with Hydrolyzed Metal Ions</i>	486
	<i>Characteristics and Quantities of Solids (Sludge) and Scum</i>	411	6-3	Chemical Precipitation for Improved Plant Performance	493
5-8	High-Rate Clarification	411		<i>Chemical Reactions in Wastewater Precipitation Applications</i>	493
	<i>Enhanced Particle Flocculation</i>	412		<i>Enhanced Removal of Suspended Solids in Primary Sedimentation</i>	497
	<i>Analysis of Ballasted Particle Flocculation and Settling</i>	412		<i>Independent Physical- Chemical Treatment</i>	498
	<i>Process Application</i>	414		<i>Estimation of Sludge Quantities from Chemical Precipitation</i>	499
5-9	Large-Scale Swirl and Vortex Separators for Combined Wastewater and Stormwater	417	6-4	Chemical Precipitation for Phosphorus Removal	500
5-10	Flotation	419			
	<i>Description</i>	419			
	<i>Design Considerations for Dissolved-Air Flotation Systems</i>	422			
5-11	Oxygen Transfer	425			
	<i>Description</i>	425			
	<i>Evaluation of Oxygen Transfer Coefficient</i>	425			
5-12	Aeration Systems	430			
	<i>Types of Aeration Systems</i>	430			
	<i>Diffused-Air Aeration</i>	430			

	Chemistry of Phosphate Precipitation	501	7-2	Composition and Classification of Microorganisms	555
	Strategies for Phosphorus Removal	503		Cell Components	555
	Phosphorus Removal Using Metal Salts and Polymers	505		Cell Composition	557
	Phosphorus Removal Using Lime	507		Environmental Factors	558
	Phosphorus Removal with Effluent Filtration	508		Microorganism Identification and Classification	559
	Comparison of Chemical Phosphorus Removal Processes	508	7-3	Use of Molecular Tools	561
	Estimation of Sludge Quantities from Phosphorus Precipitation	509		Introduction to Microbial Metabolism	563
6-5	Chemical Precipitation for Removal of Heavy Metals and Dissolved Inorganic Substances	514		Carbon and Energy Sources for Microbial Growth	563
	Precipitation Reactions	514	7-4	Nutrient and Growth Factor Requirements	565
	Coprecipitation with Phosphorus	517		Bacterial Growth and Energetics	565
6-6	Chemical Oxidation	517		Bacterial Reproduction	566
	Fundamentals of Chemical Oxidation	517		Bacterial Growth Patterns in a Batch Reactor	566
	Applications	522		Bacterial Growth and Biomass Yield	567
	Chemical Oxidation of BOD and COD	523		Measuring Biomass Growth	567
	Chemical Oxidation of Ammonia	524		Estimating Biomass Yield and Oxygen Requirements from Stoichiometry	568
6-7	Chemical Neutralization, Scale Control, and Stabilization	526		Estimating Biomass Yield from Bioenergetics	571
	pH Adjustment	526		Stoichiometry of Biological Reactions	578
	Analysis of Scaling Potential	528		Biomass Synthesis Yields for Different Growth Conditions	579
	Scaling Control	532		Observed versus Synthesis Yield	580
	Stabilization	532	7-5	Microbial Growth Kinetics	580
6-8	Chemical Storage, Feeding, Piping, and Control Systems	532		Microbial Growth Kinetics Terminology	581
	Chemical Storage and Handling	533		Rate of Utilization of Soluble Substrates	581
	Dry Chemical-Feed Systems	533		Other Rate Expressions for the Utilization of Soluble Substrate	582
	Liquid Chemical-Feed Systems	536		Rate of Soluble Substrate Production from Biodegradable Particulate Organic Matter	583
	Gas Chemical-Feed Systems	537		Rate of Biomass Growth with Soluble Substrates	584
	Initial Chemical Mixing	540		Kinetic Coefficients for Substrate Utilization and Biomass Growth	584
7	Fundamentals of Biological Treatment	545		Rate of Oxygen Uptake	585
7-1	Overview of Biological Wastewater Treatment	547		Effects of Temperature	585
	Objectives of Biological Treatment	548		Total Volatile Suspended Solids and Active Biomass	586
	Some Useful Definitions	548		Net Biomass Yield and Observed Yield	587
	Role of Microorganisms in Wastewater Treatment	548			
	Types of Biological Processes for Wastewater Treatment	551			

7-6	Modeling Suspended Growth Treatment Processes	588	7-12	Anaerobic Fermentation and Oxidation	629
	<i>Description of Suspended Growth Treatment Processes</i>	589		<i>Process Description</i>	630
	<i>Biomass Mass Balance</i>	589		<i>Microbiology</i>	631
	<i>Substrate Mass Balance</i>	592		<i>Stoichiometry of Anaerobic Fermentation and Oxidation</i>	633
	<i>Mixed Liquor Solids Concentration and Solids Production</i>	592		<i>Growth Kinetics</i>	634
	<i>The Observed Yield</i>	595		<i>Environmental Factors</i>	635
	<i>Oxygen Requirements</i>	595	7-13	Biological Removal of Toxic and Recalcitrant Organic Compounds	635
	<i>Design and Operating Parameters</i>	598		<i>Development of Biological Treatment Methods</i>	635
	<i>Process Performance and Stability</i>	600		<i>Anaerobic Degradation</i>	637
	<i>Modeling Plug-Flow Reactors</i>	601		<i>Aerobic Biodegradation</i>	638
7-7	Substrate Removal in Attached Growth Treatment Processes	602		<i>Abiotic Losses</i>	638
	<i>Substrate Flux in Biofilms</i>	604		<i>Modeling Biotic and Abiotic Losses</i>	640
	<i>Substrate Mass Balance for Biofilm</i>	605	7-14	Biological Removal of Heavy Metals	644
	<i>Substrate Flux Limitations</i>	606			
7-8	Aerobic Biological Oxidation	607	8	Suspended Growth Biological Treatment Processes	659
	<i>Process Description</i>	608			
	<i>Microbiology</i>	608	8-1	Introduction to the Activated-Sludge Process	661
	<i>Stoichiometry of Aerobic Biological Oxidation</i>	609		<i>Historical Development</i>	661
	<i>Growth Kinetics</i>	610		<i>Description of Basic Process</i>	661
	<i>Environmental Factors</i>	610		<i>Evolution of the Activated-Sludge Process</i>	663
7-9	Biological Nitrification	611		<i>Recent Process Developments</i>	664
	<i>Process Description</i>	611	8-2	Wastewater Characterization	666
	<i>Microbiology</i>	611		<i>Key Wastewater Constituents for Process Design</i>	666
	<i>Stoichiometry of Biological Nitrification</i>	612		<i>Measurement Methods for Wastewater Characterization</i>	671
	<i>Growth Kinetics</i>	614		<i>Recycle Flows and Loadings</i>	676
	<i>Environmental Factors</i>	615	8-3	Fundamentals of Process Analysis and Control	676
7-10	Biological Denitrification	616		<i>Process Design Considerations</i>	677
	<i>Process Description</i>	616		<i>Process Control</i>	689
	<i>Microbiology</i>	618		<i>Operational Problems</i>	694
	<i>Stoichiometry of Biological Denitrification</i>	619		<i>Activated-Sludge Selector Processes</i>	700
	<i>Growth Kinetics</i>	621	8-4	Processes for BOD Removal and Nitrification	703
	<i>Environmental Factors</i>	623		<i>Process Design Considerations</i>	704
7-11	Biological Phosphorus Removal	623		<i>Complete-Mix Activated-Sludge Process</i>	705
	<i>Process Description</i>	624		<i>Sequencing Batch Reactor Process</i>	720
	<i>Microbiology</i>	625		<i>Staged Activated-Sludge Process</i>	734
	<i>Stoichiometry of Biological Phosphorus Removal</i>	627			
	<i>Growth Kinetics</i>	629			
	<i>Environmental Factors</i>	629			

	<i>Alternative Processes for BOD Removal and Nitrification</i>	738		<i>Solids Separation</i>	820
	<i>Process Design Parameters</i>	740		<i>Design of Solids Separation Facilities</i>	833
	<i>Process Selection Considerations</i>	740	8-8	<i>Suspended Growth Aerated Lagoons</i>	840
8-5	<i>Processes for Biological Nitrogen Removal</i>	749		<i>Types of Suspended Growth Aerated Lagoons</i>	841
	<i>Overview of Biological Nitrogen-Removal Processes</i>	750		<i>Process Design Considerations for Flow-Through Lagoons</i>	843
	<i>Single-Sludge Biological Nitrogen-Removal Processes</i>	750		<i>Dual-Powered Flow-Through Lagoon System</i>	853
	<i>Process Design Considerations</i>	753	8-9	<i>Biological Treatment with Membrane Separation</i>	854
	<i>Anoxic/Aerobic Process Design</i>	761		<i>Overview of Membrane Biological Reactors</i>	854
	<i>Step-Feed Anoxic/Aerobic Process Design</i>	765		<i>Process Description</i>	855
	<i>Intermittent Aeration Process Design</i>	776		<i>Membrane Fouling Control</i>	857
	<i>Postanoxic Endogenous Denitrification</i>	780		<i>Process Capabilities</i>	858
	<i>Sequencing Batch Reactor Process Analysis</i>	781	8-10	<i>Simulation Design Models</i>	859
	<i>Postanoxic Denitrification with an External Carbon Source</i>	784		<i>Model Matrix Format, Components, and Reactions</i>	860
	<i>Nitrogen Removal in Anaerobic Digestion Recycle Streams</i>	788		<i>Model Applications</i>	861
	<i>Alternative Process Configurations for Biological Nitrogen Removal</i>	789	9	Attached Growth and Combined Biological Treatment Processes	887
	<i>Process Design Parameters</i>	789		9-1 Background	888
	<i>Process Selection Considerations</i>	789		<i>Evolution of Attached Growth Processes</i>	888
8-6	<i>Processes for Biological Phosphorus Removal</i>	799		<i>Mass Transfer Limitations</i>	890
	<i>Biological Phosphorus-Removal Processes</i>	799	9-2	<i>Trickling Filters</i>	890
	<i>Process Design Considerations</i>	801		<i>Trickling Filter Classification and Applications</i>	893
	<i>Process Control</i>	804		<i>Design of Physical Facilities</i>	896
	<i>Solids Separation Facilities</i>	805		<i>Process Design Considerations</i>	909
	<i>Methods to Improve Phosphorus-Removal Efficiency in BPR Systems</i>	805		<i>Nitrification Design</i>	922
	<i>Biological Phosphorus-Removal Process Performance</i>	807	9-3	<i>Rotating Biological Contactors</i>	930
	<i>Alternative Processes for Biological Phosphorous Removal</i>	809		<i>Process Design Considerations</i>	932
	<i>Process Design Parameters</i>	809		<i>Physical Facilities for RBC Process</i>	935
	<i>Process Selection Considerations</i>	809		<i>RBC Process Design</i>	937
8-7	<i>Selection and Design of Physical Facilities for Activated-Sludge Processes</i>	816	9-4	<i>Combined Aerobic Treatment Processes</i>	940
	<i>Aeration System</i>	816		<i>Trickling Filter/Solids Contact and Trickling Filter/Activated-Sludge Processes</i>	940
	<i>Aeration Tanks and Appurtenances</i>	816		<i>Activated Biofilter and Biofilter Activated-Sludge Processes</i>	943
				<i>Series Trickling Filter-Activated-Sludge Process</i>	944

	<i>Design Considerations for Combined Trickling Filter Activated-Sludge Systems</i>	944		<i>Ammonia Toxicity</i>	995
9-5	<i>Activated Sludge with Fixed-Film Packing</i>	952	10-3	<i>Liquid-Solids Separation</i>	996
	<i>Processes with Internal Suspended Packing for Attached Growth</i>	952		<i>Anaerobic Suspended Growth Processes</i>	996
	<i>Processes with Internal Fixed Packing for Attached Growth</i>	955		<i>Complete-Mix Process</i>	997
9-6	<i>Submerged Attached Growth Processes</i>	957		<i>Anaerobic Contact Process</i>	997
	<i>Downflow Submerged Attached Growth Processes</i>	957		<i>Anaerobic Sequencing Batch Reactor</i>	999
	<i>Upflow Submerged Attached Growth Processes</i>	959	10-4	<i>Design of Anaerobic Suspended Growth Processes</i>	999
	<i>Fluidized-Bed Bioreactors (FBBR)</i>	961		<i>Anaerobic Sludge Blanket Processes</i>	1005
9-7	<i>Attached Growth Denitrification Processes</i>	962		<i>Upflow Sludge Blanket Reactor Process</i>	1005
	<i>Downflow Packed-Bed Postanoxic Denitrification Processes</i>	962		<i>Design Considerations for UASB Process</i>	1007
	<i>Upflow Packed-Bed Postanoxic Denitrification Reactors</i>	967		<i>Anaerobic Baffled Reactor</i>	1016
	<i>Fluidized-Bed Reactors for Postanoxic Denitrification</i>	967	10-5	<i>Anaerobic Migrating Blanket Reactor</i>	1017
	<i>Submerged Rotating Biological Contactors</i>	969		<i>Attached Growth Anaerobic Processes</i>	1018
	<i>Attached Growth Preanoxic Denitrification Processes</i>	969		<i>Upflow Packed-Bed Attached Growth Reactor</i>	1019
10	Anaerobic Suspended and Attached Growth Biological Treatment Processes	983		<i>Upflow Attached Growth Anaerobic Expanded-Bed Reactor</i>	1020
10-1	<i>The Rationale for Anaerobic Treatment</i>	984		<i>Attached Growth Anaerobic Fluidized-Bed Reactor</i>	1020
	<i>Advantages of Anaerobic Treatment Processes</i>	984		<i>Downflow Attached Growth Processes</i>	1022
	<i>Disadvantages of Anaerobic Treatment Processes</i>	986	10-6	<i>Other Anaerobic Treatment Processes</i>	1024
	<i>Summary Assessment</i>	986		<i>Covered Anaerobic Lagoon Process</i>	1024
10-2	<i>General Design Considerations for Anaerobic Treatment Processes</i>	986		<i>Membrane Separation Anaerobic Treatment Process</i>	1026
	<i>Characteristics of the Wastewater</i>	987	11	Advanced Wastewater Treatment	1035
	<i>Solids Retention Time</i>	991	11-1	<i>Need for Advanced Wastewater Treatment</i>	1037
	<i>Expected Methane Gas Production</i>	992	11-2	<i>Technologies Used for Advanced Treatment</i>	1038
	<i>Treatment Efficiency Needed</i>	994		<i>Residual Constituents in Treated Wastewater</i>	1038
	<i>Sulfide Production</i>	994		<i>Classification of Technologies</i>	1038
				<i>Removal of Organic and Inorganic Colloidal and Suspended Solids</i>	1038
				<i>Removal of Dissolved Organic Constituents</i>	1040
				<i>Removal of Dissolved Inorganic Constituents</i>	1041
				<i>Removal of Biological Constituents</i>	1043
				<i>Process Selection and Performance Data</i>	1044

11-3	Introduction to Depth Filtration	1044		<i>Analysis and Design of Granular</i>	
	<i>Description of the Filtration Process</i>	1044		<i>Activated Carbon Contactor</i>	1152
	<i>Filter Hydraulics</i>	1050		<i>Small-Scale Column Tests</i>	1156
	<i>Analysis of the Filtration Process</i>	1057		<i>Analysis and Design of Powdered</i>	
11-4	Selection and Design Considerations			<i>Activated Carbon Contactor</i>	1159
	for Depth Filters	1069		<i>Activated Sludge with Powdered</i>	
	<i>Available Filtration Technologies</i>	1069		<i>Activated Carbon Treatment</i>	1161
	<i>Performance of Different Types of</i>		11-8	Gas Stripping	1162
	<i>Filter Technologies</i>	1078		<i>Analysis of Gas Stripping</i>	1163
	<i>Issues Related to Design and</i>			<i>Design of Stripping Towers</i>	1174
	<i>Operation of Treatment Facilities</i>	1080		<i>Application</i>	1178
	<i>Importance of Influent</i>		11-9	Ion Exchange	1180
	<i>Wastewater Characteristics</i>	1081		<i>Ion-Exchange Materials</i>	1181
	<i>Selection of Filtration Technology</i>	1081		<i>Typical Ion-Exchange Reactions</i>	1182
	<i>Filter-Bed Characteristics</i>	1084		<i>Exchange Capacity of</i>	
	<i>Filter Flowrate Control</i>	1089		<i>Ion-Exchange Resins</i>	1183
	<i>Filter Backwashing Systems</i>	1091		<i>Ion-Exchange Chemistry</i>	1185
	<i>Filter Appurtenances</i>	1093		<i>Application of Ion Exchange</i>	1189
	<i>Filter Instrumentation and</i>			<i>Operational Considerations</i>	1196
	<i>Control Systems</i>	1093	11-10	Advanced Oxidation Processes	1196
	<i>Effluent Filtration with</i>			<i>Theory of Advanced Oxidation</i>	1196
	<i>Chemical Addition</i>	1095		<i>Technologies Used to Produce</i>	
	<i>Filter Problems</i>	1096		<i>Hydroxyl Radicals (HO[•])</i>	1197
	<i>Need for Pilot-Plant Studies</i>	1096		<i>Applications</i>	1200
11-5	Surface Filtration	1098		<i>Operational Problems</i>	1202
	<i>Discfilter®</i>	1098	11-11	Distillation	1202
	<i>Cloth-Media Disk Filter®</i>	1100		<i>Distillation Processes</i>	1202
	<i>Performance Characteristics</i>	1103		<i>Performance Expectations in</i>	
11-6	Membrane Filtration Processes	1104		<i>Reclamation Applications</i>	1204
	<i>Membrane Process Terminology</i>	1104		<i>Operating Problems</i>	1205
	<i>Membrane Process Classification</i>	1104		<i>Disposal of Concentrated Waste</i>	1205
	<i>Membrane Configurations</i>	1108			
	<i>Membrane Operation</i>	1111	12	Disinfection Processes	1217
	<i>Membrane Fouling</i>	1117	12-1	Regulatory Requirements for	
	<i>Application of Membranes</i>	1121		Wastewater Disinfection	1219
	<i>Electrodialysis</i>	1131	12-2	Disinfection Theory	1219
	<i>Pilot Studies for</i>			<i>Characteristics of</i>	
	<i>Membrane Applications</i>	1134		<i>an Ideal Disinfectant</i>	1220
	<i>Disposal of Concentrated</i>			<i>Disinfection Methods and Means</i>	1220
	<i>Waste Streams</i>	1135		<i>Mechanisms of Disinfectants</i>	1223
11-7	Adsorption	1138		<i>Factors Influencing the Action</i>	
	<i>Types of Adsorbents</i>	1138		<i>of Disinfectants</i>	1223
	<i>Fundamentals of Adsorption</i>	1140	12-3	Disinfection with Chlorine	1231
	<i>Activated Carbon Adsorption Kinetics</i>	1146		<i>Characteristics of Chlorine Compounds</i>	1231
	<i>Activated Carbon Treatment</i>			<i>Chemistry of Chlorine Compounds</i>	1234
	<i>Process Applications</i>	1149			

