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Environmental Protection
Agency

Office of Drinking
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Technology Transfer

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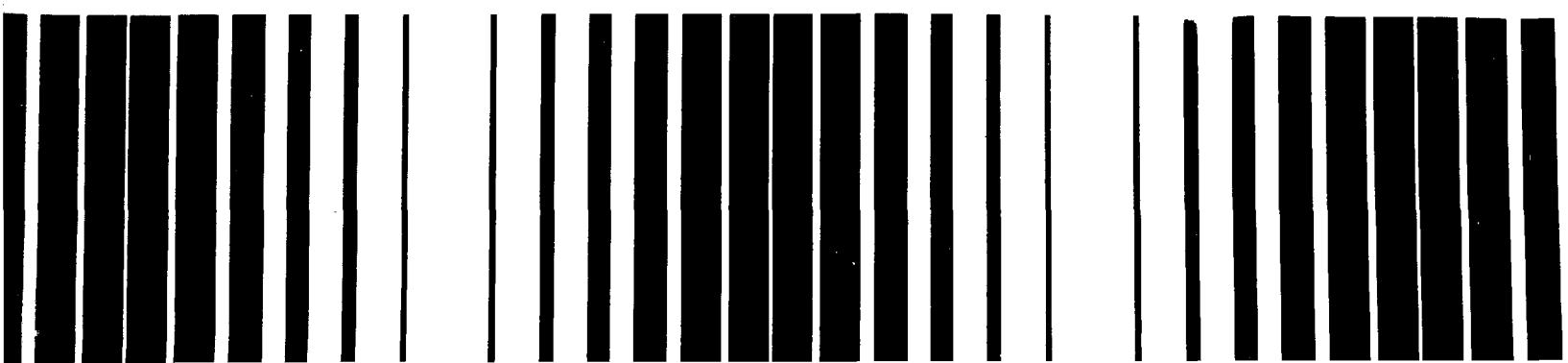
EPA

Workshop on Emerging Technologies for Drinking Water Treatment



CERI-88-23

WORKSHOP ON EMERGING TECHNOLOGIES FOR DRINKING WATER TREATMENT

April 1988

Sponsored by:

U.S. EPA Office of Drinking Water
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SDWA Amendments and Regulations

Stephen W. Clark, *Chief, Technical Section, Office of Drinking Water, US Environmental Protection Agency, Washington, DC*

EMERGING TECHNOLOGIES --

REGULATORY IMPACTS

SDWA -- MAJOR REQUIREMENTS

- **83 CONTAMINANTS BY JUNE 19, 1989**
- **TWO TREATMENT TECHNIQUES**
  - **FILTRATION (SURFACE SOURCES)**
  - **DISINFECTION (ALL)**
- **25 CONTAMINANTS IN 1991, 1994, . . . etc.**

EPA's CURRENT SCHEDULE

- **JUNE 1987 -- FLUORIDE & 8 VOCs**
- **DECEMBER 1987 -- FILTRATION**
- **JUNE 1988 -- 40 COMPOUNDS**
- **JUNE 1989 -- 34 COMPOUNDS**
- **JUNE 1991 -- DISINFECTION & BY-PRODUCTS**

BASIS OF MAXIMUM CONTAMINANT LEVELS (MCLs)

- **MCL GOAL (RISKS)**
- **MONITORING FEASIBILITY**
- **TREATMENT FEASIBILITY**
- **COSTS TO METROPOLITAN SYSTEMS**
- **NATIONAL IMPACTS**

MAJOR CONTAMINANT CATEGORIES

- **MICROBIALS**
- **DISINFECTION BY-PRODUCTS**
- **SYNTHETIC ORGANIC CHEMICALS (SOCs)**
- **INORGANIC CHEMICALS (IOCs)**
- **RADIONUCLIDES**

MICROBIALS

TREATMENT TECHNIQUES REQUIRED:

- MANDATED BY CONGRESS
- CANNOT MEASURE
- OUTBREAKS (POOR OR NO TREATMENT)
- INCREASED OUTBREAKS

SURFACE WATER TREATMENT RULE -- PERFORMANCE CRITERIA

- **99.9% REMOVAL / INACTIVATION GIARDIA**

- **99.99% REMOVAL / INACTIVATION VIRUSES**

TECHNOLOGY IMPACTS -- SURFACE WATER TREATMENT RULE

INCREASED USE OF :

- **MULTIMEDIA FILTERS**
- **OZONE**
- **POLYMERS**

DISINFECTANTS / BY-PRODUCTS

SET MCLs FOR :

- **CHLORINE**
- **CHLORAMINES**
- **CHLORINE DIOXIDE**
- **HALOMETHANES**
- **HALOACIDS**
- **HALOKETONES**
- **HALOALDEHYDES**
- **HALOPHENOLS**

DISINFECTANTS / BY-PRODUCTS -- HEALTH CONCERNS

- **BLOOD**
- **CENTRAL NERVOUS SYSTEM DEPRESSION**
- **CANCER**

CONTROL APPROACHES

- **REMOVE PRECURSORS**
- **ALTERNATE DISINFECTANTS**
- **REMOVE BY-PRODUCTS**

IMPACTS

- AFFECTS >200M PEOPLE
- HIGH COST
- BALANCE MICROBIAL SAFETY
- INCREASED USE OF :
    - COAGULANTS / POLYMERS
    - OZONE

ORGANICS -- HEALTH CONCERNS

- **VOCs : LIVER, KIDNEY, CNS, CANCER**
- **PESTICIDES : CNS, CANCER**
- **OTHER SOCs : CNS, LIVER, CANCER**

BEST AVAILABLE TECHNOLOGIES (BAT)

- **GRANULAR ACTIVATED CARBON (GAC)**
- **PACKED TOWER AERATION**

IMPACTS

- **MORE GROUND WATER TREATMENT**
- **AERATION & GAC**
- **ALSO; PAC, OZONE, MEMBRANES, AND RESINS**

KEY INORGANICS (IOCs)

- **LEAD**
- **NITRITE / NITRATE**
- **RADIONUCLIDES (Rn, U, & Ra)**
- **OTHERS (As, Se, Ba, F, etc.)**

LEAD -- HEALTH CONCERNS

- **CNS**
- **BLOOD FORMATION**
- **BLOOD PRESSURE (?)**

NITRITE / NITRATE -- HEALTH CONCERNS

- **ACUTE TOXICITY IN NEWBORNS**
- **BLUE BABY SYNDROME**
- **FATAL IF UNTREATED**

RADIONUCLIDES -- HEALTH CONCERNS

KNOWN HUMAN CARCINOGENS :

- **RADON - LUNG**
- **RADIUM - BONE**

BEST AVAILABLE TECHNOLOGIES

- **LEAD : CORROSION CONTROL**
- **NITRATE : ION EXCHANGE, REVERSE OSMOSIS**
- **RADON : AERATION**
- **RADIUM : ION EXCHANGE, REVERSE OSMOSIS**

IMPACTS

LEAD :

- CORROSION CONTROL - UNIVERSAL
- INCREASED MONITORING

OTHER IOCs :

- INCREASED TREATMENT

POINT OF ENTRY CRITERIA

- **CENTRAL CONTROL**
- **EFFECTIVE MONITORING**
- **EFFECTIVE APPLICATION**
- **MICROBIAL SAFETY**
- **PROTECT ALL CONSUMERS**

SMALL SYSTEM TECHNOLOGIES -- e.g.,

- **LIMESTONE BED (CORROSION)**
- **TANK AERATION (Rn & VOCs)**
- **SLOW SAND (FILTRATION)**

SUMMARY -- REGULATORY IMPACTS

- 83 CONTAMINANTS BY 1989
- DISINFECTION & FILTRATION TREATMENT
- DISINFECTION BY-PRODUCTS BY 1991
- FUTURE CONTAMINANTS : SOCs

SUMMARY -- TECHNOLOGY IMPACTS

- **MORE TREATMENT ($)**
- **MORE USE OF OZONE, RESINS, MEMBRANES, etc.**
- **MORE GROUND WATER TREATMENT**
- **SIMPLE TECHNOLOGIES (SMALL SYSTEMS)**

FACT SHEET

JUN 5 1987

Drinking Water Regulations under 1986 Amendments to SDWA

Significant directives to EPA's standard-setting program for drinking water contaminants included in the 1986 Amendments to the SDWA are provided below:

- o EPA is to set MCLGs and National Primary Drinking Water Regulations for 83 specific contaminants and for any other contaminant in drinking water which may have any adverse effect upon the health of persons and which is known or anticipated to occur in public water systems.