	<i>Breakpoint Reaction with Chlorine</i>	1237		<i>Effectiveness of Ozone as a Disinfectant</i>	1290
	<i>Measurement and Reporting of Disinfection Process Variables</i>	1241		<i>Modeling the Ozone Disinfection Process</i>	1290
	<i>Germicidal Efficiency of Chlorine and Various Chlorine Compounds</i>	1242		<i>Required Ozone Dosages for Disinfection</i>	1293
	<i>Factors That Affect Disinfection Efficiency of Chlorine</i>	1244		<i>Byproduct Formation and Control</i>	1293
	<i>Modeling the Chlorine Disinfection Process</i>	1248		<i>Environmental Impacts of Using Ozone</i>	1295
	<i>Review of the C_Rt Concept</i>	1252		<i>Other Benefits of Using Ozone</i>	1295
	<i>Required Chlorine Dosage for Disinfection</i>	1252	12-8	<i>Other Chemical Disinfection Methods</i>	1295
	<i>Formation and Control of Disinfection Byproducts</i>	1255		<i>Peracetic Acid</i>	1295
	<i>Environmental Impacts</i>	1257		<i>Ozone/Hydrogen Peroxide (Peroxone) Combined Chemical Disinfection Processes</i>	1297
12-4	<i>Disinfection with Chlorine Dioxide</i>	1258	12-9	<i>Ultraviolet (UV) Radiation Disinfection</i>	1298
	<i>Characteristics of Chlorine Dioxide</i>	1258		<i>Source of UV Radiation</i>	1298
	<i>Chlorine Dioxide Chemistry</i>	1259		<i>UV Disinfection System Components and Configurations</i>	1301
	<i>Effectiveness of Chlorine Dioxide as a Disinfectant</i>	1259		<i>Germicidal Effectiveness of UV Radiation</i>	1304
	<i>Byproduct Formation and Control</i>	1260		<i>Modeling the UV Disinfection Process</i>	1309
	<i>Environmental Impacts</i>	1261		<i>Estimating UV Dose</i>	1311
12-5	<i>Dechlorination</i>	1261		<i>Ultraviolet Disinfection Guidelines</i>	1316
	<i>Need for Dechlorination</i>	1261		<i>Selection and Sizing of a UV Disinfection System</i>	1324
	<i>Dechlorination of Wastewater Treated with Chlorine and Chlorine Compounds</i>	1261		<i>Troubleshooting UV Disinfection Systems</i>	1326
	<i>Dechlorination of Chlorine Dioxide with Sulfur Dioxide</i>	1264		<i>Environmental Impacts of UV Radiation Disinfection</i>	1329
12-6	<i>Design of Chlorination and Dechlorination Facilities</i>	1264	12-10	<i>Comparison of Alternative Disinfection Technologies</i>	1329
	<i>Sizing Chlorination Facilities</i>	1264		<i>Germicidal Effectiveness</i>	1330
	<i>Application Flow Diagrams</i>	1266		<i>Advantages and Disadvantages</i>	1330
	<i>Dosage Control</i>	1269			
	<i>Injection and Initial Mixing</i>	1270	13	Water Reuse	1345
	<i>Chlorine Contact Basin Design</i>	1270		<i>Wastewater Reclamation and Reuse: An Introduction</i>	1347
	<i>Chlorine Residual Measurement</i>	1283		<i>Definition of Terms</i>	1347
	<i>Chlorine Storage Facilities</i>	1284		<i>The Role of Water Recycling in the Hydrologic Cycle</i>	1347
	<i>Chlorine Containment Facilities</i>	1284		<i>Historical Perspective</i>	1349
	<i>Dechlorination Facilities</i>	1286		<i>Wastewater Reuse Applications</i>	1351
12-7	<i>Disinfection with Ozone</i>	1286	13-1	<i>Need for Water Reuse</i>	1354
	<i>Ozone Properties</i>	1287			
	<i>Ozone Chemistry</i>	1287			
	<i>Ozone Disinfection Systems Components</i>	1288			

13-2	Public Health and Environmental Issues in Water Reuse	1356		<i>Water and Salt Balances in Cooling Tower</i>	1414
	<i>Constituents in Reclaimed Water</i>	1356		<i>Common Water Quality Problems in Cooling Tower Systems</i>	1416
	<i>Public Health Issues</i>	1358			
	<i>Environmental Issues</i>	1358	13-8	Groundwater Recharge with Reclaimed Water	1422
	<i>The Evolution of Water Reuse Guidelines in the United States</i>	1358		<i>Groundwater Recharge Methods Pretreatment Requirements for Groundwater Recharge</i>	1426
	<i>Water Reclamation Criteria in Other Countries</i>	1362		<i>Fate of Contaminants in Groundwater Groundwater Recharge Guidelines</i>	1427
	<i>What Level of Treatment Is Necessary?</i>	1365			1429
13-3	Introduction to Risk Assessment	1366	13-9	Planned Indirect and Direct Potable Water Reuse	1429
	<i>Risk Assessment</i>	1366		<i>Planned Indirect Potable Water Reuse</i>	1431
	<i>Risk Management</i>	1372		<i>Planned Direct Potable Water Reuse</i>	1432
	<i>Ecological Risk Assessment</i>	1373		<i>Planned Potable Water Reuse Criteria</i>	1432
	<i>Risk Assessment for Water Reuse</i>	1373		<i>What Is the Ultimate Water Reuse Goal?</i>	1433
	<i>Limitations in Risk Assessment for Water Reuse</i>	1374	13-10	Planning for Wastewater Reclamation and Reuse	1433
13-4	Water Reclamation Technologies	1376		<i>Planning Basis</i>	1433
	<i>Constituent Removal Technologies</i>	1376		<i>Market Assessment</i>	1434
	<i>Conventional Wastewater Treatment Process Flow Diagrams for Water Reclamation</i>	1377		<i>Monetary Analyses</i>	1435
	<i>Advanced Wastewater Treatment Process Flow Diagrams</i>	1379		<i>Other Planning Factors</i>	1436
	<i>Performance Expectations for Water Reclamation Processes</i>	1379		<i>Planning Report</i>	1437
	<i>Predicting the Performance of Treatment Process Combinations</i>	1387	13-11	Epilogue on Water Reuse Issues	1438
	<i>Treatment Process Reliability</i>	1391			
13-5	Storage of Reclaimed Water	1391	14	Treatment, Reuse, and Disposal of Solids and Biosolids	1447
	<i>Need for Storage</i>	1392			
	<i>Meeting Water Quality Discharge Requirements</i>	1392	14-1	Solids Sources, Characteristics, and Quantities	1451
	<i>Operation of Storage Reservoirs</i>	1393		<i>Sources</i>	1451
	<i>Problems Involved with Storage of Reclaimed Water</i>	1397		<i>Characteristics</i>	1451
	<i>Management Strategies for Open and Enclosed Reservoirs</i>	1399		<i>Quantities</i>	1454
13-6	Agricultural and Landscape Irrigation	1401	14-2	Regulations for the Reuse and Disposal of Solids in the United States	1460
	<i>Evaluation of Irrigation Water Quality</i>	1401		<i>Land Application</i>	1461
	<i>Other Problems</i>	1410		<i>Surface Disposal</i>	1461
13-7	Industrial Water Reuse	1412		<i>Pathogen and Vector Attraction Reduction</i>	1461
	<i>Industrial Water Use</i>	1413		<i>Incineration</i>	1464
	<i>Cooling Tower Makeup Water</i>	1413	14-3	Solids Processing Flow Diagrams	1465

14-4	Sludge and Scum Pumping	1465		<i>Cocomposting with Municipal Solid Wastes</i>	1551
	<i>Pumps</i>	1465		<i>Public Health and Environmental Issues</i>	1554
	<i>Headloss Determination</i>	1475	14-12	Conditioning	1554
	<i>Sludge Piping</i>	1481		<i>Chemical Conditioning</i>	1555
14-5	Preliminary Operations	1482		<i>Other Conditioning Methods</i>	1557
	<i>Grinding</i>	1482	14-13	Dewatering	1558
	<i>Screening</i>	1482		<i>Centrifugation</i>	1559
	<i>Degritting</i>	1484		<i>Belt-Filter Press</i>	1563
	<i>Blending</i>	1484		<i>Filter Presses</i>	1565
	<i>Storage</i>	1485		<i>Sludge Drying Beds</i>	1570
14-6	Thickening	1488		<i>Reed Beds</i>	1578
	<i>Application</i>	1488		<i>Lagoons</i>	1578
	<i>Description and Design of Thickeners</i>	1489	14-14	Heat Drying	1579
14-7	Introduction to Stabilization	1499		<i>Heat-Transfer Methods</i>	1579
14-8	Alkaline Stabilization	1500		<i>Process Description</i>	1580
	<i>Chemical Reactions in Lime Stabilization</i>	1500		<i>Product Characteristics</i>	1584
	<i>Heat Generation</i>	1502		<i>Product Transport and Storage</i>	1585
	<i>Application of Alkaline Stabilization Processes</i>	1502		<i>Fire and Explosion Hazards</i>	1585
				<i>Air Pollution and Odor Control</i>	1585
14-9	Anaerobic Digestion	1505	14-15	Incineration	1586
	<i>Process Fundamentals</i>	1506		<i>Fundamental Aspects of Complete Combustion</i>	1587
	<i>Description of Mesophilic Anaerobic Digestion Processes</i>	1507		<i>Multiple-Hearth Incineration</i>	1588
	<i>Process Design for Mesophilic Anaerobic Digestion</i>	1509		<i>Fluidized-Bed Incineration</i>	1590
	<i>Selection of Tank Design and Mixing System</i>	1516		<i>Coincineration with Municipal Solid Waste</i>	1592
	<i>Methods for Enhancing Solids Loading and Digester Performance</i>	1522		<i>Air-Pollution Control</i>	1592
	<i>Gas Production, Collection, and Use</i>	1523	14-16	Solids Mass Balances	1592
	<i>Digester Heating</i>	1525		<i>Preparation of Solids Mass Balances</i>	1593
	<i>Thermophilic Anaerobic Digestion</i>	1529		<i>Performance Data for Solids-Processing Facilities</i>	1593
	<i>Two-Phased Anaerobic Digestion</i>	1531		<i>Impact of Return Flows and Loads</i>	1594
14-10	Aerobic Digestion	1533	14-17	Application of Biosolids to Land	1608
	<i>Process Description</i>	1534		<i>Site Evaluation and Selection</i>	1609
	<i>Conventional Air Aerobic Digestion</i>	1535		<i>U.S. EPA Regulations for Beneficial Use and Disposal of Biosolids</i>	1610
	<i>Dual Digestion</i>	1541		<i>Design Loading Rates</i>	1613
	<i>Autothermal Thermophilic Aerobic Digestion (ATAD)</i>	1541		<i>Application Methods</i>	1617
	<i>High-Purity Oxygen Digestion</i>	1545		<i>Application to Dedicated Lands</i>	1619
14-11	Composting	1546		<i>Landfilling</i>	1621
	<i>Process Microbiology</i>	1547	14-18	Biosolids Conveyance and Storage	1621
	<i>Process Description</i>	1547		<i>Conveyance Methods</i>	1622
	<i>Design Considerations</i>	1550		<i>Storage</i>	1622

15	Issues Related to Treatment-Plant Performance	1633	15-6	Upgrading Wastewater Treatment-Plant Performance	1708
15-1	Need for Upgrading Treatment-Plant Performance	1634		<i>Process Optimization</i>	1708
	<i>Meeting Current and Future Needs</i>	1634		<i>Upgrading Existing Wastewater Treatment Facilities</i>	1712
	<i>Meeting More Stringent Discharge Requirements</i>	1635	15-7	Important Design Considerations for New Wastewater Treatment Plants	1721
	<i>Discharge Limits for Wastewater Treatment Plants</i>	1635		<i>Process Design Considerations for Liquid Streams</i>	1721
15-2	Treatment Process Reliability and Selection of Design Values	1636		<i>Process Design Considerations for Solids Processing</i>	1721
	<i>Variability in Wastewater Treatment</i>	1636		<i>Odor Control</i>	1723
	<i>Selection of Process Design Parameters to Meet Discharge Permit Limits</i>	1640			
	<i>Performance of Combined Processes</i>	1647			
	<i>Development of Input-Output Data</i>	1649			
15-3	Odor Management	1650			
	<i>Types of Odors</i>	1650			
	<i>Sources of Odors</i>	1650			
	<i>Movement of Odors from Wastewater Treatment Facilities</i>	1654			
	<i>Strategies for Odor Management</i>	1654			
	<i>Odor-Treatment Methods</i>	1658			
	<i>Selection and Design of Odor-Control Facilities</i>	1668			
	<i>Design Considerations for Chemical Scrubbers</i>	1668			
	<i>Design Considerations for Odor-Control Biofilters</i>	1670			
15-4	Introduction to Automatic Process Control	1677			
	<i>Process Disturbances</i>	1678			
	<i>Control Systems for Wastewater Treatment Plants</i>	1679			
	<i>Control Algorithms</i>	1682			
	<i>Process Control Diagrams</i>	1690			
	<i>Description of Automatic Control System Elements</i>	1693			
15-5	Energy Efficiency in Wastewater Treatment	1703			
	<i>Overview of the Use of Electricity in Wastewater Treatment</i>	1704			
	<i>Measures for Improving Energy Efficiency</i>	1705			

Appendixes

A	Conversion Factors	1729
B	Physical Properties of Selected Gases and the Composition of Air	1737
C	Physical Properties of Water	1741
D	Solubility of Dissolved Oxygen in Water as a Function of Salinity and Barometric Pressure	1745
E	MPN Tables and Their Use	1749
F	Carbonate Equilibrium	1753
G	Moody Diagrams for the Analysis of Flow in Pipes	1757

Indexes

Name Index	1759
Subject Index	1771

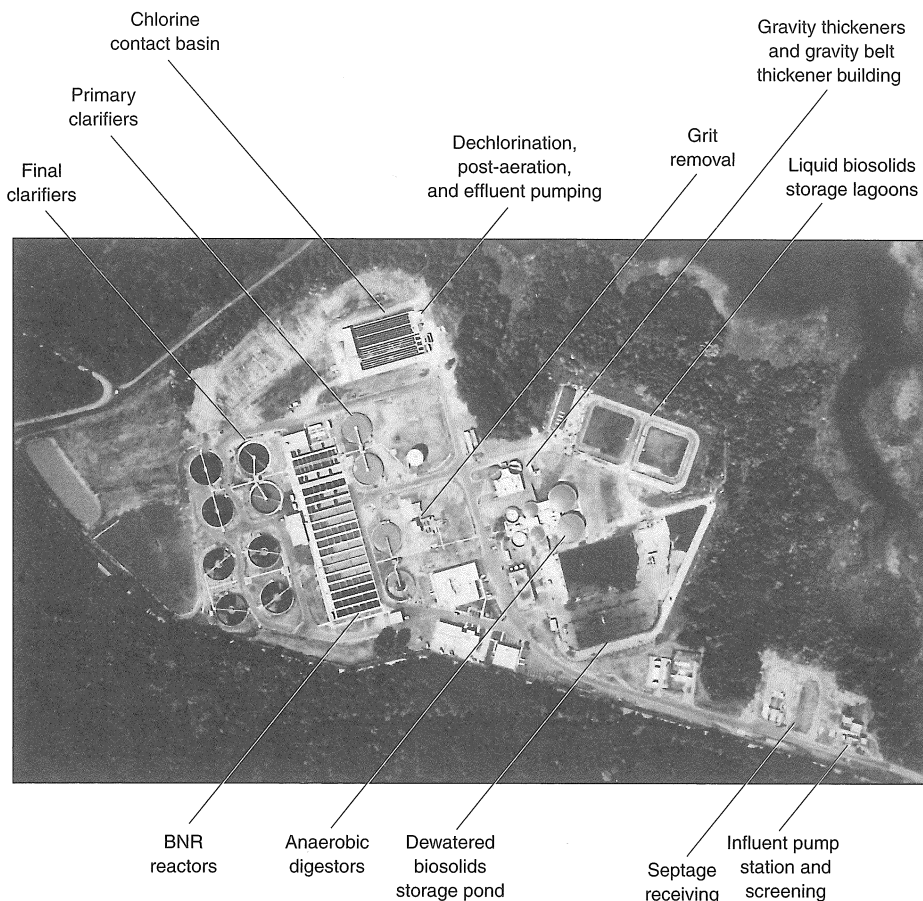
	Complete-Mix Reactor with Reaction	270
	Complete-Mix Reactors in Series with Reaction	271
	Ideal Plug-Flow Reactor with Reaction	274
	Comparison of Complete-Mix and Plug-Flow Reactors with Reaction	275
	Ideal Plug-Flow Reactor with Retarded Reaction	277
	Plug-Flow Reactor with Axial Dispersion and Reaction	279
	Other Reactor Flow Regimes and Reactor Combinations	281
4-8	TREATMENT PROCESSES INVOLVING MASS TRANSFER	283
	Basic Principle of Mass Transfer	283
	Gas-Liquid Mass Transfer	284
	Liquid-Solid Mass Transfer	293
4-9	INTRODUCTION TO PROCESS SELECTION	297
	Important Factors in Process Selection	297
	Process Selection Based on Reaction Kinetics	299
	Process Selection Based on Mass Transfer	300
	Process Design Based on Loading Criteria	301
	Bench Tests and Pilot-Plant Studies	301
	Reliability Considerations in Process Selection	301
	PROBLEMS AND DISCUSSION TOPICS	303
	REFERENCES	308

The constituents of concern found in wastewater are removed by physical, chemical, and biological methods. The individual methods usually are classified as physical unit operations, chemical unit processes, and biological unit processes. Treatment methods in which the application of physical forces predominate are known as *physical unit operations*. Examples of physical unit operations include screening, mixing, sedimentation, gas transfer, filtration, and adsorption. Treatment methods in which the removal or conversion of constituents is brought about by the addition of chemicals or by other chemical reactions are known as *chemical unit processes*. Examples of chemical unit processes include disinfection, oxidation, and precipitation. Treatment methods in which the removal of constituents is brought about by biological activity are known as *biological unit processes*. Biological treatment is used primarily to remove the biodegradable organic constituents and nutrients in wastewater. Examples of biological treatment processes include the activated-sludge and trickling-filter processes. Unit operations and processes occur in a variety of combinations in treatment flow diagrams.

From practical observations, the rates at which physical, chemical, and biological reactions and conversions occur are important, as they will affect the size of the treatment facilities that must be provided (see Fig. 4-1). The rate at which reactions and conversions occur, and the degree of their completion, is generally a function of the constituents involved, the temperature, and the type of reactor (i.e., container or tank in which the reactions take place). Hence, both the effects of temperature and the type of

Figure 4-1

Overview of Harford County, MD, Sod Run biological nutrient removal (BNR) wastewater-treatment plant. The capacity of the plant is $76,000 \text{ m}^3/\text{d}$ (20 Mgal/d).



reactor employed are important in the selection of treatment processes. In addition, a variety of environmental and other physical constraints must be considered in process selection. The fundamental basis for the analysis of the physical, chemical, and biological unit operations and processes used for wastewater treatment is the *materials mass balance principle* in which an accounting of mass is made before and after reactions and conversions have taken place.

Therefore, the purpose of this chapter is to introduce and discuss (1) the types of reactors used for wastewater treatment; (2) the preparation of mass balances to determine process performance; (3) modeling ideal flow in reactors; (4) the analysis of reactor hydraulics using tracers; (5) modeling nonideal flow in reactors; (6) reactions, reaction rates, and reaction rate coefficients; (7) modeling treatment kinetics, which involves the coupling of reactors and reaction rates; (8) treatment processes involving mass transfer; and (9) important factors involved in process analysis and selection. The information in this chapter is intended to serve as an introduction to the subject of process analysis, and to provide a basis for the analysis of the unit operations and processes that will be presented in subsequent chapters. By dealing with the basic concepts first, it will be possible to apply them (without repeating the details) in the remaining chapters. Processes

Operations used for the treatment of wastewater in which change is brought about by means of or through the application of physical forces are known as *physical unit operations*. Because physical unit operations were derived originally from observations of the physical world, they were the first treatment methods to be used. Today, physical unit operations, as shown on Fig. 5-1, are a major part of most wastewater-treatment systems.

The unit operations most commonly used in wastewater treatment include (1) screening, (2) coarse solids reduction (comminution, maceration, and screenings grinding), (3) flow equalization, (4) mixing and flocculation, (5) grit removal, (6) sedimentation, (7) high-rate clarification, (8) accelerated gravity separation (vortex separators), (9) flotation, (10) oxygen transfer, (11) aeration, and (12) volatilization and stripping of volatile organic compounds (VOCs). The principal applications of these operations and treatment devices used are summarized in Table 5-1. Physical unit operations that apply to advanced wastewater-treatment systems such as packed-bed filters, membrane separation systems, and ammonia stripping are discussed separately in Chap. 11. Unit operations associated with the processing of solids and biosolids (sludge) are covered in Chap. 14.

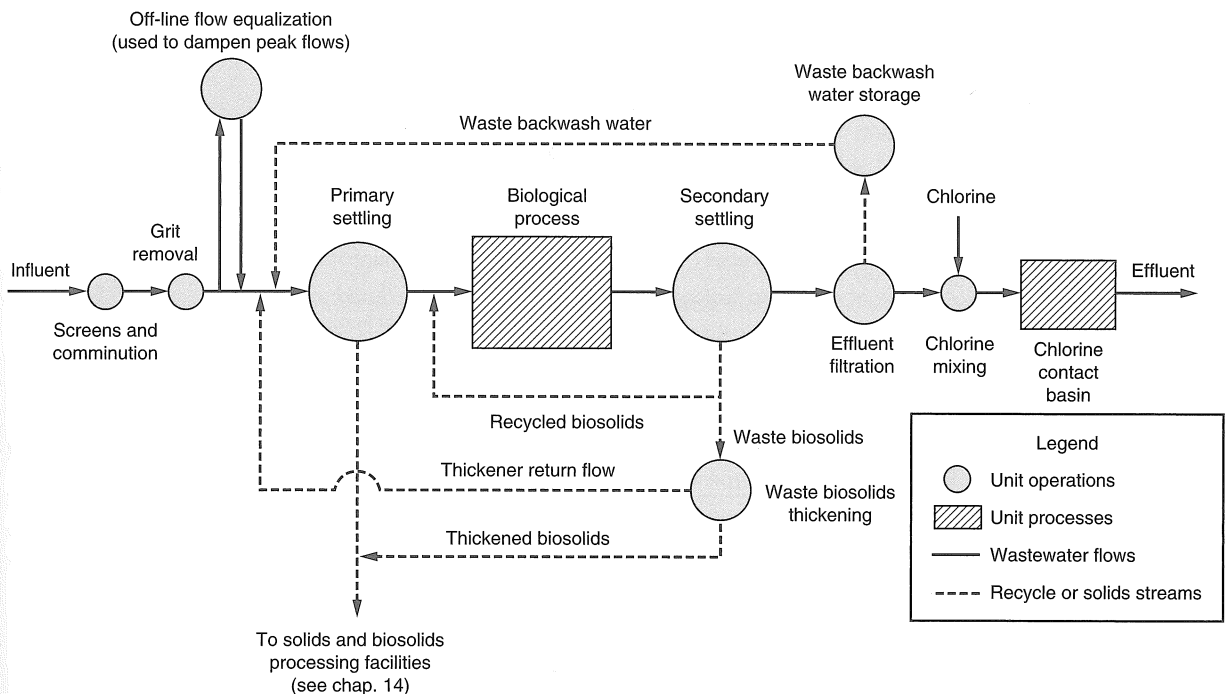


Figure 5-1

Location of physical unit operations in a wastewater-treatment plant flow diagram.

Table 5-1

Typical physical unit operations used for wastewater treatment

Operation	Application	Device	See section
Screening, coarse	Removal of coarse solids such as sticks, rags, and other debris in untreated wastewater by interception (surface straining)	Bar rack	5-1
Screening, fine	Removal of small particles	Fine screen	5-1
Screening, micro	Removal of fine solids, floatable matter, and algae	Microscreen	5-1, 11-5
Comminution	In-stream grinding of coarse solids to reduce size	Comminutor	5-2
Grinding/ maceration	Grinding of solids removed by bar racks	Screenings grinder	5-2
	Side-stream grinding of coarse solids	Macerator	5-2
Flow equalization	Temporary storage of flow to equalize flowrates and mass loadings of BOD and suspended solids	Equalization tank	5-3
Mixing	Blending chemicals with wastewater and for homogenizing and maintaining solids in suspension	Rapid mixer	5-4
Flocculation	Promoting the aggregation of small particles into larger particles to enhance their removal by gravity sedimentation	Flocculator	5-4
Accelerated sedimentation	Removal of grit	Grit chamber	5-6
	Removal of grit and coarse solids	Vortex separator	5-9
Sedimentation	Removal of settleable solids	Primary clarifier	5-7
		High-rate clarifier	5-8
	Thickening of solids and biosolids	Gravity thickener	14-6
Flotation	Removal of finely divided suspended solids and particles with densities close to that of water; also thickens biosolids	Dissolved-air flotation (DAF)	5-10 14-6
	Removal of oil and grease	Induced-air flotation	5-10
Aeration	Addition of oxygen to biological process	Diffused-air aeration	5-12
		Mechanical aerator	5-12
	Postaeration of treated effluent	Cascade aerator	5-12
VOC control	Removal of volatile and semivolatile organic compounds from wastewaters	Gas stripper	5-13
		Diffused-air and mechanical aeration	5-12, 5-13
Depth filtration	Removal of residual suspended solids	Depth filters	11-4
Surface filtration	Removal of residual suspended solids	Discfilter®	11-5
		Cloth-Media Disk Filter®	
Membrane filtration	Removal of suspended and colloidal solids and dissolved organic and inorganic matter	Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis	11-6
Air stripping	Removal of ammonia, hydrogen sulfide, and other gases from wastewater and digester supernatant	Packed tower	11-8

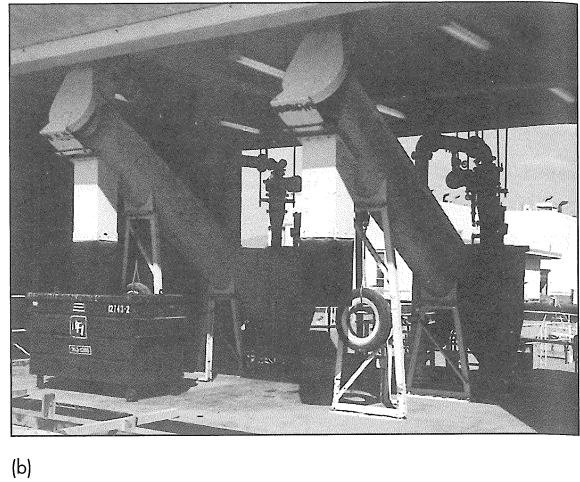
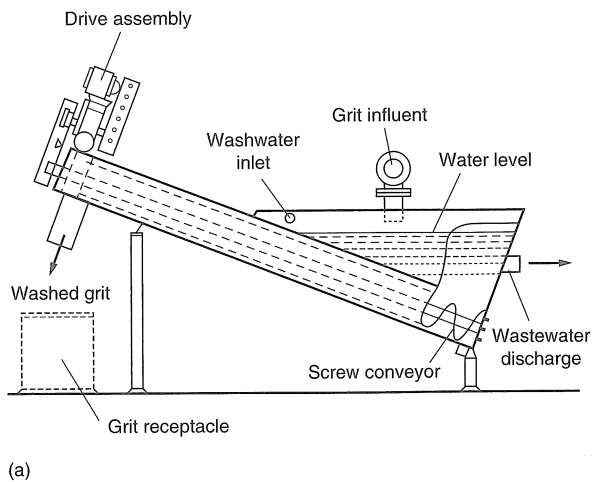


Figure 5-38

Example of grit separation and washing unit: (a) schematic and (b) view of typical installation.

the storage hoppers, by applying air beneath the grit, and by the use of hopper vibrators. Drainage facilities for collection and disposal of drippings from the bottom-loading gates are desirable. Grab buckets operating on a monorail system may also be used to load trucks directly from the grit chambers.

Pneumatic conveyors are sometimes used to convey grit short distances. Advantages of pneumatic conveying include (1) no elevated storage hoppers are required, and (2) attendant odor problems associated with storage are eliminated. The principal disadvantage is the considerable wear on piping, especially at bends.

5-7 PRIMARY SEDIMENTATION

The objective of treatment by sedimentation is to remove readily settleable solids and floating material and thus reduce the suspended solids content. Primary sedimentation is used as a preliminary step in the further processing of the wastewater. Efficiently designed and operated primary sedimentation tanks should remove from 50 to 70 percent of the suspended solids and from 25 to 40 percent of the BOD.

Sedimentation tanks have also been used as stormwater retention tanks, which are designed to provide a moderate detention period (10 to 30 min) for overflows from either combined sewers or storm sewers. The purpose of sedimentation is to remove a substantial portion of the organic solids that otherwise would be discharged directly to the receiving waters. Sedimentation tanks have also been used to provide detention periods sufficient for effective disinfection of such overflows.

The purpose of this section is to describe the various types of sedimentation facilities, to consider their performance, and to review important design considerations. Sedimentation tanks used for secondary treatment are considered in Chap. 8.

Description

Almost all treatment plants use mechanically cleaned sedimentation tanks of standardized circular or rectangular design (see Fig. 5-39). The selection of the type of sedimentation unit for a given application is governed by the size of the installation, by rules and regulations of local control authorities, by local site conditions, and by the experience and judgment of the engineer. Two or more tanks should be provided so that the process may remain in operation while one tank is out of service for maintenance and repair work. At large plants, the number of tanks is determined largely by size limitations. Typical design information and dimensions for rectangular and circular sedimentation tanks used for primary treatment are presented in Tables 5-20 and 5-21.

Rectangular Tanks. Rectangular sedimentation tanks may use either chain-and-flight solids collectors or traveling-bridge-type collectors. A rectangular tank that uses a chain-and-flight-type collector is shown on Fig. 5-40. Equipment for settled solids removal generally consists of a pair of endless conveyor chains, manufactured of alloy steel, cast iron, or thermoplastic. Attached to the chains at approximately 3-m (10-ft) intervals are scraper flights made of wood or fiberglass, extending the full width of the tank or bay. The solids settling in the tank are scraped to solids hoppers in small tanks and to transverse troughs in large tanks. The transverse troughs are equipped with collecting mechanisms (cross collectors), usually either chain-and-flight or screw-type collectors, which convey solids to one or more collection hoppers. In very long units (over 50 m), two collection mechanisms can be used to scrape solids to collection points near the middle of the tank length. Where possible, it is desirable to locate solids pumping facilities close to the collection hoppers.

Rectangular tanks may also be cleaned by a bridge-type mechanism that travels up and down the tank on rubber wheels or on rails supported on the sidewalls. One or more scraper blades are suspended from the bridge. Some of the bridge mechanisms are designed so that the scraper blades can be lifted clear of the solids blanket on the return travel.

Figure 5-39

Aerial view of wastewater-treatment plant with circular primary and secondary sedimentation basins. (Photo courtesy F. Wayne Hill Water Resources Center, Gwinnett County, GA.)

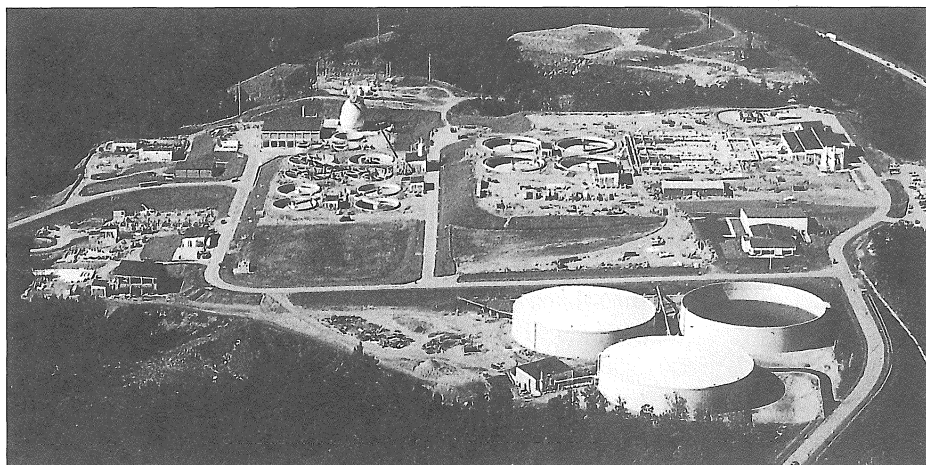


Table 5-20
Typical design information for primary sedimentation tanks^a

Item	U.S. customary units			SI units		
	Unit	Range	Typical	Unit	Range	Typical
Primary sedimentation tanks followed by secondary treatment						
Detention time	h	1.5–2.5	2.0	h	1.5–2.5	2.0
Overflow rate						
Average flow	gal/ft ² ·d	800–1200	1000	m ³ /m ² ·d	30–50	40
Peak hourly flow	gal/ft ² ·d	2000–3000	2500	m ³ /m ² ·d	80–120	100
Weir loading	gal/ft·d	10,000–40,000	20,000	m ³ /m·d	125–500	250
Primary settling with waste activated-sludge return						
Detention time	h	1.5–2.5	2.0	h	1.5–2.5	2.0
Overflow rate						
Average flow	gal/ft ² ·d	600–800	700	m ³ /m ² ·d	24–32	28
Peak hourly flow	gal/ft ² ·d	1200–1700	1500	m ³ /m ² ·d	48–70	60
Weir loading	gal/ft·d	10,000–40,000	20,000	m ³ /m·d	125–500	250

^aComparable data for secondary clarifiers are presented in Chap. 8.

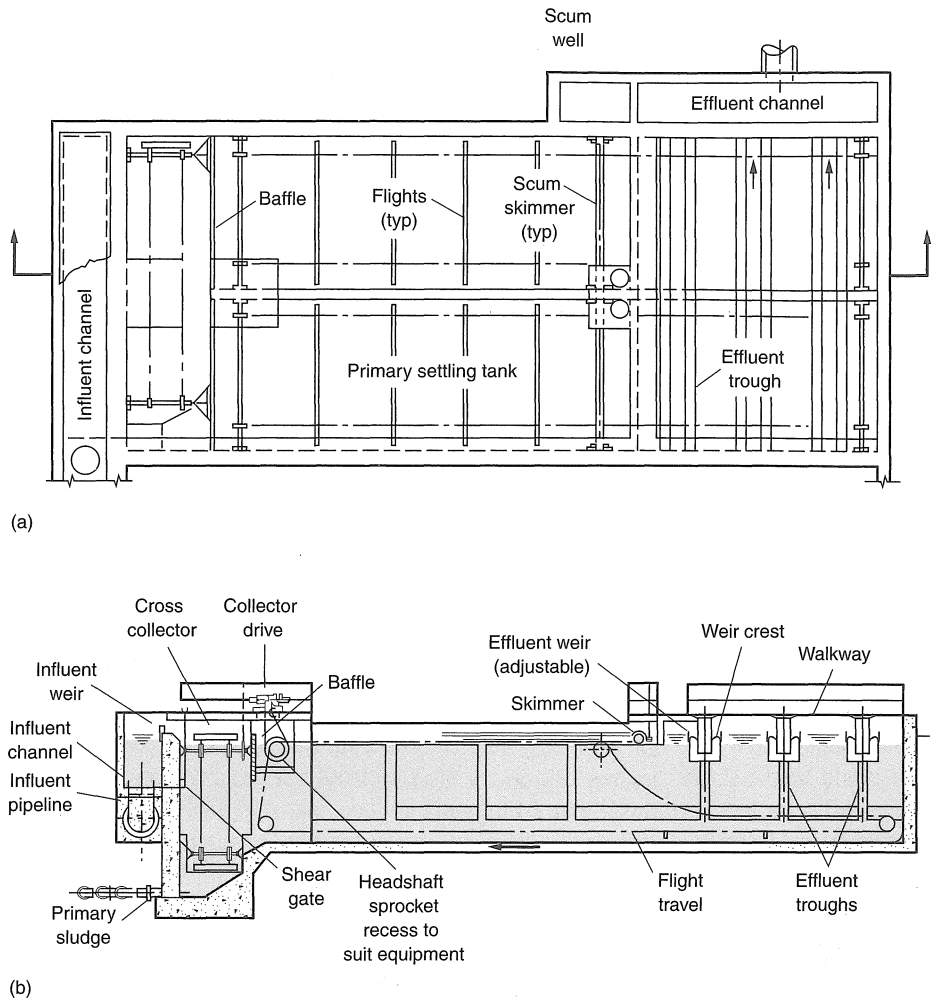
Table 5-21
Typical dimensional data for rectangular and circular sedimentation tanks used for primary treatment of wastewater

Item	U.S. customary units			SI units		
	Unit	Range	Typical	Unit	Range	Typical
Rectangular:						
Depth	ft	10–16	14	m	3–4.9	4.3
Length	ft	50–300	80–130	m	15–90	24–40
Width ^a	ft	10–80	16–32	m	3–24	4.9–9.8
Flight speed	ft/min	2–4	3	m/min	0.6–1.2	0.9
Circular:						
Depth	ft	10–16	14	m	3–4.9	4.3
Diameter	ft	10–200	40–150	m	3–60	12–45
Bottom slope	in/ft	3/4–2/ft	1.0/ft	mm/mm	1/16–1/6	1/12
Flight speed	r/min	0.02–0.05	0.03	r/min	0.02–0.05	0.03

^aIf widths of rectangular mechanically cleaned tanks are greater than 6 m (20 ft), multiple bays with individual cleaning equipment may be used, thus permitting tank widths up to 24 m (80 ft) or more.