- o Recommended Maximum Contaminant Levels (RMCLs) are now termed Maximum Contaminant Level Goals (MCLGs). No changes were made in the basis of an MCLG; i.e.:

  > MCLGs are non-enforceable health goals which are to be set at the level at which no known or anticipated adverse effects on the health persons occur and which allows an adequate margin of safety.

- o Maximum Contaminant Levels (MCLs) are to be set as close to MCLGs as is feasible. The definition of "feasible" was changed to the following:

  > Feasible means with the use of the best technology, treatment techniques and other means, which the Administrator finds, after examination for efficacy under field conditions and not solely under laboratory conditions, are generally available (taking costs into consideration).

  Granular Activated Carbon (GAC) is stated in the SDWA as feasible for the control of synthetic organic chemicals (SOCs), and any technology or other means found to be best available for control of SOCs must be at least as effective in controlling SOCs as GAC.

- o MCLGs and MCLs are to be proposed at the same time and also promulgated simultaneously.

- o MCLGs and MCLs/Monitoring requirements are to be set for 83 contaminants listed in the SDWA. The best available technology (BAT) is also to be specified for each.

  The 83 contaminants are shown in Table 1. Seven substitutes are allowed if regulation of any seven other contaminants would be more protective of public health. The list of substitutes must be proposed by June 19, 1987.

- o The timetable to produce the MCLGs and MCLs/Monitoring is as follows:
  - 9 by June 19, 1987
  - 40 by June 19, 1988
  - 34 by June 19, 1989
- o MCLGs and MCLs/Monitoring are also to be set for other contaminants in drinking water that may pose a health risk.
  - The 1986 Amendments require the EPA to publish a list (Drinking Water Priority List) of drinking water contaminants that may require regulation under the SDWA.
  - The list must be published by January 1, 1988, and every 3 years following.
  - MCLGs and MCLs/Monitoring are to be set for at least 25 contaminants on the list by January 1, 1991.
  - MCLGs and MCLs/Monitoring are to be set for at least 25 contaminants every 3 years following January 1, 1991 (i.e. 1994, 1997,...).
- o Criteria must be established from which States can determine which surface water systems must install filtration. The criteria are to be set by December 19, 1987.
- o A treatment technique regulation is to be set that will require all public water systems to use disinfection.
  - Variances are available. EPA will specify variance criteria.
  - The disinfection treatment rule must be promulgated by June 19, 1989.
- o Requirements are to be set for water systems to monitor for unregulated contaminants.
  - Minimum monitoring frequency would be five years.
  - State can add/delete contaminants from list.
  - Monitoring regulations are to be promulgated by December 19, 1987.
- o MCLGS and MCLs/Monitoring requirements are to be reviewed by EPA every three years.

o Other requirements/provisions of the 1986 Amendments:

- Public notification regulations are to be changed to provide for different types and frequencies of notice depending upon the potential health risk. Final regulations are due September 19, 1987.

- BAT for issuance of variances is to be set when MCLs are set. BAT may vary depending upon the size of systems and other factors, including costs.

- Exemptions can be extended for systems with 500 connections or less. No limit is placed on the number of extensions but certain criteria will have to be met.

o A summary of deadlines pertinent to standard-setting is presented in Table 2.

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TABLE 1
Contaminants Required to be Regulated
under the SDWA of 1986

Volatile Organic Chemicals

Trichloroethylene
Tetrachloroethylene
Carbon tetrachloride
1,1,1-Trichloroethane
1,2,-Dichloroethane
Vinyl chloride
Methylene chloride
Benzene
Chlorobenzene
Dichlorobenzene
Trichlorobenzene
1,1-Dichloroethylene
trans-1,2,Dichloroethylene
cis-1,2,-Dichloroethylene

Microbiology and Turbidity

Total coliforms
Turbidity
Giardia lamblia
Viruses
Standard plate count
Legionella

Inorganics

Arsenic
Barium
Cadmium
Chromium
Lead
Mercury
Nitrate
Selenium
Silver
Fluoride
Aluminum
Antimony
Molybdenum
Asbestos
Sulfate
Copper
Vanadium
Sodium
Nickel
Zinc
Thallium
Beryllium
Cyanide

Organics

Endrin
Lindane
Methoxychlor
Toxaphene
2,4,-D
2,4,5-TP
Aldicarb
Chlordane
Dalapon
Diquat
Endothall
Glyphosate
Carbofuran
Alachlor
Epichlorohydrin
Toluene
Adipates
2,3,7,8-TCDD (Dioxin)
1,1,2-Trichloroethane
Vydate
Simazine
PAH's
PCB's
Atrazine
Phthalates
Acrylamide
Dibromochloropropane (DBCP)
1,2-dichloropropane
Pentachlorophenol
Pichloram
Dinoseb
Ethylene dibromide (EDB)
Dibromomethane
Xylene
Hexachlorocyclopentadiene

Radionuclides

Radium 226 and 228
Beta particle and photon radioactivity
Uranium
Gross alpha particle activity
Radon

TABLE 2

Summary of Deadlines
for Standards under SDWA of 1986

What	When
9 MCLGs and MCLs/Monitoring	June 19, 1987
Propose Seven Substitutes	June 19, 1987
Public Notice Revisions	Sept. 19, 1987
Filtration Criteria	Dec. 19, 1987
Monitoring for Unregulated Contaminants	Dec. 19, 1987
List of Contaminants	Jan. 01, 1988
40 MCLGs and MCLs/Monitoring	June 19, 1988
34 MCLGs and MCLs/Monitoring	June 19, 1989
Disinfection Treatment	June 19, 1989
25 MCLGs and MCLs/Monitoring	Jan. 01, 1991

Status: National Primary Drinking Water Regulations

Volatile Organic Chemicals (VOCs)

- ANPRM March 4, 1982 (47 FR 9350)
- Proposed MCLGs June 12, 1984 (49 FR 24330)
- Final MCLGs, proposed MCLs, Monitoring Nov. 13, 1985
- November 13, 1985 Federal Register
  - Extension of public comment period for 45 days on tetrachloroethylene MCLG.
  - NTP Report recently released
- Public Briefing: December 19, 1985 Washington, D.C.
- Public Hearing: January 13-14, 1986 Washington, D.C.

Final MCL and Monitoring June 1987: Summary

VOCs: Final MCLGs and MCLs (in mg/l)

	Final MCLG*	Final MCL
Trichloroethylene	zero	0.005
Carbon Tetrachloride	zero	0.005
Vinyl Chloride	zero	0.002
1,2-Dichloroethane	zero	0.005
Benzene	zero	0.005
para-Dichlorobenzene	0.075	0.075
1,1-Dichloroethylene	0.007	0.007
1,1,1-Trichloroethane	0.2	0.2

*Final MCLGs were published Nov. 13, 1985. The MCLG and MCL for p-dichlorobenzene were reproposed at zero and 0.005 mg/l on April 17, 1987; comment was requested on levels of 0.075 mg/l and 0.075 mg/l, respectively.

BAT for 1412 (MCLs):

° Packed tower aeration (PTA) and granular activated carbon (GAC) for the eight VOCs, except vinyl chloride.

° PTA for vinyl chloride.

BAT for 1415 (Variances):

° Same as BAT for 1412.

Compliance Monitoring:

° Initial Monitoring: All systems must monitor each sour at least once in four years.

- Surface waters: 4 quarterly samples
- Ground waters: 4 quarterly samples; state can exempt systems from subsequent monitoring if no VOCs detected in first sample,
- Composite samples of up to five sources allowed

° Phase in by system size (start monitoring: January 1, 1988).