Figure 5-40

Typical rectangular primary sedimentation tank: (a) plan and (b) section.



Where cross collectors are not provided, multiple solids hoppers must be installed. Solids hoppers have operating difficulties, notably solids accumulation on the slopes and in the corners and arching over the solids drawoff piping. Wastewater may also be drawn through the solids hopper, bypassing some of the accumulated solids, resulting in a "rathole" effect. A cross collector is more advisable, except possibly in small plants, because a more uniform and concentrated solids can be withdrawn and many of the problems associated with solids hoppers can be eliminated.

Because flow distribution in rectangular tanks is critical, one of the following inlet designs is used: (1) full-width inlet channels with inlet weirs, (2) inlet channels with submerged ports or orifices, (3) or inlet channels with wide gates and slotted baffles. Inlet weirs, while effective in spreading flow across the tank width, introduce a vertical

velocity component into the solids hopper that may resuspend the solids particles. Inlet ports can provide good distribution across the tank width if the velocities are maintained in the 3 to 9 m/min (10 to 30 ft/min) range. Inlet baffles are effective in reducing the high initial velocities and distribute flow over the widest possible cross-sectional area. Where full-width baffles are used, they should extend from 150 mm (6 in) below the surface to 300 mm (12 in) below the entrance opening.

For installations of multiple rectangular tanks, below-grade pipe and equipment galleries can be constructed integrally with the tank structure and along the influent end. The galleries are used to house the sludge pumps and sludge drawoff piping. The galleries also provide access to the equipment for operation and maintenance. Galleries can also be connected to service tunnels for access to other plant units.

Scum is usually collected at the effluent end of rectangular tanks with the flights returning at the liquid surface. The scum is moved by the flights to a point where it is trapped by baffles before removal. Water sprays can also move the scum. The scum can be scraped manually up an inclined apron, or it can be removed hydraulically or mechanically, and for scum removal a number of means have been developed. For small installations, the most common scum drawoff facility consists of a horizontal, slotted pipe that can be rotated by a lever or a screw. Except when drawing scum, the open slot is above the normal tank water level. When drawing scum, the pipe is rotated so that the open slot is submerged just below the water level, permitting the scum accumulation to flow into the pipe. Use of this equipment results in a relatively large volume of scum liquor.

Another method for removing scum is by a transverse rotating helical wiper attached to a shaft. Scum is removed from the water surface and moved over a short inclined apron for discharge to a cross-collecting scum trough. The scum may then be flushed to a scum ejector or hopper ahead of a scum pump. Another method of scum removal consists of a chain-and-flight type of collector that collects the scum at one side of the tank and scrapes it up a short incline for deposit in scum hoppers, whence it can be pumped to disposal units. Scum is also collected by special scum rakes in rectangular tanks that are equipped with the carriage or bridge type of sedimentation tank equipment. In installations where appreciable amounts of scum are collected, the scum hoppers are usually equipped with mixers to provide a homogeneous mixture prior to pumping. Scum is usually disposed of with the solids and biosolids produced at the plant; however, separate scum disposal is used at many plants.

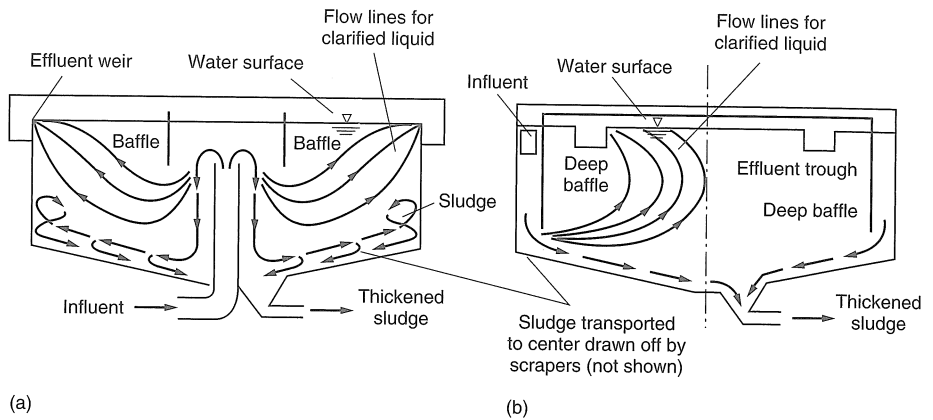
Multiple rectangular tanks require less land area than multiple circular tanks and find application where site space is at a premium. Rectangular tanks also lend themselves to nesting with preaeration tanks and aeration tanks in activated-sludge plants, thus permitting common wall construction and reducing construction costs. They are also used generally where tank roofs or covers are required.

Circular Tanks. In circular tanks the flow pattern is radial (as opposed to horizontal in rectangular tanks). To achieve a radial flow pattern, the wastewater to be settled can be introduced in the center or around the periphery of the tank, as shown on Fig. 5-41. Both flow configurations have proved to be satisfactory generally, although the center-feed type is more commonly used, especially for primary treatment. In the center-feed design (see Fig. 5-41a), the wastewater is transported to the center of the tank in a pipe suspended from the bridge, or encased in concrete beneath the tank floor.

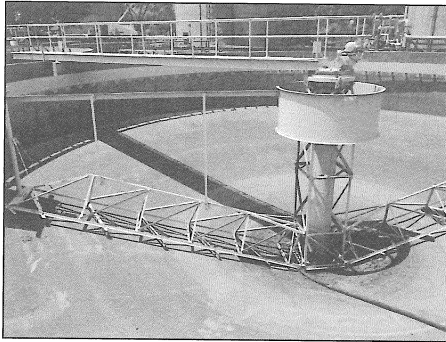
Figure 5-41

Typical circular primary sedimentation tanks:
(a) center feed and
(b) peripheral feed.

(Crites and Tchobanoglous, 1998.)

**Figure 5-42**

Typical circular primary sedimentation tank.



At the center of the tank, the wastewater enters a circular well designed to distribute the flow equally in all directions (see Fig. 5-42). The center well has a diameter typically between 15 and 20 percent of the total tank diameter and ranges from 1 to 2.5 m (3 to 8 ft) in depth and should have a tangential energy-dissipating inlet within the feedwell.

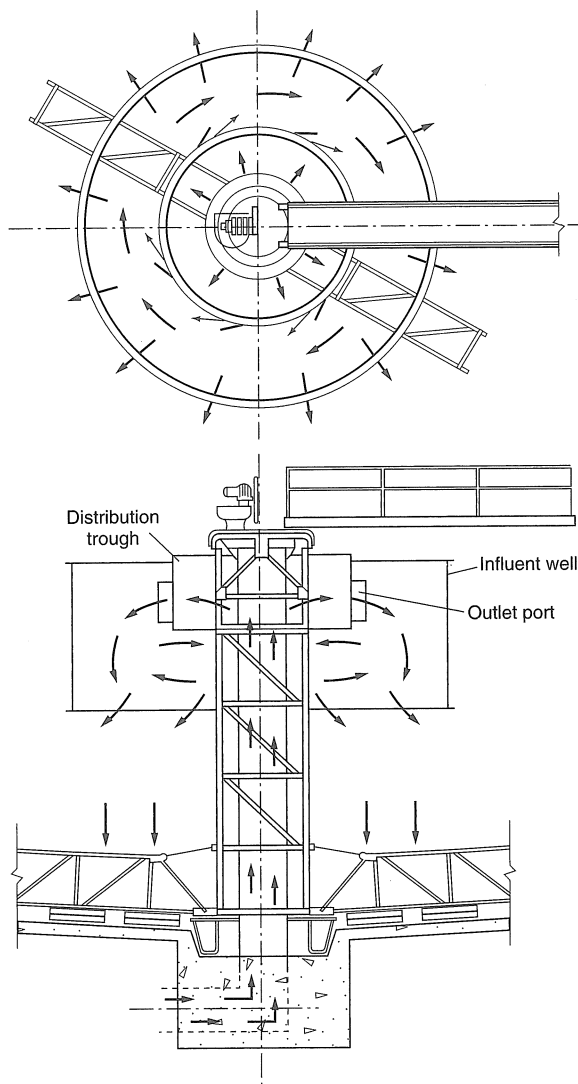
The energy-dissipating device (see Fig. 5-43) functions to collect influent from the center column and discharge it tangentially into the upper 0.5 to 0.7 m of the feedwell. The discharge ports are sized to produce a velocity of ≤ 0.75 m/s at maximum flow and 0.30 to 0.45 m/s at average flow. The feedwell should be sized so that the maximum downward velocity does not exceed 0.75 m/s. The depth of the feedwell should extend about 1 meter below the energy-dissipating inlet ports (Randall et al., 1992).

In the peripheral-feed design (see Fig. 5-41b), a suspended circular baffle forms an annular space into which the inlet wastewater is discharged in a tangential direction. The wastewater flows spirally around the tank and underneath the baffle, and the clarified liquid is skimmed off over weirs on both sides of a centrally located weir trough. Grease and scum are confined to the surface of the annular space. Peripheral feed tanks are used generally for secondary clarification.

Circular tanks 3.6 to 9 m (12 to 30 ft) in diameter have the solids-removal equipment supported on beams spanning the tank. Tanks 10.5 m (35 ft) in diameter and larger have a central pier that supports the mechanism and is reached by a walkway or bridge.

Figure 5-43

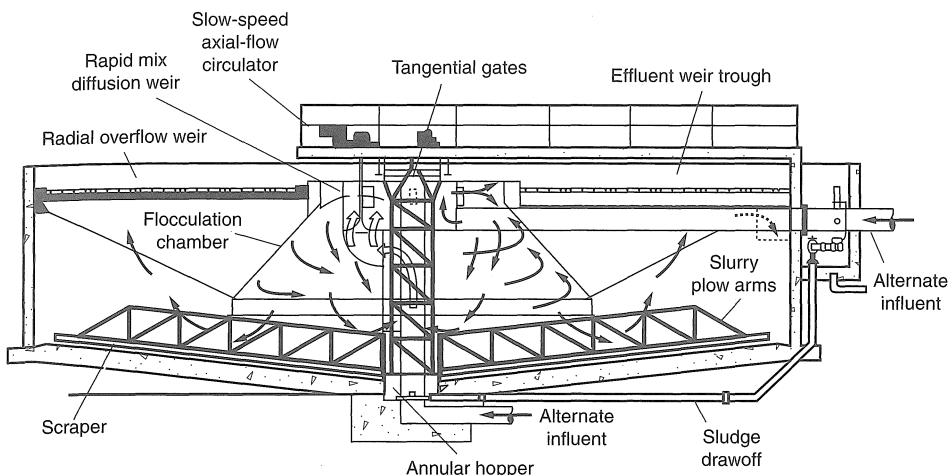
Typical energy-dissipating and flow distribution inlet for a center-feed sedimentation tank. The inner ring is used to create a tangential flow pattern. (Randall, et al., 1992.)



The bottom of the tank is sloped at about 1 in 12 (vertical:horizontal) to form an inverted cone, and the solids are scraped to a relatively small hopper located near the center of the tank.

Multiple tanks are customarily arranged in groups of two or four. The flow is divided among the tanks by a flow-split structure, commonly located between the tanks. Solids are usually withdrawn by sludge pumps for discharge to the solids processing and disposal units.

Combination Flocculator-Clarifier. Combination flocculator-clarifiers are often used in water treatment and sometimes used for wastewater treatment, especially in cases where enhanced settling, such as for industrial wastewater treatment or for



(a)

Figure 5-44

Typical flocculator-clarifier: (a) schematic and (b) view of empty tank. In some designs, turbine or propeller mixers are included in the flocculation chamber.

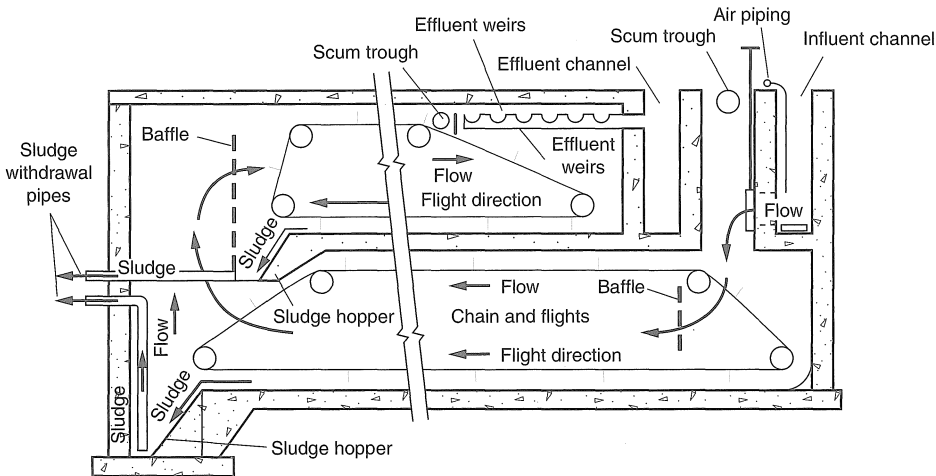


(b)

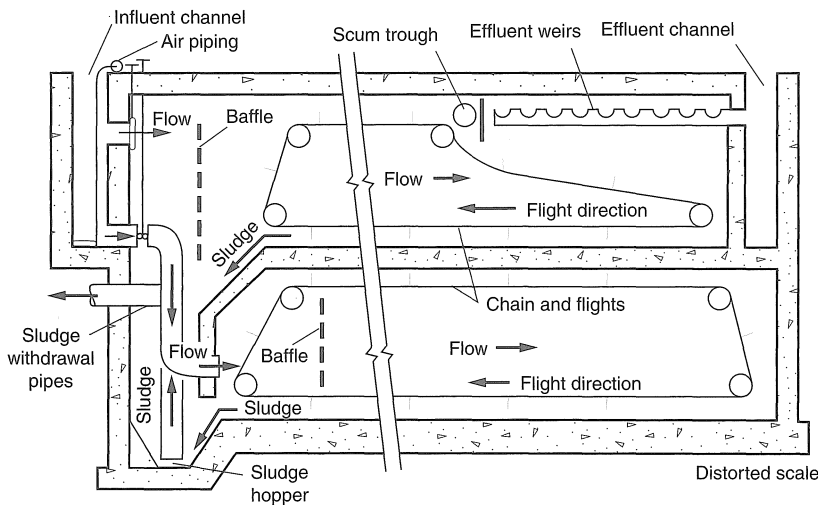
biosolids concentration, is required. Inorganic chemicals or polymers can be added to improve flocculation. Circular clarifiers are ideally suited for incorporation of an inner, cylindrical flocculation compartment (see Fig. 5-44). Wastewater enters through a center shaft or well and flows into the flocculation compartment, which is generally equipped with a paddle-type or low-speed mixer. The gentle stirring causes flocculent particles to form. From the flocculation compartment, flow then enters the clarification zone by passing down and radially outward. Settled solids and scum are collected in the same way as in a conventional clarifier.

Stacked (Multilevel) Clarifiers. Stacked clarifiers originated in Japan in the 1960s where limited land area is available for the construction of wastewater-treatment facilities. Since that time, stacked clarifiers have been used in the United States, the most notable installation of which is at the Deer Island Wastewater Treatment Plant constructed in Boston harbor. Design of these types of clarifiers recognizes the importance of settling area to settling efficiency. Operation of stacked rectangular clarifiers is similar to conventional rectangular clarifiers in terms of influent and effluent flow patterns and solids collection and removal. The stacked clarifiers are actually two (or

more) tanks, one located above the other, operating on a common water surface (see Fig. 5-45). Each clarifier is fed independently, resulting in parallel flow through the lower and upper tanks. Settled solids are collected from each tank with chain and flight solids collectors, discharging to a common hopper. In addition to saving space, advantages claimed for stacked clarifiers include less piping and pumping requirements.



(a)



(b)

Figure 5-45

Typical section through a stacked clarifier: (a) series flow and (b) parallel flow type used at the Deer Island Wastewater Treatment Plant, Boston, MA. Note: In the parallel flow type, the upper effluent weirs serve both the upper and lower clarifiers. Channels for the discharge of effluent from the lower to the upper clarifier are located on either side of the sludge collection mechanism in the upper clarifier.

Because the facilities are more compact and have less exposed surface area, better control of odors and volatile organic compound emissions is possible. Disadvantages include higher construction cost than conventional clarifiers and more complex structural design. Design criteria for stacked clarifiers, as regards overflow and weir rates, are similar to conventional primary and secondary clarifiers.

Sedimentation Tank Performance

The efficiency of sedimentation basins with respect to the removal of BOD and TSS is reduced by (1) eddy currents formed by the inertia of the incoming fluid, (2) wind-induced circulation cells formed in uncovered tanks, (3) thermal convection currents, (4) cold or warm water causing the formation of density currents that move along the bottom of the basin and warm water rising and flowing across the top of the tank, and (5) thermal stratification in hot arid climates (Fair and Geyer, 1954). Factors that affect performance are considered in the following discussion.

BOD and TSS Removal. Typical performance data for the removal of BOD and TSS in primary sedimentation tanks, as a function of the detention time and constituent concentration, are presented on Fig. 5-46. The curves shown on Fig. 5-46 are derived from observations of the performance of actual sedimentation tanks. The curvilinear relationships in the figure can be modeled as rectangular hyperbolas using the following relationship (Crites and Tchobanoglous, 1998).

$$R = \frac{t}{a + bt} \quad (5-45)$$

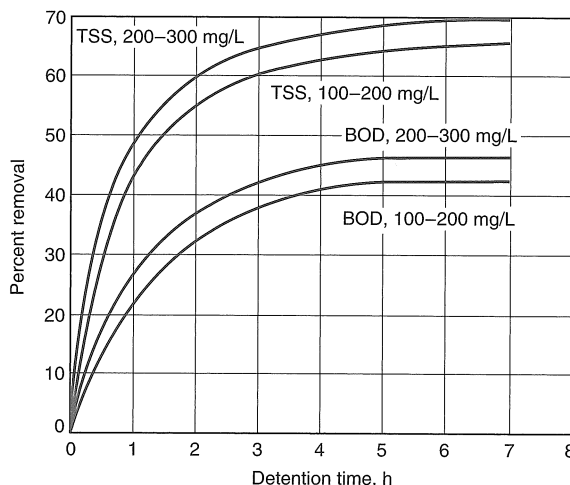
where R = expected removal efficiency

t = nominal detention time T

a, b = empirical constants

Figure 5-46

Typical BOD and TSS removal in primary sedimentation tanks. (Greeley, 1938.)



cle, Hudson and Wolfner (1967) noted that "coagulants hydrolyze and begin to polymerize in a fraction of second after being added to water." Hahn and Stumm (1968) studied the coagulation of silica dispersions with Al(III). They reported that the time required for the formation of mono- and polynuclear hydroxide species appears to be extremely short, on the order of 10^{-3} s. The time of formation for the polymer species was on the order of 10^{-2} s. Further, they found that the rate-limiting step in the coagulation process was the time required for the colloidal transport step brought about by Brownian motion (i.e., perikinetic flocculation) which was estimated to be on the order of 1.5 to 3.3×10^{-3} s. The importance of initial and rapid mixing is also discussed by Amirtharajah and Mills (1982) and Vrale and Jorden (1971). Clearly, based on the literature and actual field evaluations, the instantaneous rapid and intense mixing of metal salts is of critical importance, especially where the metal salts are to be used as coagulants to lower the surface charge of the colloidal particles. It should be noted that although achieving extremely low mixing times in large treatment plants is often difficult, low mixing times can be achieved by using multiple mixers. Typical mixing times for various chemicals are reported in Table 6-19 in Sec. 6-8.

6-3 CHEMICAL PRECIPITATION FOR IMPROVED PLANT PERFORMANCE

Chemical precipitation, as noted previously, involves the addition of chemicals to alter the physical state of dissolved and suspended solids and facilitate their removal by sedimentation. In the past, chemical precipitation was often used to enhance the degree of TSS and BOD removal: (1) where there were seasonal variations in the concentration of the wastewater (such as in cannery wastewater), (2) where an intermediate degree of treatment was required, and (3) as an aid to the sedimentation process. Since about 1970, the need to provide more complete removal of the organic compounds and nutrients (nitrogen and phosphorus) contained in wastewater has brought about renewed interest in chemical precipitation. In current practice, chemical precipitation is used (1) as a means of improving the performance of primary settling facilities, (2) as a basic step in the independent physical-chemical treatment of wastewater, (3) for the removal of phosphorus, and (4) for the removal of heavy metals. The first two applications are considered in the following discussion. Phosphorus and heavy metals removal is considered in Secs. 6-4 and 6-5, respectively.

Aside from the determination of the required chemical dosages, the principal design considerations related to the use of chemical precipitation involve the analysis and design of the necessary sludge processing facilities, and the selection and design of the chemical storage, feeding, piping, and control systems. Chemical storage, feeding, piping, and control systems are considered in Sec. 6-8.

Chemical Reactions in Wastewater Precipitation Applications

Over the years a number of different substances have been used as precipitants. The degree of clarification obtained depends on the quantity of chemicals used and the care with which the process is controlled. It is possible by chemical precipitation to obtain a clear effluent, substantially free from matter in suspension or in the colloidal state. The chemicals added to wastewater interact with substances that are either normally present in the wastewater or added for this purpose. The most common chemicals are listed in

Table 6-3

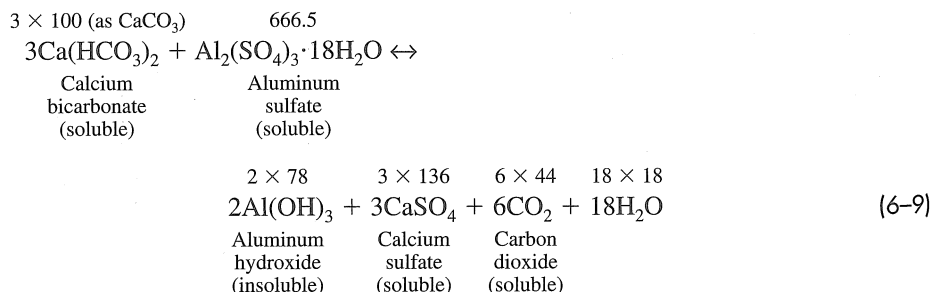
Inorganic chemicals used most commonly for coagulation and precipitation processes in wastewater treatment

Chemical	Formula	Molecular weight	Equivalent weight	Availability	
				Form	Percent
Alum	Al ₂ (SO ₄) ₃ ·18H ₂ O ^a	666.5	114	Liquid	8.5 (Al ₂ O ₃)
				Lump	17 (Al ₂ O ₃)
	Al ₂ (SO ₄) ₃ ·14H ₂ O ^a	594.4		Liquid	8.5 (Al ₂ O ₃)
				Lump	17 (Al ₂ O ₃)
Aluminum chloride	AlCl ₃	133.3	44	Liquid	
Calcium hydroxide (lime)	Ca(OH) ₂	56.1 as CaO	40	Lump	63–73 as CaO
				Powder	85–99
				Slurry	15–20
Ferric chloride	FeCl ₃	162.2	91	Liquid	20 (Fe)
				Lump	20 (Fe)
Ferric sulfate	Fe ₂ (SO ₄) ₃	400	51.5	Granular	18.5 (Fe)
Ferrous sulfate (copperas)	FeSO ₄ ·7H ₂ O	278.1	139	Granular	20 (Fe)
Sodium aluminate	Na ₂ Al ₂ O ₄	163.9	100	Flake	46 (Al ₂ O ₃)

^aNumber of bound water molecules will typically vary from 14 to 18.

Table 6-3. Information on the handling, storage, and feeding of these compounds may be found in Sec. 6-8. The reactions involved with (1) alum, (2) lime, (3) ferrous sulfate (copperas) and lime, (4) ferric chloride, (5) ferric chloride and lime, and (6) ferric sulfate and lime are considered in the following discussion (Metcalf & Eddy, 1935).

Alum. When alum is added to wastewater containing calcium and magnesium bicarbonate alkalinity, a precipitate of aluminum hydroxide will form. The overall reaction that occurs when alum is added to water may be illustrated as follows:



The numbers above the chemical formulas are the combining molecular weights of the different substances and, therefore, denote the quantity of each one involved. The pre-

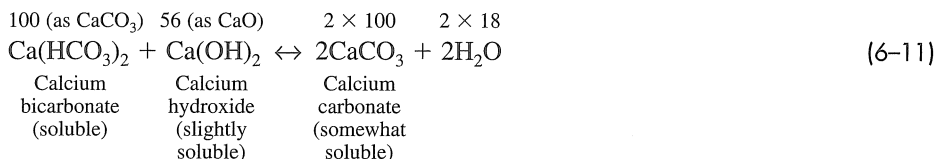
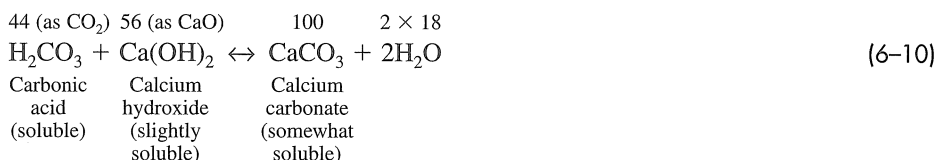
cipitation reaction given above also occurs with the addition of aluminum chloride (AlCl_3). The insoluble aluminum hydroxide is a gelatinous floc that settles slowly through the wastewater, sweeping out suspended material and producing other changes. The reaction is exactly analogous when magnesium bicarbonate is substituted for the calcium salt.

Because alkalinity in Eq. (6-9) is reported in terms of calcium carbonate (CaCO_3), the molecular weight of which is 100, the quantity of alkalinity required to react with 10 mg/L of alum is

$$(10.0 \text{ mg/L}) \left[\frac{3(100 \text{ g/mole})}{(666.5 \text{ g/mole})} \right] = 4.5 \text{ mg/L}$$

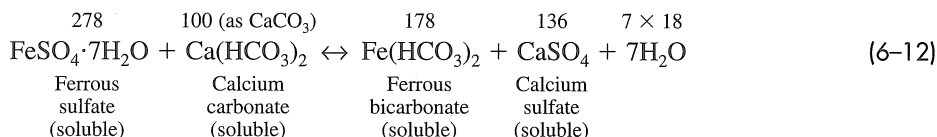
If less than this amount of alkalinity is available, it must be added. Lime is commonly used for this purpose when necessary, but it is seldom required in the treatment of wastewater.

Lime. When lime alone is added as a precipitant, the principles of clarification are explained by the following reactions for the carbonic acid [Eq. (6-10)] and the alkalinity [Eq. (6-11)]:



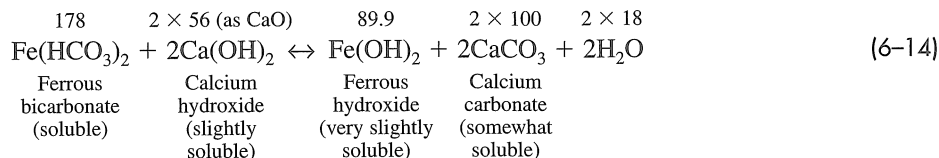
A sufficient quantity of lime must therefore be added to combine with all the free carbonic acid and with the carbonic acid of the bicarbonates (half-bound carbonic acid) to produce calcium carbonate. Much more lime is generally required when it is used alone than when sulfate of iron is also used (see the following discussion). Where industrial wastes introduce mineral acids or acid salts into the wastewater, these must be neutralized before precipitation can take place.

Ferrous Sulfate and Lime. In most cases, ferrous sulfate cannot be used alone as a precipitant because lime must be added at the same time to form a precipitate. When ferrous sulfate alone is added to wastewater, the following reactions occur:

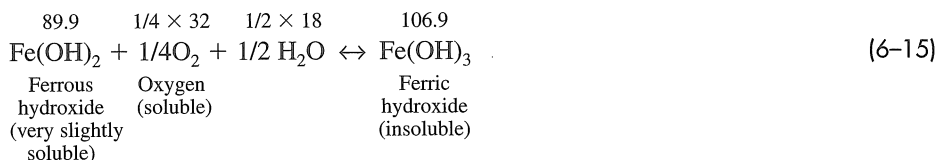




If sufficient alkalinity is not available, lime is often added in excess in conjunction with ferrous sulfate. The resulting reaction is



The ferrous hydroxide can be oxidized to ferric hydroxide, the final form desired, by oxygen dissolved in the wastewater. The reaction is:



The insoluble ferric hydroxide is formed as a bulky, gelatinous floc similar to the alum floc. The alkalinity required for a 10 mg/L dosage of ferrous sulfate [see Eq. (6-12)] is

$$(10.0 \text{ mg/L}) \left[\frac{(100 \text{ g/mole})}{(278 \text{ g/mole})} \right] = 3.6 \text{ mg/L}$$

The lime required [see Eq. (6-14)] is

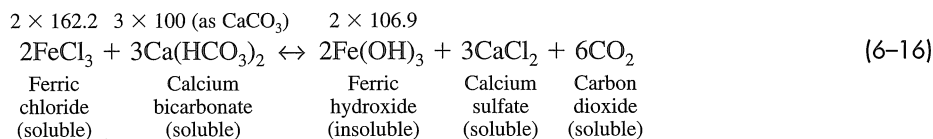
$$(10.0 \text{ mg/L}) \left[\frac{2(56 \text{ g/mole})}{(278 \text{ g/mole})} \right] = 4.0 \text{ mg/L}$$

The oxygen required [see Eq. (6-15)] is

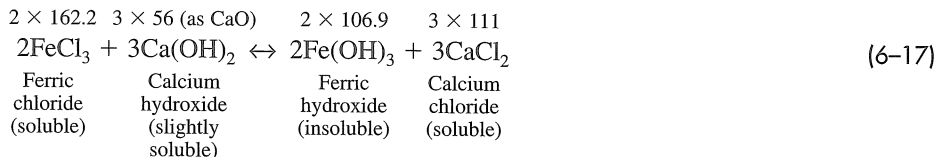
$$(10.0 \text{ mg/L}) \left[\frac{(32 \text{ g/mole})}{4(278 \text{ g/mole})} \right] = 0.29 \text{ mg/L}$$

Because the formation of ferric hydroxide is dependent on the presence of dissolved oxygen, the reaction given in Eq. (6-15) cannot be completed in most wastewaters, and, as a result, ferrous sulfate is not used commonly in wastewater.

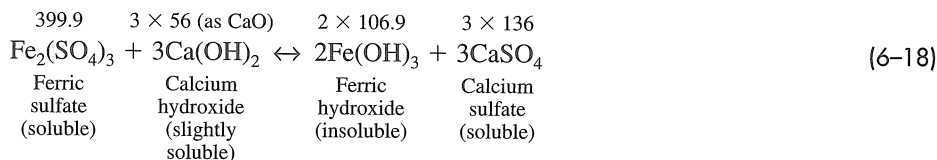
Ferric Chloride. Because of the many problems associated with the use of ferrous sulfate, ferric chloride is the iron salt used most commonly in precipitation applications. When ferric chloride is added to wastewater, the following reactions take place.



Ferric Chloride and Lime. If lime is added to supplement the natural alkalinity of the wastewater, the following reaction can be assumed to occur:



Ferric Sulfate and Lime. The overall reaction that occurs when ferric sulfate and lime are added to wastewater may be represented as follows:



Enhanced Removal of Suspended Solids in Primary Sedimentation

The degree of clarification obtained when chemicals are added to untreated wastewater depends on the quantity of chemicals used, mixing times, and the care with which the process is monitored and controlled. With chemical precipitation, it is possible to remove 80 to 90 percent of the total suspended solids (TSS) including some colloidal particles, 50 to 80 percent of the BOD, and 80 to 90 percent of the bacteria. Comparable removal values for well-designed and well-operated primary sedimentation tanks without the addition of chemicals are 50 to 70 percent of the TSS, 25 to 40 percent of the BOD, and 25 to 75 percent of the bacteria. Because of the variable characteristics of wastewater, the required chemical dosages should be determined from bench- or pilot-scale tests. Recommended surface loading rates for various chemical suspensions to be used in the design of the sedimentation facilities are given in Table 6-4.

Table 6-4
Recommended
surface loading rates
for sedimentation
tanks for various
chemical suspensions

Suspension	Overflow rate			
	gal/ft ² ·d		m ³ /m ² ·d	
	Typical range	Peak flow	Typical range	Peak flow
Alum floc ^a	700–1400	1200	30–70	80
Iron floc ^a	700–1400	1200	30–70	80
Lime floc ^a	750–1500	1500	35–80	90
Untreated wastewater	600–1200	1200	30–70	80

^aMixed with the settleable suspended solids in the untreated wastewater and colloidal or other suspended solids swept out by the floc.

Note: m³/m²·d × 24.5424 = gal/ft²·d

5. Prepare a summary table of sludge masses and volumes without and with chemical precipitation.

Treatment	Sludge	
	Mass, kg/d	Volume, m ³ /d
Without chemical precipitation	132.0	2.14
With chemical precipitation	802.3	10.0

Comment The magnitude of the sludge disposal problem associated with high lime treatment for phosphorus removal as compared to biological phosphorus removal is illustrated in this example.

6-5 CHEMICAL PRECIPITATION FOR REMOVAL OF HEAVY METALS AND DISSOLVED INORGANIC SUBSTANCES

The technologies available for the removal of heavy metals from wastewater include chemical precipitation, carbon adsorption, ion exchange, and reverse osmosis. Of these technologies, chemical precipitation is most commonly employed for most of the metals. Common precipitants include hydroxide (OH) and sulfide (S²⁻). Carbonate (CO₃²⁻) has also been used in some special cases. Metal may be removed separately or coprecipitated with phosphorus.