Size	Complete by	Date
> 10,000	1 year	December 31, 1988
3300-10,000	2 years	December 31, 1989
< 3300	4 years	December 31, 1991

° Repeat monitoring: varies from quarterly to once per five years. The frequency is based on whether VOCs are detected in the first round of monitoring and whether system is vulnerable to contamination.

Monitoring for Unregulated VOCs:

° Initial monitoring: all systems required to sample each drinking water source once for unregulated VOCs during a four year period.

° Same phase-in schedules as compliance monitoring.

° 50 VOCs specified:

- List 1: required for all systems (33 VOCs)
- List 2: required for vulnerable systems (2 VOCs)
- List 3: required at State discretion (15 VOCs)

° Repeat monitoring: Every five years; EPA will specify a new list.

Analytical Methods: GC or GC/MS

° Methods 504, 502.1, 503.1, 524.1, 524.2, 502.2

Laboratory Certification Criteria:

° Seven VOCs: $\pm$ 20% $\geq$ 0.004 mg/l

$\pm$ 40% < 0.004 mg/l

° Vinyl Chloride: $\pm$ 40% < 0.004 mg/l

Non-transient Non-community Water Systems (NTWS):

° Non-community water systems which regularly serve at least 25 of the same persons over 6 months per year (i.e., NTWS) are required to meet all requirements in this rule.

Point-of-Entry (POE), Point-of-Use (POU), and Bottled Water:

- POE may be used to achieve compliance with MCLs but is not BAT.
- POU and bottled water cannot be used to meet MCLs.

Variances and Exceptions

- As a condition of issuing a variance or exemption, states have the authority to require the water system to implement additional interim control measures. If an unreasonable risk to health exists, the state must require either installation of point-of-use devices or distribution of bottled water to each customer.

IOCs, SOCs, Microbials

- ANPRM October 5, 1983
- Proposed MCLGs, November 13, 1985, Federal Register (50 FR 46936)
- Repoprosed MCLGs, proposed MCLs/Monitoring scheduled for September 1987. Final June 1988.

Proposed MCLGs for SOCs

SOC	Existing NIPDWR (mg/l)	Proposed MCLG (mg/l)
Acrylamide	--	zero
Alachlor	--	zero
Aldicarb, aldicarb sulfoxide and aldicarb sulfone	--	0.009
Carbofuran	--	0.036
Chlordane	--	zero
cis-1,2-Dichloroethylene	--	0.07
DBCP	--	zero
1,2-Dichloropropane	--	0.006

Proposed MCLGs for SOCs continued

SOC	Existing NIPDWR (mg/l)	Proposed MCLG (mg/l)
1,2-Dichloropropane	--	0.006
o-Dichlorobenzene	--	0.62
2,4-D	0.1	0.07
EDB	--	zero
Epichlorohydrin	--	zero
Ethylbenzene	--	0.68
Heptachlor	--	zero
Heptachlor epoxide	--	zero
Lindane	0.004	0.0002
Methoxychlor	0.1	0.34
Monochlorobenzene	--	0.06
PCBs	--	zero
Pentachlorophenol	--	0.22
Styrene	--	0.14
Toluene	--	2.0
2,4,5-TP	0.01	0.052
Toxaphene	0.005	zero
trans-1,2-Dichloroethylene	--	0.07
Xylene	--	0.44

Proposed MCLGs for IOCs

IOC	Existing NIPDWR (mg/l)	Proposed MCLG mg/l
Arsenic	0.05	0.050
Asbestos	--	7.1 MFL
Barium	1.0	1.5
Cadmium	0.010	0.005
Chromium	0.05	0.12
Copper	--	1.3
Lead	0.05	0.020
Mercury	0.002	0.003
Nitrate	10	10
Nitrite	--	1.0
Selenium	0.01	0.045

MFL = million fibers per liter

Proposed MCLGs for Microbiological Parameters

Parameter	Existing NIPDWR	Proposed MCLG
Total Coliforms	1-4/100 ml	Zero
Turbidity	1-5 NTU	0.1 NTU**
Giardia*	--	Zero
Viruses*	--	Zero

*Analytical methods do exist but they are not considered to be technically and economically available for Giardia or viruses for use in compliance monitoring. Are included in filtration rule.

**Nephelometric Turbidity Unit.

Fluoride

° ANPRM October 5, 1983

° Proposed MCLG May 14, 1985

° Final MCLG, Proposed MCL, SMCL, Monitoring Nov. 14, 1985

° Final MCL, SMCL, Monitoring April 2, 1986

Final MCLG	4 mg/l
Final MCL	4 mg/l
Final SMCL	2 mg/l
Final Monitoring	1 per year surface waters 1 per 3 years ground waters Minimum repeat: 1 per 10 years

Radionuclides

° ANPRM September 30, 1986

Draft MCLGs for Radionuclides

Radionuclide	Draft MCLG
Radium 226	zero
Radium 228	zero
Uranium	zero

Draft MCLGs for Radionuclides (continued)

Radionuclide	Draft MCLG
Uranium	zero
Radon	zero
Gross Alpha particle article	zero
Beta particle and photon radioactivity	zero

° Proposed MCLGs/MCLs/Monitoring scheduled for January 1988. Final December 1988.

Other IOCs and SOCs

° Proposed MCLGs/MCLs/Monitoring scheduled for June 1988. Final June 1989.

° IOCs and SOCs:

Methylene Chloride
Antimony
Endrin
Dalapon
Diquat
Endothall
Glyphosate
Adipates
2,3,7,8-TCDD (Dioxin)
Trichlorobenzene
Standard plate count
Legionella
Sulfate
Nickel
Thallium
Beryllium
Cyanide
1,1,2-Trichloroethane
Vydate
Simazine
PAH's
Atrazine
Phthalates
Pichloram
Dinoseb
Hexachlorocyclopentadiene

Substitutes and Drinking Water Priority List

° Proposal June 19, 1987. Final January 1, 1988.

° Candidates for removal from SDWA List of 83:

- Zinc
- Silver
- Sodium
- Molybdenum
- Vanadium
- Dibromomethane

In addition, other candidates listed for public comment are:

- Sulfate
- Phthalates

° Candidates for Substitution into List of 83:

- Aldicarb sulfoxide
- Aldicarb sulfone
- Ethylbenzene
- Heptachlor
- Heptachlor epoxide
- Styrene
- Nitrite

Drinking Water Priority List

Zinc	2,4-Dinitrotoluene
Silver	1,3-Dichloropropane
Sodium	Bromobenzene
Aluminum	Chloromethane
Molybdenum	Bromomethane
Vanadium	1,2,3-Trichloropropane
Dibromomethane	1,1,1,2-Tetrachloroethane
Chlorine	Chloroethane
Hypochlorite ion	2,2-Dichloropropane
Chlorine dioxide	o-chlorotoluene
Chlorite	p-chlorotoluene
Chloramine	hexachlorobenzene
Ammonia	hexachloroethane
Trihalomethanes (chloroform, dibromochloromethane, bromodichloromethane, bromoform)	hexachlorobutadiene
	1,1-dichloropropene
	2,4,5-T
Chlorophenols	Isophorone
Halonitriles	Ethylene thiourea
Selected disinfection related chlorinated acids, alcohols, aldehydes, and ketones	Boron
	Strontium
	Cryptosporidium
Chloropicrin	

Filtration/Coliforms

° Surface Water Treatment Rule (filtration and Disinfection) to be proposed August 1987. Draft includes following:

General Requirements and Definitions

- Coverage: all public water systems using any surface water.

- Treatment technique requirements in lieu of MCLs for Giardia, viruses, heterotrophic plate count bacteria, Legionella, Turbidity

- Treatment definition is at least 99.9 percent removal or inactivation of Giardia lamblia cysts and at least 99.99 percent removal or inactivation of enteric viruses.

- Technical definitions are provided for "surface" water and appropriate treatment processes.

° Criteria under which filtration is required

- Source water quality conditions under which disinfection only is considered safe (fecal coliform concentrations less than 20 per 100 ml or total coliforms less than 100 per 100 ml in 90 percent of the samples and a maximum turbidity level of less than 5 NTU).

- Site-specific conditions to be met including disinfectant levels, monitoring, watershed management programs, sanitary surveys, waterborne disease outbreak history, total coliform and total trihalomethane MCL compliance history.

- Primacy Agency must determine that all conditions are met or filtration is required.

° Disinfection requirements for unfiltered water supplies

- All systems must disinfect.

- Performance criteria: achieve 99.9 percent inactivation of Giardia lamblia cysts and 99.99 percent inactivation of enteric viruses (as appropriate).

- Operating criteria: disinfectant concentration and disinfectant contact times required to obtain the inactivation rates specified in the performance criteria are published in the rule.

- Design criteria: redundancy of components, and auxiliary power supply.

- Monitoring requirements: continuously monitor disinfectant concentration at the plant and demonstrate a disinfectant residual concentration in 95 percent of the distribution system samples.

° Disinfection requirements for filtered water supplies

- Disinfection with filtration must achieve at least 99.9 percent and 99.99 percent removal/inactivation of

Giardia and viruses, respectively. Primacy agency defines level of disinfection required, depending on technology and source water quality.

- Monitoring requirements: continuously monitor disinfectant concentration at the plant and demonstrate a disinfectant residual concentration in 95 percent of the distribution system samples.

° Filtration requirements

- Filtration must be installed when the system fails to meet source water quality or site-specific conditions.

- Performance requirements in terms of turbidity levels are set for commonly used filtration technologies (e.g., conventional, direct, slow sand and diatomaceous earth filtration technologies).

- Other technologies (including emerging and innovative technologies) can be approved by the Primacy Agency if they achieve the performance criteria for Giardia lamblia and virus removal/inactivation.

° Monitoring and Analytical Requirements

- EPA approved methods for total coliforms, fecal coliform, turbidity, disinfectant residual, temperature, and pH are proposed.

- Specified frequency of monitoring for each parameter and numbers of analyses required, varies according to population served.

° Reporting, Public Notice and Recordkeeping

- Requirements include monthly reports to the Primacy Agency on coliform concentrations, turbidity levels, disinfectant concentration, pH, water temperature, disinfectant contact time and disinfectant residuals.

- Unfiltered water systems must also report annually on their watershed control program and sanitary surveys.

- Water-borne outbreaks must be reported within 48 hours.

° Violations

- All systems with unfiltered surface water sources must meet source water quality and site-specific conditions within 48 months of promulgation. If they fail to meet these criteria within 30 months, filtration would be required, but they would not be in violation until failing to meet such criteria after 48 months.

- Monitoring requirements for unfiltered, raw water quality must be met within 30 months of promulgation.

- Performance criteria and monitoring/reporting requirements for the filtered and disinfection treatment techniques must be met within 48 months of promulgation.

Total Coliform MCL

° Maximum contaminant level goal--zero

° Maximum contaminant levels

- Based on presence or absence of total coliforms in sample, rather than density.

- Monthly MCL

  -- No more than 1 coliform-positive sample/month for systems which analyze fewer than 40 samples/month.

  -- No more than 5% of samples can be coliform-positive if system analyzes at least 40 samples/month.

- Long-term MCL

  -- No more than 5% of most recent 60 samples coliform-positive if system analyzes fewer than 60 samples/year.

  -- No more than 5% of all samples in most recent 12-month period can be coliform-positive if system analyzes at least 60 samples/year.

° Monitoring frequency

- For systems serving 3,300 persons or fewer:

  -- 5 samples/month, with less monitoring for systems which:

     (a) filter and disinfect surface water and disinfect ground water; and

     (b) have a sanitary survey at the frequency specified in the proposed regulation.

- For systems serving more than 3,300 persons:

  -- Based on population served

  -- Similar to current minimum monitoring requirements for coliforms, but with smaller number of population categories.

° Repeat samples

- If system has coliform-positive sample, system must collect five repeat samples all on the same day from same location as original sample, except some may be from the next service connection.

- If any repeat sample is coliform-positive, system must:

  -- Analyze positive culture medium to determine if it contains fecal coliforms; and

  -- Collect and analyze another set of five repeat samples all on the same day, unless the MCL has been violated and the system has notified the State.

° Heterotrophic bacteria (HPC)

- No MCLG/MCL is proposed.

- Proposed regulation based on HPC interference with total coliform analysis and considers effectiveness of disinfection and filtration controlling HPC levels.

- If coliform sample produces a turbid culture in the absence of gas production, using the Multiple-Tube Fermentation Technique or produces confluent growth or a colony number that is "too numerous to count" using the membrane filter technique, the system may either accept the sample as coliform-positive or declare the sample invalid and collect and analyze another water sample. Second sample is analyzed for both total coliforms and HPC. If HPC is greater than 500 colonies/ml, then sample is considered coliform-positive, even if total coliform analysis is negative.

° Variances and exemptions--none allowed

° Waterborne disease outbreaks--States must search for and investigate possible occurrences of such outbreaks.

State Implementation of the SDWA
Frederick A. Marrocco, *Vice President, Association of State Drinking Water Administrators and Chief, Division of Water Supplies, Pennsylvania Department of Environmental Resources, Harrisburg*

Handout materials not available.

Current and Emerging Treatment Technologies

Robert M. Clark, *Director, Drinking Water Research Division, US Environmental Protection Agency, Cincinnati, OH*

Treatment Techniques (Robert M. Clark, Director, Drinking Water Research Division, US Environmental Protection Agency, Cincinnati, OH).

The Safe Drinking Water Act (SDWA) of 1974 requires that EPA establish maximum contaminant level goals (MCLG) for each contaminant in drinking water which may have an adverse effect on the health of persons. Each Goal is required to be set at a level at which no known or anticipated adverse effects on health occur, allowing an adequate margin of safety. The SDWA also requires that National Primary Drinking Water Regulations (NPDWRs) establishing maximum contaminant levels (MCLs) or treatment techniques, and secondary drinking water regulations be established. The purpose of this paper is to describe the activities of the Drinking Water Research Division (DWRD) of EPA in evaluating the various technologies that may be available for achieving these MCLs.

In addition to conducting research into technological alternatives, the DWRD provides technical advice and assistance to State agencies, EPA regional offices, water utilities and professional organizations. Amendments to the SDWA have increased regulatory pressure and accelerated the timetable for establishing MCLs. DWRD's activities and its role in satisfying the amendments will be discussed in terms of the following SDWA admendment categories: contaminants to be regulated; surface water filtration; mandatory disinfection; and prohibition of use of lead materials. In addition DWRD's work which is intended to study and characterize the factors that lead to deterioration of water quality in distribution systems will be discussed.

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REGULATED CONTAMINANTS

DWRD is conducting research in three major areas associated with regulated contaminants. These areas are: disinfection by-products; organic contaminants; and, inorganic contaminants.

DISINFECTION BY-PRODUCTS

Disinfection by-products research is perhaps the most significant and controversial area of research ever undertaken by EPA in the drinking water field. The major and most important disinfection by-products are total trihalomethanes (TTHM). In addition over 500 additional disinfection by-products have been identified. An objective of this research is to establish the feasibility of lowering the TTHM standard which of course will have many ramifications for the water supply industry. In addition, a limited number of additional disinfection by-products are being quantified.

Two major pathways of research are currently being pursued. One is the identification and characterization of the by-products of chlorination disinfection and the second is the evaluation of various treatment techniques to control byproducts using results from in-house pilot plant studies. By-products of all other types of disinfection are being studied as well. Because of the complexity of the research effort a disinfection by-product workgroup has been formed to bring various groups within ORD together with the Office of Drinking Water to maintain communication in this research area.

Identification of By-Products

DWRD has been actively developing methods for identifying the various by-products associated with chlorine disinfection. Most of this work has been conducted at the bench scale. The Division has also been working closely with the Technical Services Division of ODW to isolate the various by-products identified in field studies.

The major disinfection by-products found to-date include the following: trihaolmethanes (4 compounds), dihaloacetonitrile (3 compounds), chloroacetic acid (3 compounds), chlorohydrate, chloropicrin, 1,1,1-trichloropropenone, Table 1 lists these compounds and the general ranges within which they have been found. From 30-60% of TOX in drinking water is associated with these disinfection by-products.