Precipitation Reactions

Metals of interest include arsenic (As), barium (Ba), cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), selenium (Se), and zinc (Zn). Most of these metals can be precipitated as hydroxides or sulfides. Solubility products for free metal concentrations in equilibrium with hydroxide and sulfide precipitates are reported in Table 6-9. In wastewater treatment facilities, metals are precipitated most commonly as metal hydroxides through the addition of lime or caustic to a pH of minimum solubility. However, several of these compounds are, as discussed previously, amphoteric (i.e., capable of either accepting or donating a proton) and exhibit a point of minimum solubility. The pH value at minimum solubility varies with the metal in question as illustrated on Fig. 6-17 for hydroxide precipitation. The solid line on Fig. 6-17 represents the total metal in solution in equilibrium with the precipitate. The curves were developed based on the mononuclear hydroxide species using the same procedures as illustrated on Fig. 6-8 for Al³⁺ and Fe³⁺. It is important to remember that the location of the minimum solubility will vary depending on the constituents in the wastewater. The curves given on Fig. 6-17 are useful in establishing the pH ranges for testing. Metals can also be precipitated as the sulfides as illustrated on Fig. 6-18. The minimum effluent concentration levels that

Table 6-9
Solubility products
for free metal ion
concentrations in
equilibrium with
hydroxides and
sulfides^{a,b}

Disinfectant	Half reaction	pK_{sp}
Cadmium hydroxide	$Cd(OH)_2 \leftrightarrow Cd^{2+} + 2OH^-$	13.93
Cadmium sulfide	$CdS \leftrightarrow Cd^{2+} + S^{2-}$	28
Chromium hydroxide	$Cr(OH)_3 \leftrightarrow Cr^{3+} + 3OH^-$	30.2
Copper hydroxide	$Cu(OH)_2 \leftrightarrow Cu^{2+} + 2OH^-$	19.66
Copper sulfide	$CuS \leftrightarrow Cu^{2+} + S^{2-}$	35.2
Iron (III) hydroxide	$Fe(OH)_2 \leftrightarrow Fe^{2+} + 2OH^-$	14.66
Iron (III) sulfide	$FeS \leftrightarrow Fe^{2+} + S^{2-}$	17.2
Lead hydroxide	$Pb(OH)_2 \leftrightarrow Pb^{2+} + 2OH^-$	14.93
Lead sulfide	$PbS \leftrightarrow Pb^{2+} + S^{2-}$	28.15
Mercury hydroxide	$Hg(OH)_2 \leftrightarrow Hg^{2+} + 2OH^-$	23
Mercury sulfide	$HgS \leftrightarrow Hg^{2+} + S^{2-}$	52
Nickel hydroxide	$Ni(OH)_2 \leftrightarrow Ni^{2+} + 2OH^-$	15
Nickel sulfide	$NiS \leftrightarrow Ni^{2+} + S^{2-}$	24
Silver hydroxide	$AgOH \leftrightarrow Ag^+ + OH^-$	14.93
Silver sulfide	$(Ag)_2S \leftrightarrow 2Ag^+ + S^{2-}$	28.15
Zinc hydroxide	$Zn(OH)_2 \leftrightarrow Zn^{2+} + 2OH^-$	16.7
Zinc sulfide	$ZnS \leftrightarrow Zn^{2+} + S^{2-}$	22.8

^aAdapted from Bard (1966).

^bTo obtain the complete solubility of a metal, all of the complex species must be considered such as reported in Table 6-2 for aluminum and iron.

Figure 6-17

Residual soluble metal concentration as a function of pH for the precipitation of metals as hydroxides. Because of the wide variation in the solubility and formation constants for the various metal hydroxides, the curves presented in this figure should only be used as a reference guide (see also Table 6-10).

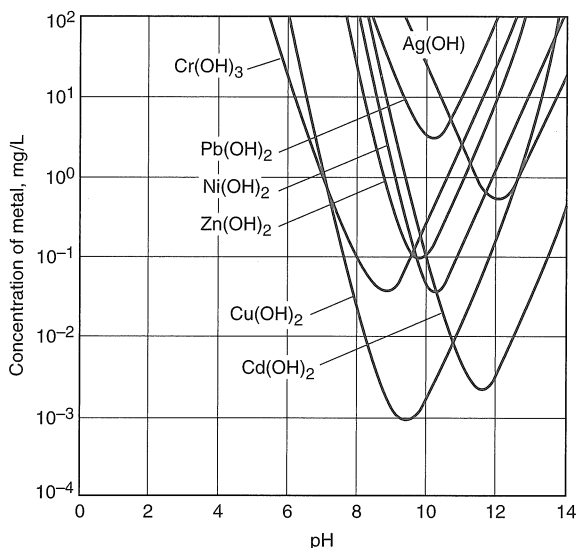


Figure 6-18

Residual soluble metal concentration as a function of pH for the precipitation of metals as sulfides. Because of the wide variation in the solubility and formation constants for the various metal sulfides, the curves presented in this figure should only be used as a reference guide (see also Table 6-10).

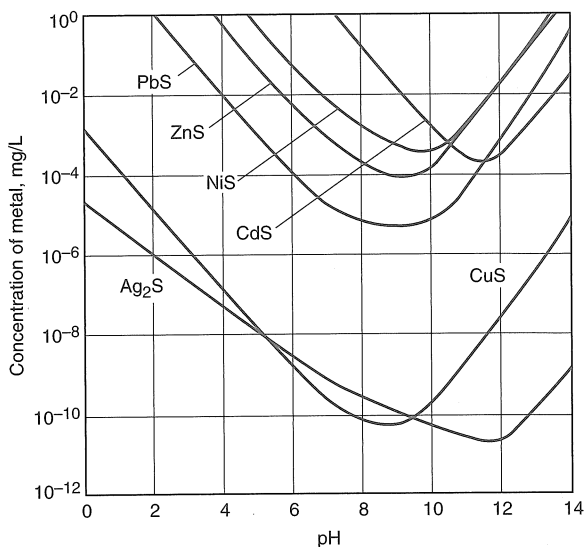


Table 6-10
Practical effluent concentration levels achievable in heavy metals removal by precipitation^a

Metal	Achievable effluent concentration, mg/L	Type of precipitation and technology
Arsenic	0.05	Sulfide precipitation with filtration
	0.005	Ferric hydroxide coprecipitation
Barium	0.5	Sulfate precipitation
Cadmium	0.05	Hydroxide precipitation at pH 10–11
	0.05	Coprecipitation with ferric hydroxide
	0.008	Sulfide precipitation
Copper	0.02–0.07	Hydroxide precipitation
	0.01–0.02	Sulfide precipitation
Mercury	0.01–0.02	Sulfide precipitation
	0.001–0.01	Alum coprecipitation
	0.0005–0.005	Ferric hydroxide coprecipitation
	0.001–0.005	Ion exchange
Nickel	0.12	Hydroxide precipitation at pH 10
Selenium	0.05	Sulfide precipitation
Zinc	0.1	Hydroxide precipitation at pH 11

^aFrom Eckenfelder (2000).

can be achieved in the chemical precipitation of heavy metals are reported in Table 6-10. In practice, the minimum achievable residual metal concentrations will also depend on the nature and concentration of the organic matter in the wastewater as well as the temperature. Because of the many uncertainties associated with the precipitation of metals, laboratory bench-scale or pilot-plant testing should be conducted.

Objectives of Biological Treatment

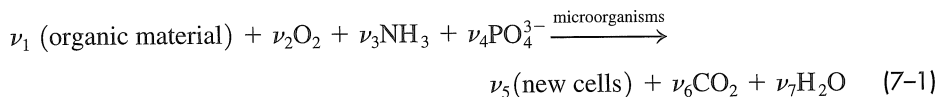
The overall objectives of the biological treatment of domestic wastewater are to (1) transform (i.e., oxidize) dissolved and particulate biodegradable constituents into acceptable end products, (2) capture and incorporate suspended and nonsettleable colloidal solids into a biological floc or biofilm, (3) transform or remove nutrients, such as nitrogen and phosphorus, and (4) in some cases, remove specific trace organic constituents and compounds. For industrial wastewater, the objective is to remove or reduce the concentration of organic and inorganic compounds. Because some of the constituents and compounds found in industrial wastewater are toxic to microorganisms, pretreatment may be required before the industrial wastewater can be discharged to a municipal collection system. For agricultural irrigation return wastewater, the objective is to remove nutrients, specifically nitrogen and phosphorus, that are capable of stimulating the growth of aquatic plants. Schematic flow diagrams of various treatment processes for domestic wastewater incorporating biological processes are shown on Fig. 7-1.

Some Useful Definitions

Common terms used in the field of biological wastewater treatment and their definitions are presented in Table 7-1. All of the terms presented in Table 7-1 are discussed in greater detail in the remainder of this chapter and in Chaps. 8, 9, and 10, which follow. The first five entries in Table 7-1 refer to the metabolic function of the processes. As reported, the principal processes used for the biological treatment of wastewater can be classified with respect to their metabolic function as aerobic processes, anaerobic processes, anoxic processes, facultative processes, and combined processes. Terminology used to describe the types of treatment processes is presented in the second group of entries in Table 7-1. The principal processes used for wastewater treatment are classified as suspended-growth, attached-growth, or combinations thereof. The third group of terms are descriptors for the different types of treatment functions.

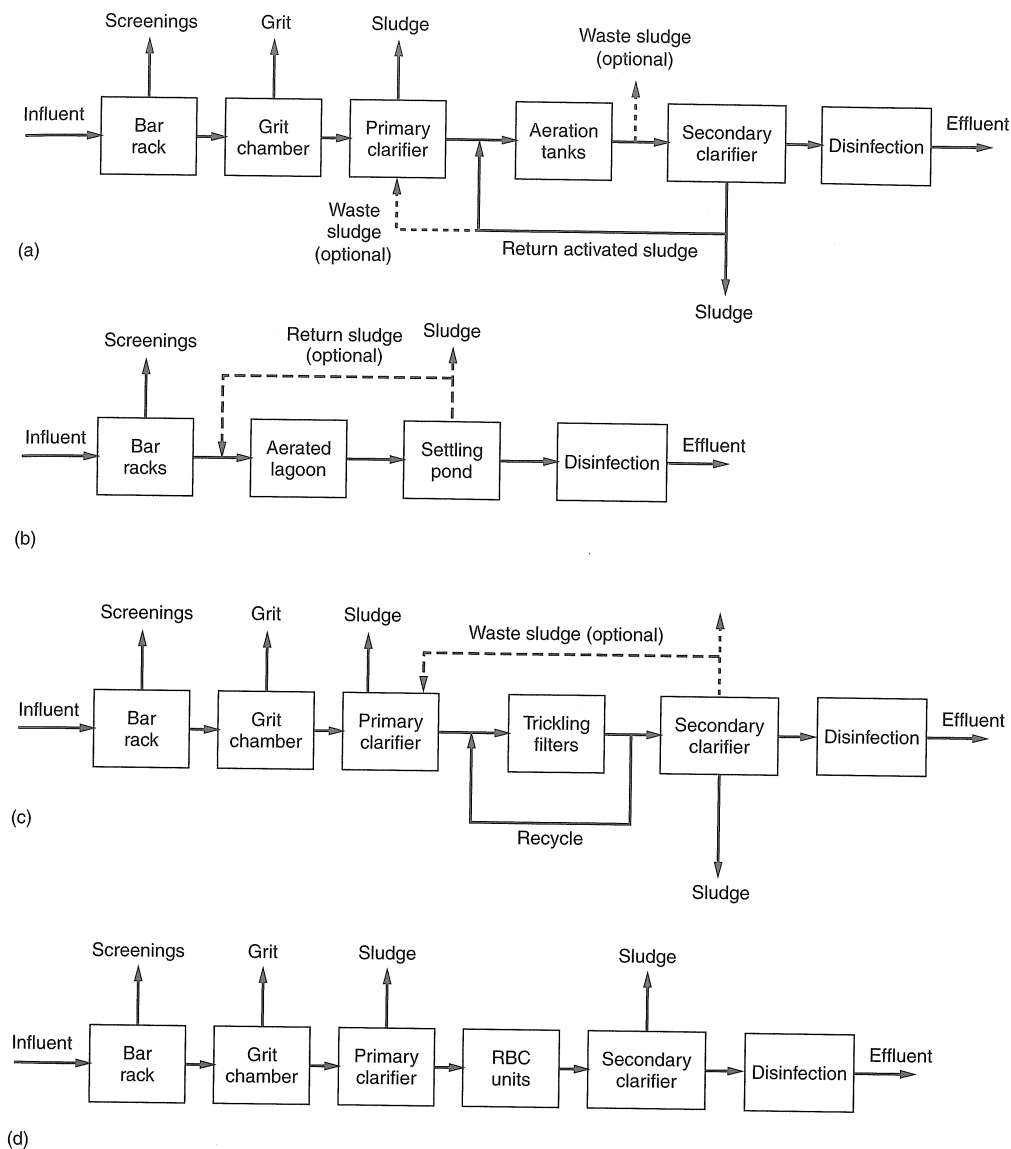
Role of Microorganisms in Wastewater Treatment

The removal of dissolved and particulate carbonaceous BOD and the stabilization of organic matter found in wastewater is accomplished biologically using a variety of microorganisms, principally bacteria. Microorganisms are used to oxidize (i.e., convert) the dissolved and particulate carbonaceous organic matter into simple end products and additional biomass, as represented by the following equation for the aerobic biological oxidation of organic matter.



where ν_i = the stoichiometric coefficient, as defined previously in Sec. 4-6 in Chap. 4.

In Eq. (7-1), oxygen (O_2), ammonia (NH_3), and phosphate (PO_4^{3-}) are used to represent the nutrients needed for the conversion of the organic matter to simple end products [i.e., carbon dioxide (CO_2) and water]. The term shown over the directional arrow is used to denote the fact that microorganisms are needed to carry out the oxidation process. The term *new cells* is used to represent the biomass produced as a result of the oxidation of the organic matter. Microorganisms are also used to remove nitrogen and

**Figure 7-1**

Typical (simplified) flow diagrams for biological processes used for wastewater treatment: (a) activated-sludge process, (b) aerated lagoons, (c) trickling filters, and (d) rotating biological contactors.

phosphorus in wastewater treatment processes. Specific bacteria are capable of oxidizing ammonia (nitrification) to nitrite and nitrate, while other bacteria can reduce the oxidized nitrogen to gaseous nitrogen. For phosphorus removal, biological processes are configured to encourage the growth of bacteria with the ability to take up and store large amounts of inorganic phosphorus.

Because the biomass has a specific gravity slightly greater than that of water, the biomass can be removed from the treated liquid by gravity settling. It is important to note that unless the biomass produced from the organic matter is removed on a periodic basis, complete treatment has not been accomplished because the biomass, which itself is organic, will be measured as BOD in the effluent. Without the removal of biomass from the treated liquid, the only treatment achieved is that associated with the bacterial oxidation of a portion of the organic matter originally present.

Types of Biological Processes for Wastewater Treatment

The principal biological processes used for wastewater treatment can be divided into two main categories: *suspended growth* and *attached growth* (or *biofilm*) processes (see Table 7-1). Typical process applications for suspended and attached growth biological treatment processes are given in Table 7-2, along with other treatment processes. The successful design and operation of the processes listed in Table 7-2 require an understanding of the types of microorganisms involved, the specific reactions that they perform, the environmental factors that affect their performance, their nutritional needs, and their reaction kinetics. These subjects are considered in the sections that follow.

Suspended Growth Processes. In suspended growth processes, the microorganisms responsible for treatment are maintained in liquid suspension by appropriate mixing methods. Many suspended growth processes used in municipal and industrial wastewater treatment are operated with a positive dissolved oxygen concentration (aerobic), but applications exist where suspended growth anaerobic (no oxygen present) reactors are used, such as for high organic concentration industrial wastewaters and organic sludges. The most common suspended growth process used for municipal wastewater treatment is the activated-sludge process shown on Fig. 7-2 and discussed below.

The activated-sludge process was developed around 1913 at the Lawrence Experiment Station in Massachusetts by Clark and Gage (Metcalf and Eddy, 1930), and by Ardern and Lockett (1914) at the Manchester Sewage Works in Manchester, England. The activated-sludge process was so named because it involved the production of an activated mass of microorganisms capable of stabilizing a waste under aerobic conditions. In the aeration tank, contact time is provided for mixing and aerating influent wastewater with the microbial suspension, generally referred to as the mixed liquor suspended solids (MLSS) or mixed liquor volatile suspended solids (MLVSS). Mechanical equipment is used to provide the mixing and transfer of oxygen into the process. The mixed liquor then flows to a clarifier where the microbial suspension is settled and thickened. The settled biomass, described as *activated sludge* because of the presence of active microorganisms, is returned to the aeration tank to continue biodegradation of the influent organic material. A portion of the thickened solids is removed daily or periodically as the process produces excess biomass that would accumulate along with the nonbiodegradable solids contained in the influent wastewater. If the accumulated solids are not removed, they will eventually find their way to the system effluent.

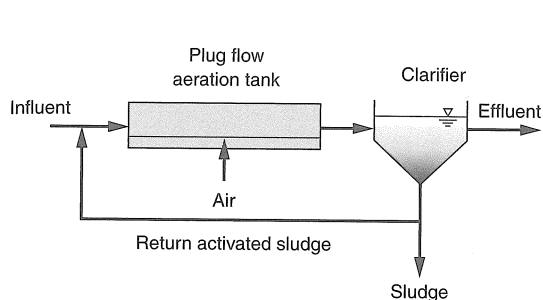
An important feature of the activated-sludge process is the formation of floc particles, ranging in size from 50 to 200 μm , which can be removed by gravity settling, leaving a relatively clear liquid as the treated effluent. Typically, greater than 99 percent of the suspended solids can be removed in the clarification step. As will be discussed in

Table 7-2

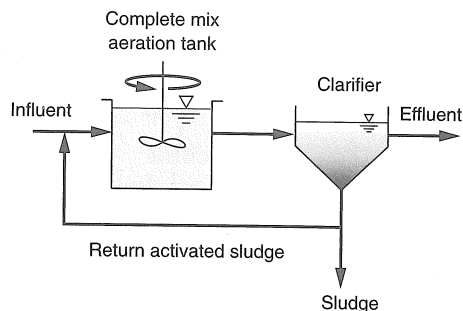
Major biological treatment processes used for wastewater treatment.