TABLE 1. COMMON DISINFECTION BY-PRODUCTS

General Compound Identification	Number of Individual Compounds	Nominal Concentration in ug/L		
		< 10	10-100	> 100
Trihalomethanes	4			X
Dihaloacetonitriles	3	X		
Chloracetic Acids	3	X	X	X
Chloral Hydrate				X
Chloropicrin		X		
1,1,1-Trichloropropanone		X		

Control of Disinfection By-Products

Figure 1 is a schematic of DWRD's in-house pilot plant. Two parallel channels are being evaluated. The channel at the top of the figure is a control in which the pilot-plant is being operated as a conventional filtration plant with chlorine added at the head works. In the bottom channel the point-of-chlorination has been moved to minimize disinfection by-products, primarily total trihalomethanes, and to simultaneously maintain control of microbiological quality throughout the plant. The influent to both channels is spiked with coliform, phage and raw sewage. A side stream from the lower channel is passed through granular activated carbon (GAC).

Based on work conducted to-date, microbiological quality has been maintained and TTHMs minimized when chlorination was moved to a point just before the filter. Assimable Organic Carbon (AOC) is also being measured throughout the plant in order to characterize the biological quality of the water that might enter the distribution system. Based on preliminary work AOC is also reduced when chlorination is moved to a point just before filtration.

Recent results indicate that with a properly optimized treatment system chloramines can minimize TTHM formation and also maintain microbiological control. This area of investigation is continuing

ORGANIC CONTAMINANTS

Despite the complexity of setting MCLs for health threatening agents, Congress has been placing great pressure on EPA to regulate organic contaminants more extensively. A number of drinking water contaminants have yet to be regulated. At this time only a few revisions of existing regulations have been made although the SDWA requires a review of regulations at least every three years.

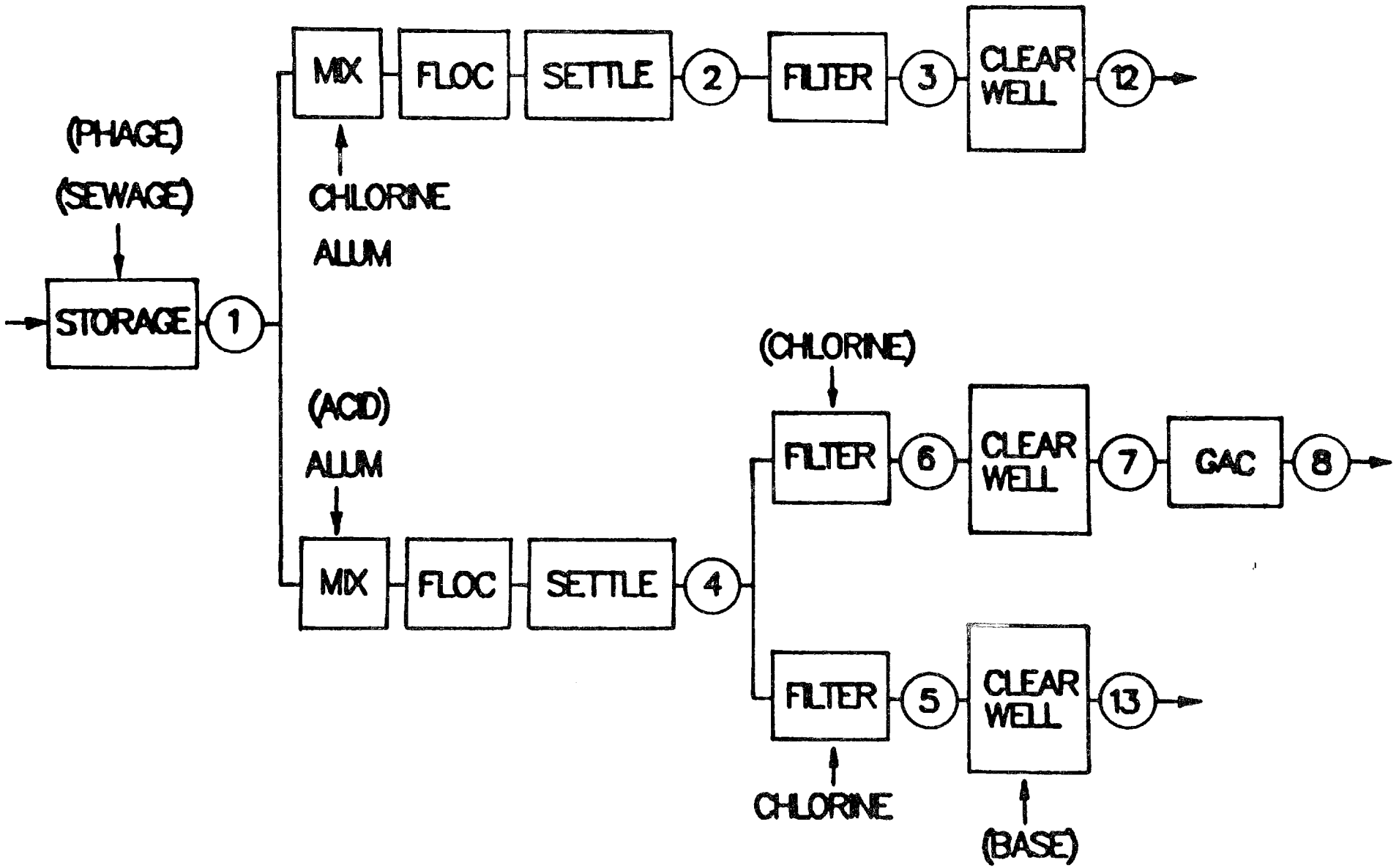

FIGURE 1. PILOT PLANT SCHEMATIC FOR DISINFECTION BY—PRODUCT CONTROL

Traditionally EPA's technology program has utilized the approach of carefully evaluating process kinetics on the bench, scaling up for engineering feasibility at the pilot-scale, and making field-scale evaluations to evaluate process economics. This approach may take several years for completion and involve several million dollars for each unit process examined. Regulatory pressure will no longer allow for a contaminant-by-contaminant and process-by-process evaluation.

As mentioned previously, recent amendments to the SDWA require a large number of Synthetic Organic Chemicals (SOCs) to be considered for regulation under stringent time deadlines.[1] A key provision for potential regulation under the SDWA is that a feasible technology be available to remove each contaminant regulated. For SOCs, granular activated carbon (GAC) by law is feasible technology. Table 2 summarizes the synthetic organic compounds for which DWRD is currently developing carbon usage rate data. In order to calculate these data several approaches are being taken. One approach is to develop usage rate data based on microcolumn data and the other is to calculate usage rates based on field scale studies. These approaches will be described in the following sections.

TABLE 2. CARBON USAGE RATES FOR SELECTED ORGANICS

2,4-D	Endrin	EDB
Silvex	Phthalate(s)	DBCP
Lindane	Adipate(s)	1,2-Dichloropropane
Methoxychlor	PAH(s)	Cis-1,2-Dichloroethylene
Toxaphene	Hexachlorocyclopentadiene	Trans-1,2-dichloroethylene
Chlordane	Dioxin	Chlorobenzene
Heptachlor	Simazine	o-Dichlorobenzene
Heptachlor Epoxide	Atrazine	Toluene
PCS(s)	Diquat	Styrene
Pentachlororophenol	Endothall	Ethyl Benzene
Alachlor	Picloram	o-Xylene
Carbofuran	Dalapon	m-Xylene
Aldicarb	Dinoseb	p-Xylene
Aldicarb Sulfone	Glyphosate	Dibromomethane
Aldicarb Sulfoxide	Oxamyl	1,1,2-Trichloroethane

Microcolumn Data

Microcolumns are being used to study GAC adsorption. The adsorption protocol involves developing a set of single solute isotherms in both distilled and natural waters. Using the Freundlich isotherm parameters, the homogeneous surface diffusion adsorption model (HSDM) is employed to generate breakthrough curves and predict carbon usage rates for fixed-bed GAC column operation both at microcolum and at full-scale. Other inputs to the HSDM are kinetic parameters estimated from correlations given in the literature and parameters defining the carbon type and the system hydraulics.

For some SOCs, predicted full-scale usage rates are found to be cost effective, i.e., typically beyond a two-year service life, and these full-scale usage rates are used as inputs to cost models. A typical HSDM-generated full-scale breakthrough curve is given in Figure 2.

For poorer adsorbed SOCs, full-scale predications show shorter service lives, and microcolumn operations are conducted. Because microcolumn breakthrough curves represent empirical kinetic phenomenon rather than correlated estimates, the microcolumn breakthrough curves are scaled-up to full-scale conditions. These scaled-up usage rates are used as inputs to cost models.

The microcolumns were designed to give constant-pattern breakthrough curves based on the HSDM. The apparatus consists of a 4 mm Inside Diameter (ID) glass column packed with US Standard Seive 100 x 200 mesh Filtrasorb 400 GAC at a depth sufficient to contain the mass transfer zone for the compound. Other requirements are a prefilter to prevent excessive head loss across the column, dampers to smooth out pump delivery and maintain constant pressure on the column, and a flexible head space bag to restrict loss of volatile contaminants. The apparatus is described in Figure 3. For SOCs having full-scale service lives of less than two years, microcolumn breakthrough curves may be

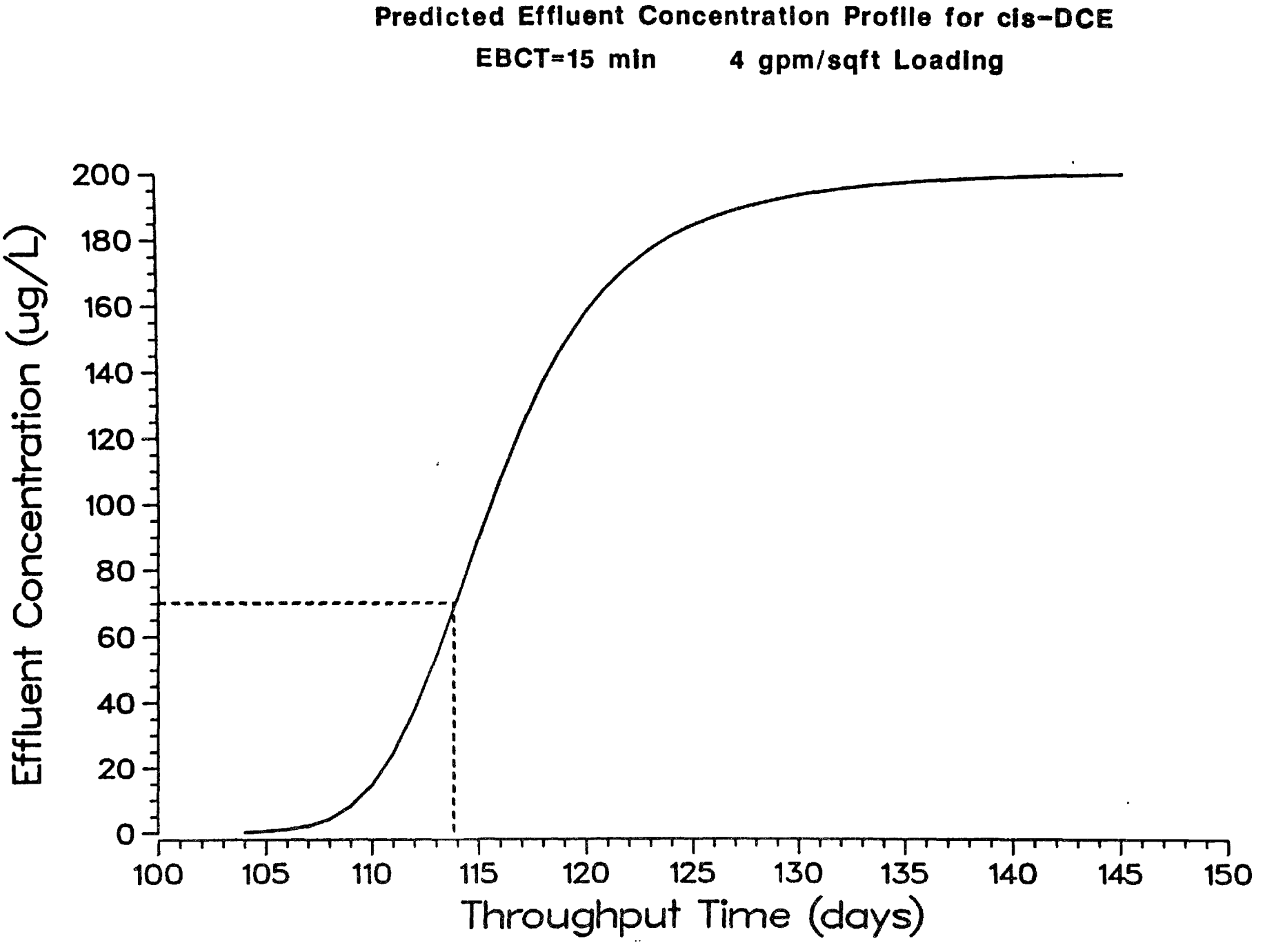

FIGURE 2. TYPICAL BREAKTHROUGH CURVE FOR FULL SCALE SYSTEM

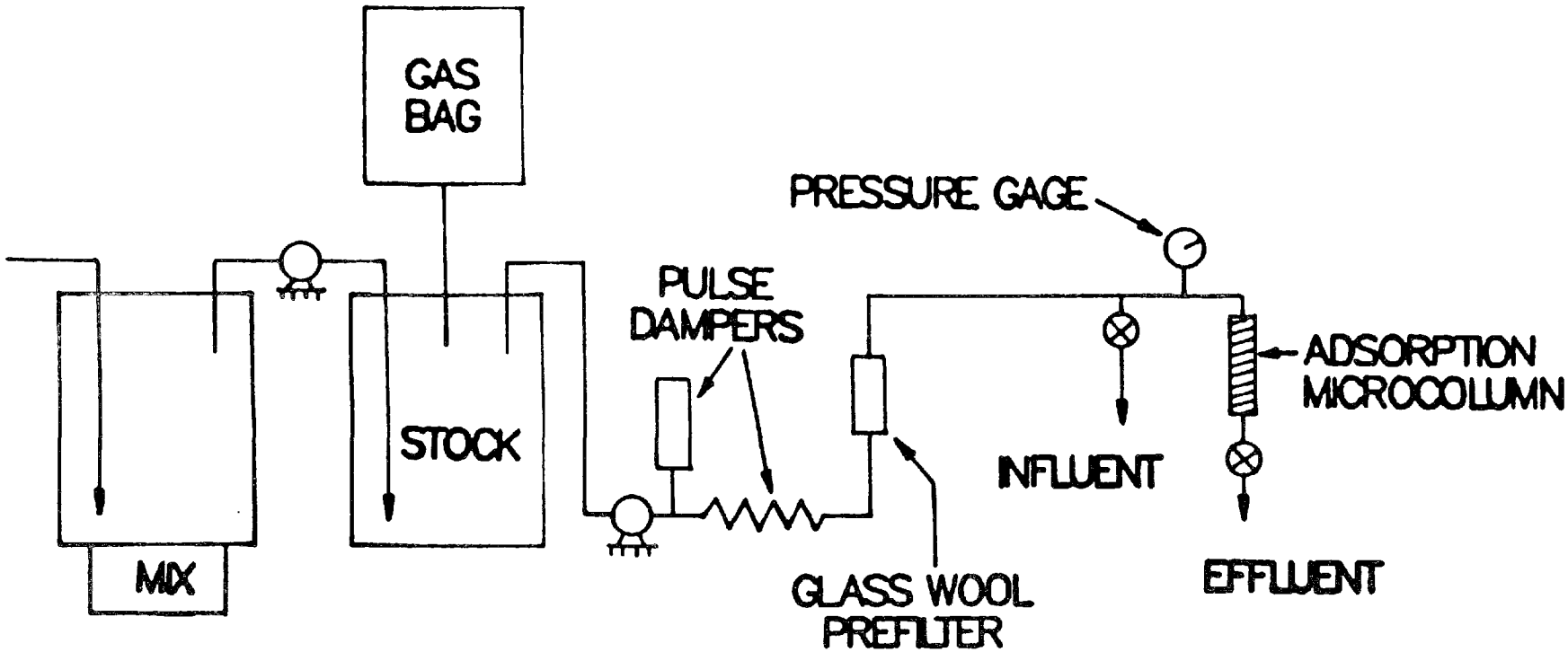

FIGURE 3. ADSORPTION MICROCOLUMN SCHEMATIC

generated in less than 5 days. This is compatible with the short regulatory time frame. Figure 4 shows a typical microcolumn breakthrough curve.