Type	Common name	Use ^a
Aerobic processes		
Suspended growth	Activated-sludge process(es)	Carbonaceous BOD removal, nitrification
	Aerated lagoons	Carbonaceous BOD removal, nitrification
	Aerobic digestion	Stabilization, carbonaceous BOD removal
Attached growth	Trickling filters	Carbonaceous BOD removal, nitrification
	Rotating biological contactors	Carbonaceous BOD removal, nitrification
	Packed-bed reactors	Carbonaceous BOD removal, nitrification
Hybrid (combined) suspended and attached growth processes	Trickling filter/activated sludge	Carbonaceous BOD removal, nitrification
Anoxic processes		
Suspended growth	Suspended-growth denitrification	Denitrification
Attached growth	Attached-growth denitrification	Denitrification
Anaerobic processes		
Suspended growth	Anaerobic contact processes	Carbonaceous BOD removal
	Anaerobic digestion	Stabilization, solids destruction, pathogen kill
Attached growth	Anaerobic packed and fluidized bed	Carbonaceous BOD removal, waste stabilization, denitrification
Sludge blanket	Upflow anaerobic sludge blanket	Carbonaceous BOD removal, especially high-strength wastes
Hybrid	Upflow sludge blanket/attached growth	Carbonaceous BOD removal
Combined aerobic, anoxic, and anaerobic processes		
Suspended growth	Single- or multistage processes, various proprietary processes	Carbonaceous BOD removal, nitrification, denitrification, and phosphorus removal
Hybrid	Single- or multistage processes with packing for attached growth	Carbonaceous BOD removal, nitrification, denitrification, and phosphorus removal
Lagoon processes		
Aerobic lagoons	Aerobic lagoons	Carbonaceous BOD removal
Maturation (tertiary) lagoons	Maturation (tertiary) lagoons	Carbonaceous BOD removal, nitrification
Facultative lagoons	Facultative lagoons	Carbonaceous BOD removal
Anaerobic lagoons	Anaerobic lagoons	Carbonaceous BOD removal, waste stabilization

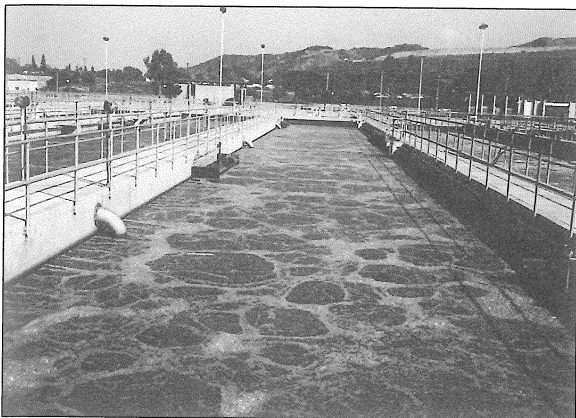
^aAdapted from Tchobanoglous and Schroeder (1985).



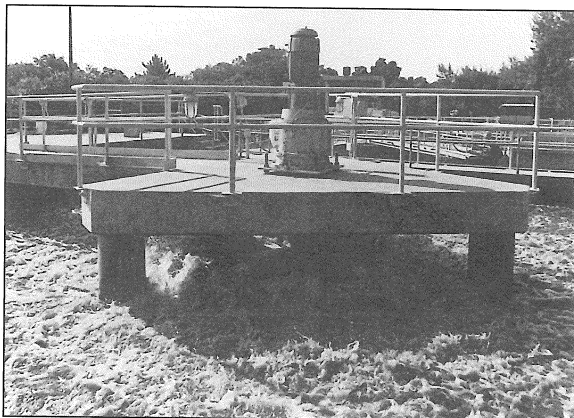
(a-1)



(b-1)



(a-2)



(b-2)

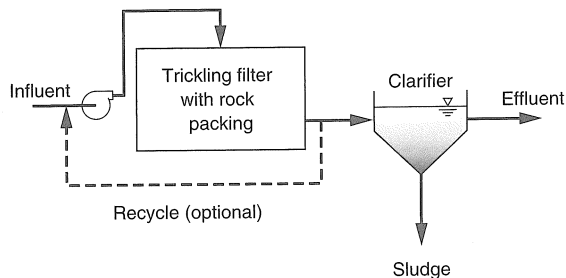
Figure 7-2

Suspended growth biological treatment process (a-1) schematic and (a-2) view of plug-flow activated-sludge process and (b-1) schematic and (b-2) view of complete-mix activated-sludge process.

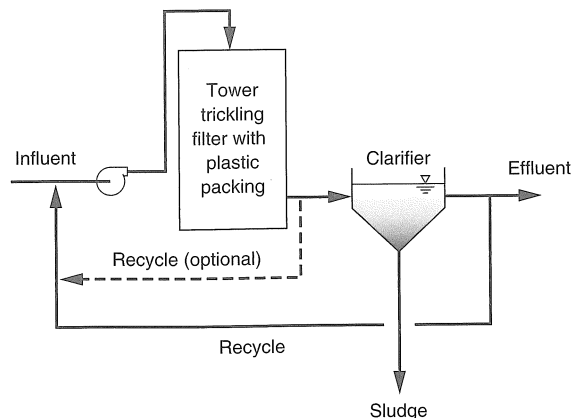
Chap. 8, the characteristics and thickening properties of the flocculent particles will affect the clarifier design and performance.

Attached Growth Processes. In attached growth processes, the microorganisms responsible for the conversion of organic material or nutrients are attached to an inert packing material. The organic material and nutrients are removed from the wastewater flowing past the attached growth also known as a biofilm. Packing materials used in attached growth processes include rock, gravel, slag, sand, redwood, and a wide range of plastic and other synthetic materials. Attached growth processes can also be operated as aerobic or anaerobic processes. The packing can be submerged completely in liquid or not submerged, with air or gas space above the biofilm liquid layer.

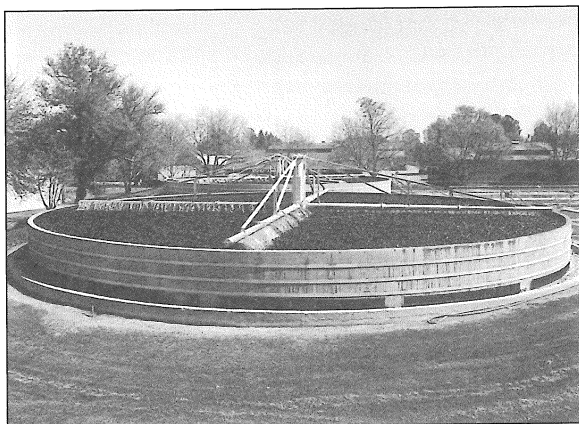
The most common aerobic attached growth process used is the trickling filter in which wastewater is distributed over the top area of a vessel containing nonsubmerged packing material (see Fig. 7-3). Historically, rock was used most commonly as the packing material for trickling filters, with typical depths ranging from 1.25 to 2 m (4 to



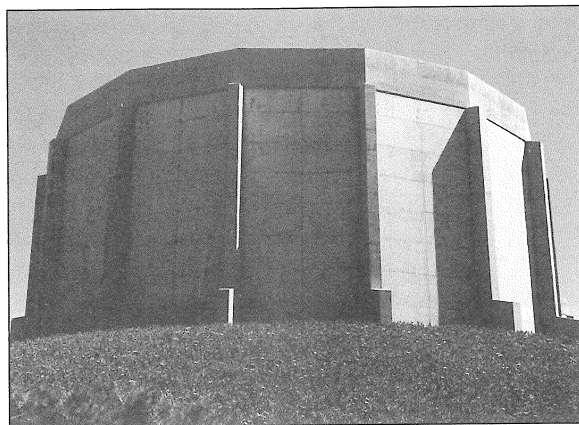
(a-1)



(b-1)



(a-2)



(b-2)

Figure 7-3

Attached growth biological treatment process (a-1) schematic and (a-2) view of trickling filter with rock packing and (b-1) schematic and (b-2) view of tower trickling filter with plastic packing (see Fig. 7-15b). The tower filter is 10 m high and 50 m in diameter.

6 ft). Most modern trickling filters vary in height from 5 to 10 m (16 to 33 ft) and are filled with a plastic packing material for biofilm attachment. The plastic packing material is designed such that about 90 to 95 percent of the volume in the tower consists of void space. Air circulation in the void space, by either natural draft or blowers, provides oxygen for the microorganisms growing as an attached biofilm. Influent wastewater is distributed over the packing and flows as a nonuniform liquid film over the attached biofilm. Excess biomass sloughs from the attached growth periodically and clarification is required for liquid/solids separation to provide an effluent with an acceptable suspended solids concentration. The solids are collected at the bottom of the clarifier and removed for waste-sludge processing.

Metals. Metals are also of concern for nitrifiers, and Skinner and Walker (1961) have shown complete inhibition of ammonia oxidation at 0.25 mg/L nickel, 0.25 mg/L chromium, and 0.10 mg/L copper.

Un-ionized Ammonia. Nitrification is also inhibited by un-ionized ammonia (NH_3) or free ammonia, and un-ionized nitrous acid (HNO_2). The inhibition effects are dependent on the total nitrogen species concentration, temperature, and pH. At 20°C and pH 7.0, the $\text{NH}_4\text{-N}$ concentrations at 100 mg/L and 20 mg/L may initiate inhibition of $\text{NH}_4\text{-N}$ and $\text{NO}_2\text{-N}$ oxidation, respectively, and $\text{NO}_2\text{-N}$ concentrations at 280 mg/L may initiate inhibition of $\text{NO}_2\text{-N}$ oxidation (U.S. EPA, 1993).

7-10 BIOLOGICAL DENITRIFICATION

The biological reduction of nitrate to nitric oxide, nitrous oxide, and nitrogen gas is termed *denitrification*. Biological denitrification is an integral part of biological nitrogen removal, which involves both nitrification and denitrification. Compared to alternatives of ammonia stripping (see Chap. 11), breakpoint chlorination (see Chap. 12), and ion exchange (see Chap. 11), biological nitrogen removal is generally more cost-effective and used more often. Biological nitrogen removal is used in wastewater treatment where there are concerns for eutrophication, and where groundwater must be protected against elevated $\text{NO}_3\text{-N}$ concentrations where wastewater-treatment plant effluent is used for groundwater recharge and other reclaimed water applications.

Process Description

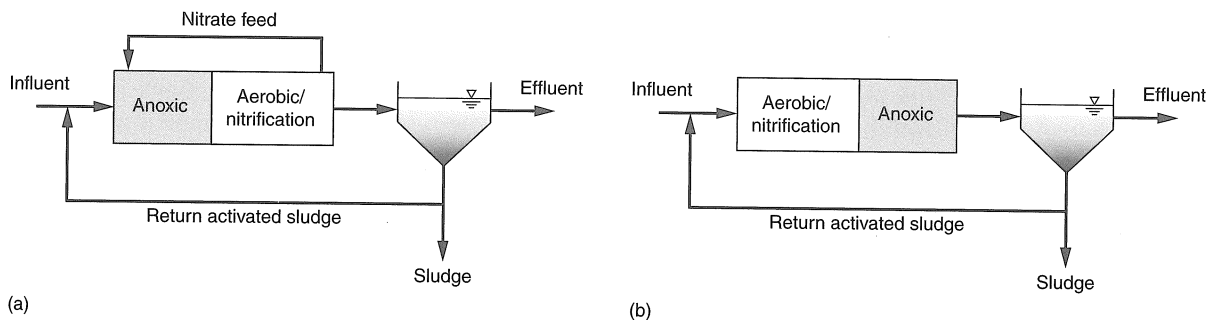
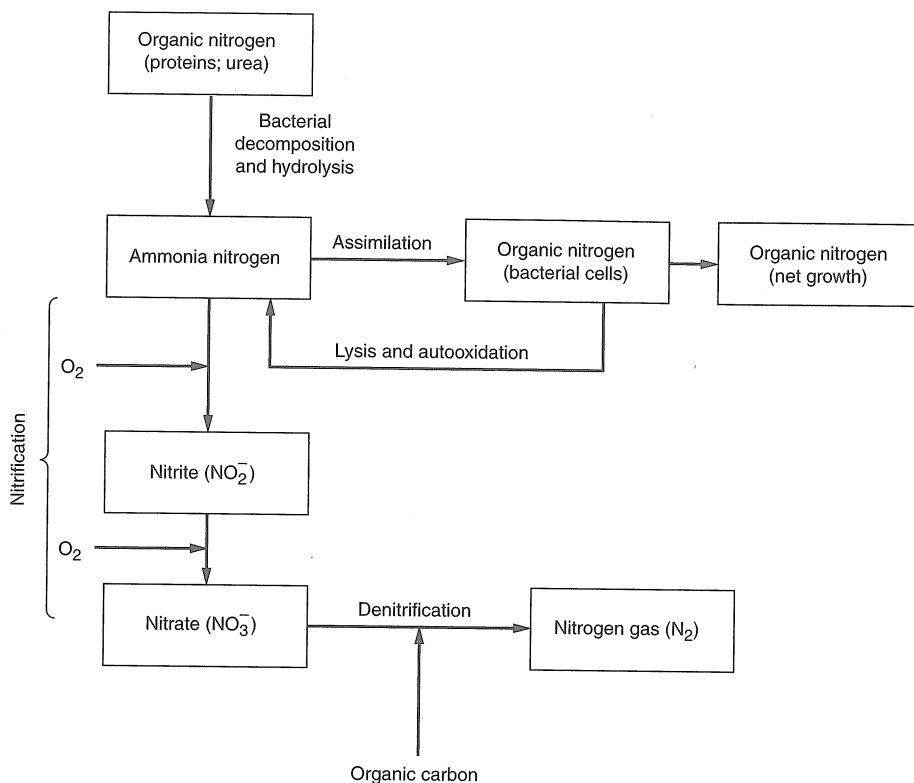
Two modes of nitrate removal can occur in biological processes, and these are termed assimilating and dissimilating nitrate reduction (see Fig. 7-20). Assimilating nitrate reduction involves the reduction of nitrate to ammonia for use in cell synthesis. Assimilation occurs when $\text{NH}_4\text{-N}$ is not available and is independent of DO concentration. On the other hand, dissimilating nitrate reduction or biological denitrification is coupled to the respiratory electron transport chain, and nitrate or nitrite is used as an electron acceptor for the oxidation of a variety of organic or inorganic electron donors.

Two basic flow diagrams for activated-sludge denitrification and the conditions that drive the denitrification reaction rates are illustrated on Fig. 7-21. The first flow diagram (Fig. 7-21a) is for the Modified Ludzak-Ettinger (MLE) process (U.S. EPA, 1993), the most common process used for biological nitrogen removal in municipal wastewater treatment. The process consists of an anoxic tank followed by the aeration tank where nitrification occurs. Nitrate produced in the aeration tank is recycled back to the anoxic tank. Because the organic substrate in the influent wastewater provides the electron donor for oxidation reduction reactions using nitrate, the process is termed *substrate denitrification*. Further, because the anoxic process precedes the aeration tank, the process is known as a *preanoxic denitrification*.

In the second process shown on Fig. 7-21b, denitrification occurs after nitrification and the electron donor source is from endogenous decay. The process illustrated on Fig. 7-21b is generally termed a *postanoxic denitrification* as BOD removal has occurred first and is not available to drive the nitrate reduction reaction. When a postanoxic denitrification process depends solely on endogenous respiration for energy, it has a much slower rate of reaction than for the preanoxic processes using wastewater

Figure 7-20

Nitrogen transformations in biological treatment processes. (Adapted from Sedlak, 1991.)

**Figure 7-21**

Types of denitrification processes and the reactors used for their implementation: (a) substrate driven (preanoxic denitrification) and (b) endogenous driven (postanoxic denitrification).

BOD. Often an exogenous carbon source such as methanol or acetate is added to postanoxic processes to provide sufficient BOD for nitrate reduction and to increase the rate of denitrification. Postanoxic processes include both suspended and attached growth systems. In one attached growth granular-medium filtration process, both nitrate reduction and effluent suspended solids removal occur in the same reactor.

centrations. A dissolved oxygen concentration of 0.2 mg/L and above has been reported to inhibit denitrification for a *Pseudomonas* culture (Skerman and MacRae, 1957; Terai and Mori, 1975) and by Dawson and Murphy (1972) for activated-sludge treating domestic wastewater. Nelson and Knowles (1978) reported that denitrification ceased in a highly dispersed growth at a DO concentration of 0.13 mg/L. The effect of nitrate and DO concentration on the biokinetics is accounted for by two correction factors to Eq. (7-109) expressed in the form of two saturation terms as follows:

$$r_{su} = - \left(\frac{kXS}{K_s + S} \right) \left(\frac{NO_3}{K_{s,NO_3} + NO_3} \right) \left(\frac{K'_0}{K'_0 + DO} \right) (\eta) \quad (7-110)$$

where K'_0 = DO inhibition coefficient for nitrate reduction, mg/L

K_{s,NO_3} = half velocity coefficient for nitrate limited reaction, mg/L

Other terms are as defined previously.

The value of K'_0 is system-specific. Values in the range from 0.1 to 0.2 mg/L have been proposed for K'_0 and 0.1 mg/L for K_{s,NO_3} (Barker and Dold, 1997). Assuming a K'_0 value of 0.1 mg/L the rate of substrate utilization with nitrate as the electron acceptor at DO concentrations of 0.10, 0.20, and 0.50 mg/L would be at 50, 33, and 17 percent of the maximum rate, respectively.

Effect of Simultaneous Nitrification-Denitrification. In activated-sludge systems, the issue of DO concentration is confounded by the fact that the measured bulk liquid DO concentration does not represent the actual DO concentration within the activated-sludge floc. Under low DO concentration conditions, denitrification can occur in the floc interior, while nitrification is occurring at the floc exterior. Also in activated-sludge tanks operated at low DO concentrations, both aerobic and anaerobic zones exist depending on mixing conditions and distance from the aeration point, so that nitrification and denitrification can be occurring in the same tank. Under these conditions, nitrogen removal that occurs in a single aeration tank is referred to as simultaneous nitrification and denitrification. Although both nitrification and denitrification are occurring at reduced rates as indicated by the DO effects described for both processes, if a sufficient SRT and τ exist, the overall nitrogen removal can be significant. Rittman and Langeland (1985) reported greater than 90 percent nitrogen removal by nitrification and denitrification in an activated-sludge system used to treat municipal wastewater at DO concentrations below 0.50 mg/L and with values of τ greater than 25 hours.

Environmental Factors

Alkalinity is produced in denitrification reactions and the pH is generally elevated, instead of being depressed as in nitrification reactions. In contrast to nitrifying organisms, there has been less concern about pH influences on denitrification rates. No significant effect on the denitrification rate has been reported for pH between 7.0 and 8.0, while Dawson and Murphy (1972) showed a decrease in the denitrification rate as the pH was decreased from 7.0 to 6.0 in batch unacclimated tests.