Once the full-scale breakthrough curves are developed for each compound, field-verified cost equations are used to generate full-scale costs.[2] A computer program has been developed that uses breakthrough curve data to calculate carbon usage rates, and ultimately calculate costs for a wide number of carbon systems. A set of costs generated from this procedure at various sizes of application has been developed. For the data prepared for this analysis, it is assumed that the carbon systems were consistent with the following conditions: EBCT = 15 minutes; loading rate = 4 gpm/ft^2; carbon type = Filtersorb 400. These were full-scale conditions that were used in the HSDM.

Several treatment plant sizes were assumed with emphasis on small systems. Steel pressure contactors were assumed for GAC adsorption in systems with a design capacity less than or equal to 1 mgd. Concrete gravity contactors were assumed in larger systems. All systems were assumed to operate at 50% plant capacity. Spent carbon replacement versus reactivation alternatives were selected based on least cost. Cost parameters used in the analysis are presented in Table 3.

TABLE 3. COST PARAMETERS USED IN ANALYSIS

Item	Value
GAC Price	$0.70/lb @ 40,000 lbs
Capital Recovery Interest Rate	10%
Amortization Period	20 years
ENR Construction Cost Index	4229
Producers Price Index	294
Labor Rate	$11/manhour
Electric Rate	$0.07/kwh
Fuel Oil Rate	$0.90/gallon
Process Water Rate	$0.50/1000 gallons
GAC Bulk Density	30 lbs/ft^3
GAC Loss Rate from Reactivation	11%

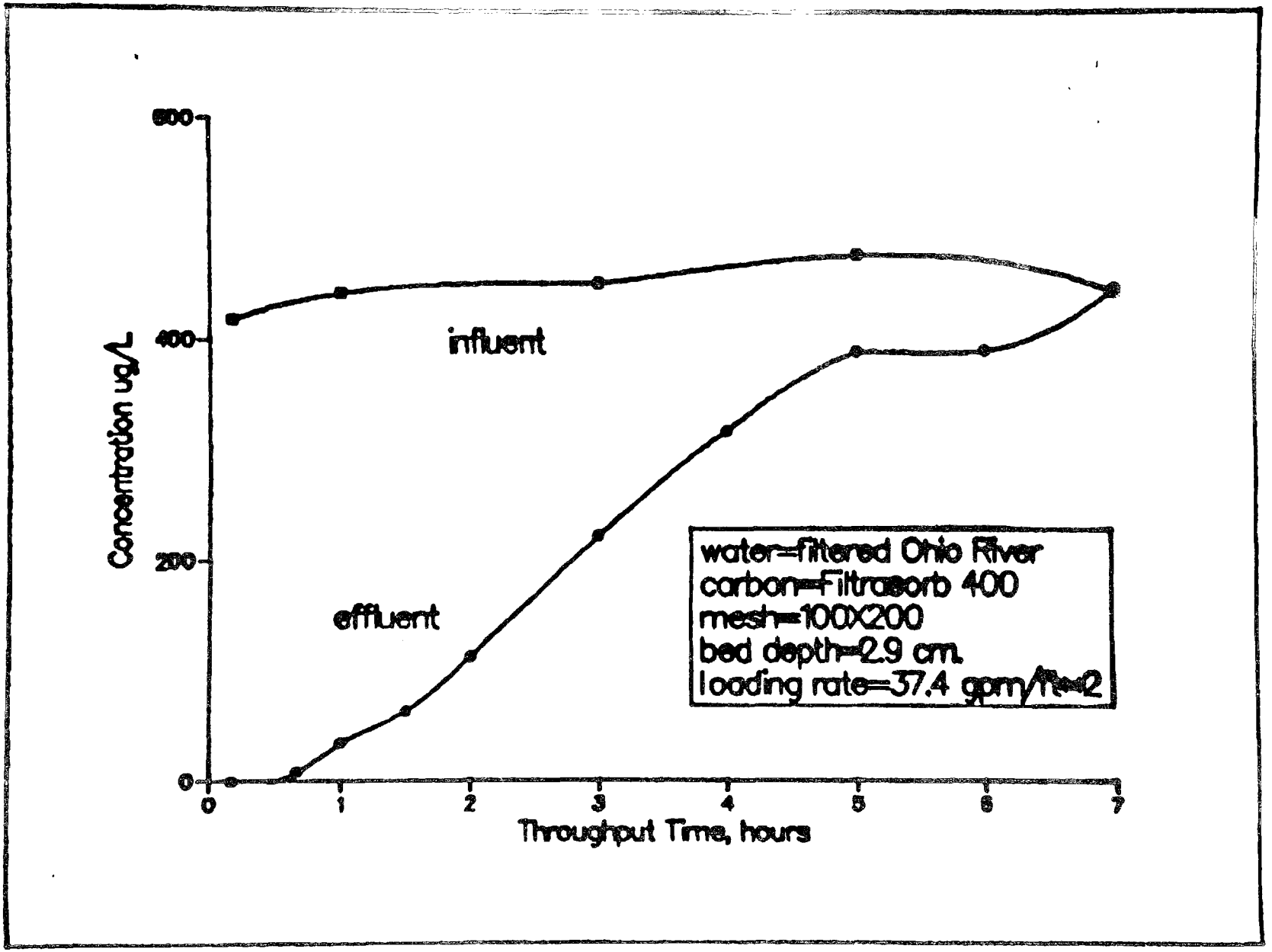

FIGURE 4. MICROCOLUMN ADSORPTION OF TRANS—1,2—DICHLOROETHYLENE

An example of the SOCs examined, their influent and effluent concentrations, and type of water studied in each case are given in Table 4. Most of the scenarios are worst-case situations which provide conservative cost estimates for removal of the single-solute SOCs. Table 4 presents a matrix of GAC system costs for various usage rates and plant capacities. All estimates are determined using 1986-year prices and cost indices. Using the data in Table 4, two sets of cost-curves were generated: (1) a set of graphs displaying cost as a function of system capacity at a fixed usage rate (designated by specific SOC removal), (2) a set of graphs displaying cost as a function of usage rate or GAC bed life at a fixed system capacity. These cost-curves can be very useful in analyzing cost sensitivity with variations in system size, use rate and bed life.

In general, the most significant cost impacts appear to be with systems that have a capacity of less than 5 mgd and/or a GAC bed life shorter than 4 months (>0.4 lbs/1000 gal). At system capacities greater than 40 mgd the cost curve has a fairly flat response showing small changes in cost with variations in system size. Likewise, when the GAC bed life is longer than 1 year, the change in cost with variation in usage-rate is small. For systems larger than 10 mgd, the fairly flat response of the cost curve extends down to a GAC bed life of 6 months (<0.23 lbs/1000 gal). It appears that for strongly adsorbed compounds the GAC bed life could be reduced by as much as 100% and the cost would only increase by approximately 10 to 20%. An interesting example is as follows: if the GAC usage-rate increases by a factor of 10 (1000% increase) from 0.0572 lbs/1000 gal (2-year bed life) to 0.6 lbs/1000 gal (69-day bed life), the cost increases by only a factor of 2 (100% cost increase).