7-11 BIOLOGICAL PHOSPHORUS REMOVAL

The removal of phosphorus by biological means is known as *biological phosphorus removal*. Phosphorus removal is generally done to control eutrophication because

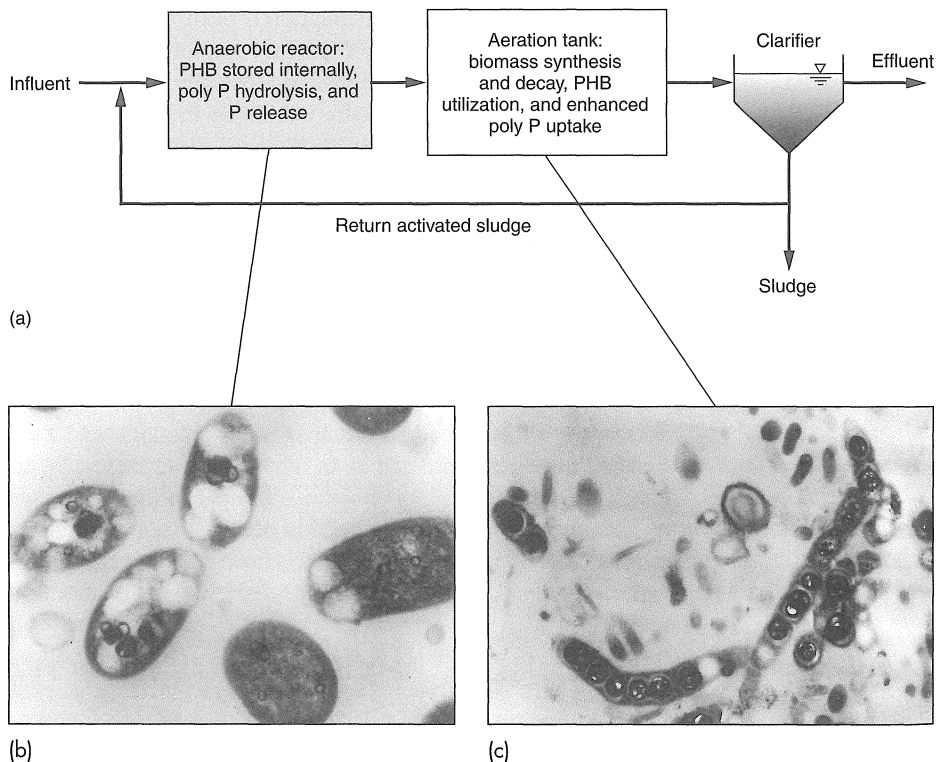
phosphorus is a limiting nutrient in most freshwater systems. Treatment plant effluent discharge limits have ranged from 0.10 to 2.0 mg/L of phosphorus depending on plant location and potential impact on receiving waters. Chemical treatment using alum or iron salts is the most commonly used technology for phosphorus removal (see Sec. 6–4 in Chap. 6), but since the early 1980s success in full-scale plant biological phosphorus removal has encouraged further use of the technology. The principal advantages of biological phosphorus removal are reduced chemical costs and less sludge production as compared to chemical precipitation.

Process Description

In the biological removal of phosphorus, the phosphorus in the influent wastewater is incorporated into cell biomass, which subsequently is removed from the process as a result of sludge wasting. Phosphorus accumulating organisms (PAOs) are encouraged to grow and consume phosphorus in systems that use a reactor configuration that provides PAOs with a competitive advantage over other bacteria. The reactor configuration utilized for phosphorus removal is comprised of an anaerobic tank having a τ value of 0.50 to 1.0 h that is placed ahead of the activated-sludge aeration tank (see Fig. 7–22). The contents of the anaerobic tank are mixed to provide contact with the return activated sludge and influent wastewater. Anaerobic contact tanks have been placed in front of many different types of suspended growth processes (see detailed discussion in Sec. 8–6 in Chap. 8), with aerobic SRT values ranging from 2 to 40 d.

Figure 7–22

Biological phosphorus removal: (a) typical reactor configuration. Photos below flow diagram are of (b) transmission electron microscope images of polyhydroxybutyrate storage and (c) polyphosphate storage granules.



7-14 BIOLOGICAL REMOVAL OF HEAVY METALS

Metal removal in biological treatment processes is mainly by adsorption and complexation of the metals with the microorganisms. In addition, processes that result in transformations and precipitation of metals are possible. Microorganisms combine with metals and adsorb them to cell surfaces because of interactions between the metal ions and the negatively charged microbial surfaces. Metals may also be complexed by carboxyl groups found in microbial polysaccharides and other polymers, or absorbed by protein materials in the biological cell.

The removal of metals in biological processes has been found to fit adsorption characteristics displayed by the Freundlich isotherm model (see Sec. 11-7 in Chap. 11) (Mullen et al., 1989; Kunz et al., 1976). A significant amount of soluble metal removal has been observed in biological processes, with removals ranging from 50 to 98 percent depending on the initial metal concentration, the biological reactor solids concentrations, and system SRT. In anaerobic processes the reduction of sulfate to hydrogen sulfide can promote the precipitation of metal sulfides. A classic example is the addition of ferric or ferrous chloride to anaerobic digesters to remove sulfide toxicity by the formation of iron sulfide precipitates. The precipitation of heavy metals by hydrogen sulfide is discussed in Sec. 6-5 in Chap. 6.

PROBLEMS AND DISCUSSION TOPICS

- 7-1** Prepare a recipe for an inorganic medium to be used in a laboratory chemostat to grow 500, 1000, or 1200 mg VSS/d (value to be selected by instructor) of bacteria biomass, assuming that the chemical formula for the biomass can be described as $C_5H_7NO_2$. Determine the concentration of essential inorganic compounds as reported in Table 7-4 for a feed rate of 1 L/d. Assume that phosphorus is added as KH_2PO_4 , sulfur as Na_2SO_4 , nitrogen as NH_4Cl , and other cations associated with chloride.
- 7-2** Protein is a major component of bacterial enzymes. List the key cell components involved and the major steps that lead to protein production.
- 7-3** From the literature (e.g., *Journal of Applied and Environmental Microbiology*) identify the key physiological, metabolic characteristics, and phylogenetic classification of a bacteria that may have a role in biological wastewater treatment or toxic degradation. Cite a minimum of 3 references.
- 7-4** From the literature, describe an application using molecular biology (e.g., molecular probes or other methods) techniques that can be related to biological wastewater treatment. Cite a minimum of 3 references.
- 7-5** A 1-L sample contains 20, 28, or 36 g (value to be selected by instructor) of casein ($C_8H_{12}O_3N_2$). If 18 g of bacterial cell tissue ($C_5H_7NO_2$) is synthesized per 50 g of casein consumed, determine the amount of oxygen required to complete the oxidation of casein to end products and cell tissue. The end products of the oxidation are carbon dioxide (CO_2), ammonia (NH_3), and water. Assume that the nitrogen not incorporated in cell-tissue production will be converted to ammonia.

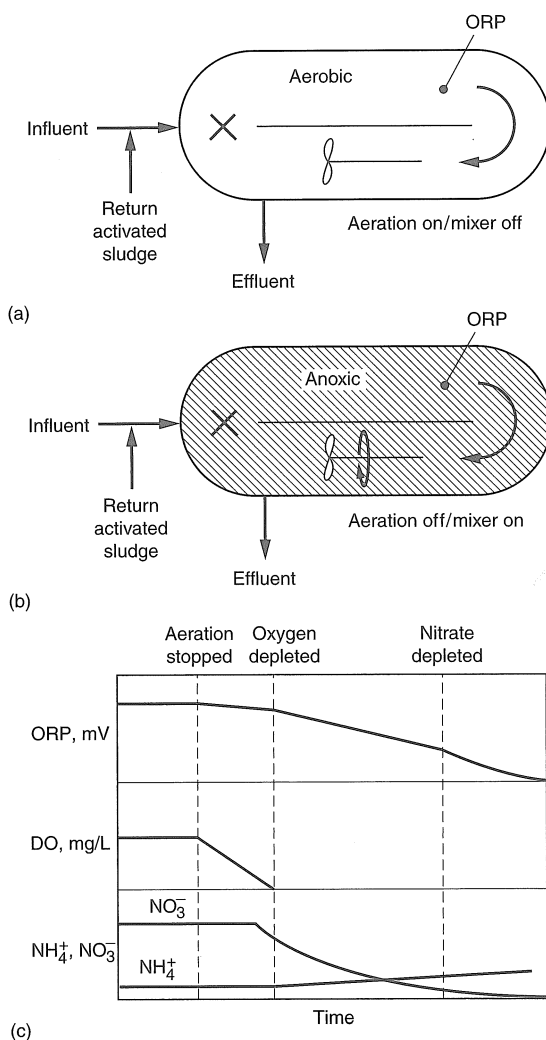
Intermittent Aeration Process Design

Long SRT systems, such as oxidation ditch processes, may employ intermittent aeration to accomplish both nitrification and denitrification in a single tank. During the aeration-off period, the aeration tank operates essentially as an anoxic reactor as nitrate is used in lieu of DO for BOD removal. During the anoxic period, the tank operation is similar to a preanoxic tank because influent BOD is added continuously to drive the denitrification reaction.

Operation of an oxidation ditch using intermittent aeration is shown on Fig. 8–28. Intermittent aeration systems typically are operated with SRT values in the range of 18 to 40 d and hydraulic detention times in excess of 16 h. During the anoxic reaction

Figure 8–28

Operation of a Nitrox™ oxidation ditch process using intermittent aeration: (a) aerobic conditions, (b) anoxic conditions, and (c) variations in ORP, DO, ammonia, and nitrate.



period (Fig. 8-28b), aeration is stopped, a submerged mixer is turned on, and nitrate is used as the electron acceptor. The reactor is operated as a complete-mix activated-sludge anoxic process. During the anoxic period, DO and nitrate are depleted and the ammonia concentration increases (see Fig. 8-28c). The time for the anoxic and aerobic periods is important in determining the system's treatment performance.

The anoxic/aerobic cycle times may be adjusted manually as part of the system operation to optimize the process performance. Alternatively, a patented process, Nitrox™, uses an oxidation-reduction potential (ORP) measurement to control the intermittent operation. The ORP response during an aeration-off period is shown on Fig. 8-28c. As the DO concentrations decline, the ORP value decreases. When the $\text{NO}_3\text{-N}$ is depleted, a dramatic decline in the ORP value occurs. The ORP decline is called the *ORP knee* and can be identified by calculating the ORP slope with time. In the Nitrox™ process, the ORP values are logged onto a computer, which is programmed to turn on the aeration based on the changing slope of the ORP. The aeration-off periods are selected to occur during different times of the day; the more ideal time is when the influent BOD concentration is high so that nitrate reduction occurs at a faster rate. The process behaves much like an anoxic selector as improved SVIs have been reported (Stensel et al., 1995).

Reported plant performance data for intermittent aeration processes indicate effluent $\text{NO}_3\text{-N}$ concentrations range from 3.0 to 4.8 mg/L. The processes are also predicted to produce effluent total nitrogen (TN) concentrations <8.0 mg/L (U.S. EPA, 1993). The relatively long τ values used provide sufficient dilution to minimize the effluent $\text{NH}_4\text{-N}$ concentrations during the OFF period. A sufficiently long SRT is also needed to provide enough nitrification capacity to allow the aeration system to be operated intermittently.

Because of the long SRT and τ , the denitrification kinetics are related to the overall degradation of bCOD, pbCOD, and endogenous decay and are not as strongly influenced by the rbCOD fraction as for the preanoxic denitrification application with the relatively short τ . During the complete-mix anoxic period in an intermittent oxidation ditch operation or in the anoxic zone of a continuously aerated oxidation ditch, the specific denitrification rate is affected by both the endogenous respiration rate and the bCOD in the influent wastewater as continuous feeding occurs. The average specific denitrification rate, which includes these effects, can be estimated by the following equation [based on Stensel (1981) and modified to account for the rate as a function of active heterotrophic biomass]:

$$\text{SDNR}_b = \frac{0.175A_n}{(Y_{\text{net}})\text{SRT}} \quad (8-54)$$

where SDNR_b = specific denitrification rate relative to heterotrophic biomass concentration, g $\text{NO}_3\text{-N/g}$ biomass $\cdot\text{d}$

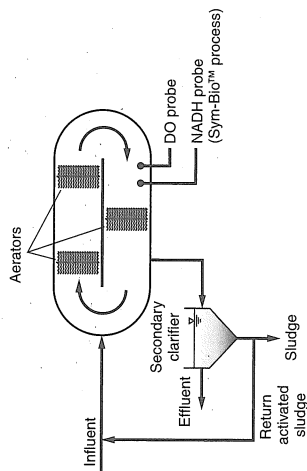
A_n = net oxygen utilization coefficient, g O_2/g bCOD removed

Y_{net} = net yield for heterotrophic biomass, g VSS/g bCOD

0.175 = based on 2.86 g O_2 equivalent/g $\text{NO}_3\text{-N}$ and the assumption that only 50% of heterotrophic biomass can use nitrate in place of oxygen

Simultaneous nitrification/denitrification

(k) Low DO oxidation ditch



Oxidation ditches that have sufficient volume available are able to accommodate both nitrification and denitrification at lower rates under low DO conditions. An oxidation ditch may be used to maintain DO concentrations below 0.5 mg/L with manual or automated DO control. Where multiple aerators are used, for example, with brush aerators, a low to zero DO is maintained throughout the channel. Besides DO control, other methods may be used, and one such method using NADH measurement is the Sym-Bio™ process.

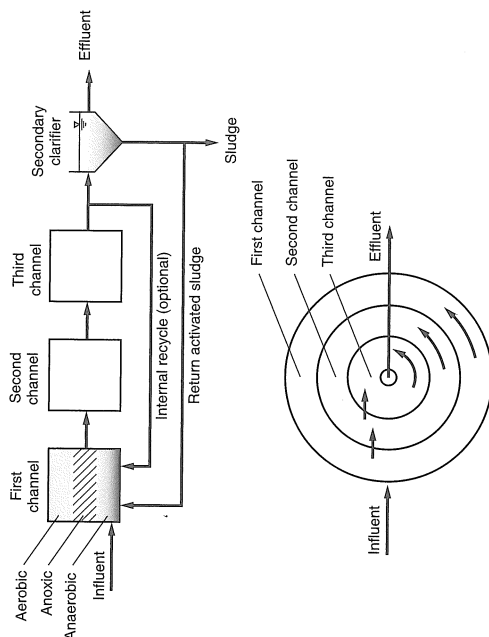
The Sym-Bio™ process uses both a DO probe and an NADH probe to control simultaneous nitrification/denitrification (Trivedi and Heinen, 2000). The bacteria content of the reduced form of coenzyme nicotinamide adenine dinucleotide (NADH) is measured by the emitted fluorescence after exposed to ultraviolet light emission by the NADH probe. NADH plays a significant role in bacteria reactions that involve the transfer of hydrogen. Under more reduced conditions, the ratio of NADH/NAD will increase in the bacteria cell. The NADH probe can be used to accomplish SNIEN by (1) monitoring the changes in NADH in the activated sludge and (2) controlling the operation of activated-sludge systems operated at low to zero DO concentrations. The process involves a series of steps; the DO is lowered and when the NADH/NAD ratio reaches a set value, the DO is increased to a higher level for a predetermined time. Effluent $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations of less than 3.0 and 1.0 mg/L, respectively, have been achieved

(continued)

Process

Simultaneous nitrification/denitrification (Continued)

(l) Orbal™

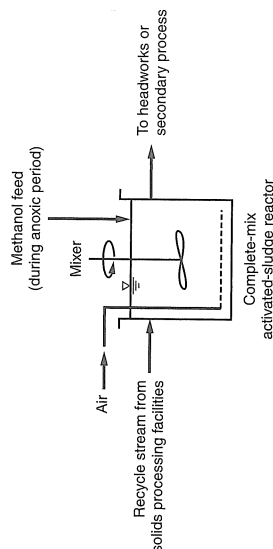


Description

The channels in the Orbal process are operated in series with a zero to low DO (<0.3 mg/L) concentration in the first channel, a 0.5 to 1.5 mg/L DO concentration in the second channel, and a higher DO concentration (2 to 3 mg/L) in the third channel. The first channel receives the influent wastewater and return activated sludge and generally contains about one-half the total basin volume. Volumes of the second and third channels are about one-third and one-sixth of the total basin volumes, respectively. Recycle of mixed liquor from the inner loop to the outer loop allows denitrification of nitrates resulting from nitrification in the inner channels. Variations of the process include operation with and without internal recycle flow (Bionutire™ process) from the third channel to the first channel. An oxygen supply rate of about 50% of the estimated design requirement has been recommended to support SNDn in the first zone

Nitrogen removal from digested sludge processing recycle flows

(m) Sharon (single-reactor high-activity ammonia removal over nitrite)



A sidestream treatment process, the Sharon process, has been developed at Delft University of Technology in the Netherlands to remove nitrogen biologically from recycle flows from dewatering of anaerobically digested solids (Hellinga et al. 1998). The recycle stream is also characterized by a relatively high temperature and high pH. The process takes advantage of high-temperature effects on nitrification kinetics, which favors more rapid growth of ammonia-oxidizing bacteria and inhibition of nitrite-oxidizing bacteria. A short residence time (1 to 2 d) is then used to favor mainly nitrite production with an on/off aeration operation that provides an anoxic operating period to reduce nitrite. Methanol is added during the anoxic period to provide an electron donor for nitrite reduction. Alternatively, the nitrite stream can be returned to the headworks to provide an electron acceptor for odor control

9-7 ATTACHED GROWTH DENITRIFICATION PROCESSES

Biological denitrification processes have been applied following secondary treatment nitrification processes to reduce the nitrate/nitrite produced. Typically, an exogenous carbon source is added to provide an electron donor that can be oxidized biologically using nitrate or nitrite. Both attached growth and suspended growth processes have been used for postanoxic denitrification with success. Suspended growth processes used for denitrification are discussed in Sec. 8-5 in Chap. 8. The different types of attached growth postanoxic processes, illustrated on Fig. 9-28, include (1) downflow and upflow packed-bed reactors, (2) upflow fluidized-bed reactors, and (3) submerged rotating biological contactors. All of the processes require carbon addition in the form of methanol to the influent. Methanol to $\text{NO}_3\text{-N}$ dose ratios are in the range of 3.0 to 3.5 kg methanol/kg $\text{NO}_3\text{-N}$. The general physical designs of the downflow Biocarbone® and upflow Biofor® and Biostyr® systems have been described in Sec. 9-6. Specific design loadings used for the various systems for attached growth postanoxic denitrification are presented and discussed in this section. Attached growth preanoxic denitrification processes are also considered.

Downflow Packed-Bed Postanoxic Denitrification Processes

Downflow packed-bed denitrification filters (see Fig. 9-28a) are deep bed filters [1.2 to 2.0 m (4 to 6.5 ft)] that have been used in many installations (U.S. EPA, 1993) for

Figure 9-28

Postanoxic attached growth denitrification processes: (a) downflow packed-bed reactor, (b) upflow packed-bed reactor, (c) fluidized-bed denitrification reactor, and (d) submerged rotating biological contactor.