Table 4. GAC COSTS FOR VARIOUS USE RATES AND SYSTEM SIZES

Use Rate, lbs/1000 gal	.0572	.0626	.0734	.0832	.1176	.178	.2191	.2336	.2713	.378	.45	.6046	1.2
Service Life, days	730	667	569	502	355	234	191	179	154	110	93	69	35
	A	B	C	D	E	F	G	H	I	J	K	L	M
Design Capacity (MGD)	Total System Cost (¢/1000 gal)												
.25	83.8	84.6	86.2	87.6	92.6	101.1	106.9	108.9	114.1	128.7	138.5	159.3	237.8
.75	79.1	79.8	81.3	82.7	87.4	95.6	101.1	103.0	108.0	122.1	132.9	151.3	228.0
1	67.9	68.6	70.1	71.5	76.1	84.2	89.7	91.6	96.5	110.4	119.6	139.3	213.7
2	40.2	40.9	42.3	43.7	48.2	56.1	61.4	63.2	68.0	81.5	90.5	109.7	121.0
3	35.2	35.9	37.3	38.6	43.1	50.8	56.0	57.9	62.6	71.1	73.7	79.4	100.8
5	30.3	31.0	32.4	33.6	38.0	45.6	48.5	49.1	50.5	54.4	57.0	62.5	83.4
7	27.7	28.4	29.8	31.0	35.4	39.4	40.9	41.5	42.9	46.7	49.3	54.7	75.4
10	25.4	26.1	27.4	28.7	31.1	33.4	34.9	35.4	36.7	40.5	43.1	48.5	68.8
20	21.1	21.3	21.7	22.0	23.3	25.4	26.9	27.4	28.7	32.4	34.9	39.9	55.4
30	18.0	18.2	18.6	19.0	20.2	22.3	23.7	24.2	25.5	29.2	31.1	35.2	56.8
50	15.2	15.4	15.7	16.1	17.3	19.4	20.8	21.2	22.2	25.0	30.5	34.6	53.6
70	13.7	13.9	14.3	14.6	15.8	17.8	18.9	19.2	20.2	25.0	27.5	31.5	51.9
100	12.4	12.6	13.0	13.3	14.5	16.1	18.9	19.4	20.2	23.1	24.9	30.8	49.5

A = two-year service life
B = chlorobenzene, Ci = 600 ug/L, Ce = 6 ug/L, Milli-Q distilled water
C = chlorobenzene, Ci = 600 ug/L, Ce = 6 ug/L, filtered Ohio River water
D = aldicarb, Ci = 500 ug/L, Ce = 1.3 ug/L, filtered Ohio River water
E = EDB, Ci = 100 ug/L, Ce = 1, Milli-Q distilled water
F = 1,2-dichloropropane, Ci = 100 ug/L, Ce = 2 ug/L Milli-Q distilled water
G = trans-DCE, Ci = 100 ug/L, Ce = 70 ug/L filtered Ohio River water
H = 1,2-dichloropropane, Ci = 100 ug/L, Ce = 2 ug/L filtered Ohio River water
I = toluene, Ci = 5000 ug/L, Ce = 100 ug/L, distilled Wausau water
J = cis-DCE, Ci = 200 ug/L, Ce = 70 ug/L, filtered Ohio River water
K = 93 day service life
L = trans-DCE, Ci = 500 ug/L, Ce = 70 ug/L, filtered Ohio River water
M = 35 day service life

This cost analysis suggests that highly accurate predictions of GAC adsorption performance for many SOCs may not be necessary because of the apparent insensitivity of cost with mild changes in usage rate. From the cost curves this appears to be valid for situations where the GAC bed life is longer than 6 months. It was found that capacities and thus costs are most sensitive to the parameters in the Freundlich isotherm equation. The costs presented herein were generated using a computer program written for the IBM-PC/AT.

Other Technologies Studies

Other technologies being examined at the bench and pilot scale for control of organics include ozone oxidation, reverse osmosis, ultraviolet treatment, and ultrafiltration.

Ozone Oxidation

Ozone oxidation is being studied extensively in DWRD's in-house pilot plant facilities.[3] Controlled pilot plant ozone treatment tests have been conducted on 29 VOCs in distilled water and groundwater. Results showed that aromatic compounds, alkenes and certain pesticides are well removed by ozone treatment but that alkanes are poorly removed. Also, removal efficiency improved for the alkenes and aromatic compounds with increasing ozone dosage and for some alkanes with increasing pH. For most compounds, the efficacy of ozone was not affected by the background water matrix. Information from the literature concerning the ozone treatment of pure materials in the gaseous or liquid phase generally predicted the effectiveness of ozone in treating aqueous solutions.

Reverse Osmosis

Revesrse osmosis (RO) has shown some promise in removing both VOCs and SOCs from groundwater.[4] Most of the efforts by DWRD to date have been on a pilot- or bench-scale basis, with some limited application of reverse osmosis for the removal of organics at one field site. Primary indications are that certain RO membranes are very effective in removing a wide range of organic chemicals.

Ultraviolet Treatment

Ultraviolet light also shows some promise for removing organic contaminants, particularly when combined with ozone. DWRD is in the process of funding a project with the Los Angeles Water and Power Company that deals with the removal of VOCs from groundwater using these two technologies. If successful, these chemicals will be oxidized to CO_2 and water, and the need to deal with off-gas control problems will be eliminated.

Ultrafiltration

Studies have been conducted to evaluate the costs and performance of low pressure membrane processes (ultrafiltration) for TTHM precursor reduction in small systems. A 150 day pilot-plant of two highly organic contaminanted ground waters (both of which produced more than 400 ug/L THMs when conventionally treated) produced a finished water that easily met the Trihalomethane Maximum Contaminant Level (100 ug/L). Costs appears to be reasonable.[12] More extensive testing of this technology is underway.

Field-Tested Technologies

Carbon Adsorption

Extensive field scale studies have been conducted on the use of granular activated carbon (GAC) treatment with onsite regeneration. Past research has

devoted to demonstrating the effectiveness of GAC for surface water treatment.[5] Extensive field testing has been conducted at Jefferson Parish and Cincinnati, Ohio. Other field sites include: Manchester, New Hampshire; Evansville, Indiana; Miami, Florida; Huntington, West Virginia; Beaver Falls, Pennsylvanis; and Passaic, New Jersey.

More recently, DWRD has been conducting studies that incorporate the use of carbon treatment for removal of VOCs and SOCs from groundwater at Suffolk County, New York, California's San Joaquin Valley, and Wausau, Wisconsin. Each of these projects is designed to examine a different aspect of GAC application and except for Wausau, are intended to deal with the little-understood pesticide contamination problem.

A typical project is in Suffolk County, New York, where the removal of organics, pesticides, and nitrates is being studied under various flow situations. Two parallel treatment systems (one consisting of GAC and ion exchange and the other consisting of reverse osmosis) are being operated at low flows similar to home usage. Costs for these two systems will be established along with unit operating efficiency so that a large public water supply system can be designed and tested. The results from this study will be applicable to other areas, especially in farming communities, where multiple contamination of groundwater is identified.

Two principle objectives of a project being conducted in the San Joaquin Valley study are to (1) develop cost-effective design criteria for the removal of DBCP and other pesticides from water supplies by GAC, (2) to compare treatment methods other than GAC for the removal of these compounds, and (3) to improve and strengthen existing administrative guidelines and jurisdictional responsibilities pertaining to both community water systems and private wells

containing the compounds of interest. Pilot studies will be conducted with GAC, and results will be compared with those existing operating systems. These comparisons should lead to recommendations for more effective design and operational criteria for GAC units used by water systems. The focus in this study will be on point-of-use GAC units that are now in use by small systems, individual homeowners, and farmers in the area. Disposal of treatment residues is also being studied.

The third site, in Wausau, Wisconsin, has multiple contaminants in its groundwater source from a nearby superfund site. Figure 5 shows a typical breakthrough curve from the Wausau carbon field study.

GAC is the primary technology being studied, but air-stripping is being examined as a companion technology. The Wausau project is unique in that modeling techniques are being used to predict full-scale design criteria for a GAC plant. These predictions will be evaluated against the actual cost and performance associated with building of GAC contactors onsite. the results from this study are expected to provide a useful methodology for extension to other GAC applications. Modeling techniques will be particularly useful in studying the long list of SOCs and VOCs that may be proposed for regulation under the current and future provisions of the Safe Drinking Water Act. In addition to modeling, minicolumn technology is also being studied. This methodology allows investigators to acquire water from a given site and to study the performance of a small, high-pressure column in the presence of a natural water background. Results from these minicolumn experiments are expected to reproduce the breakthrough curves normally seen in pilot- and full-scale facilities.

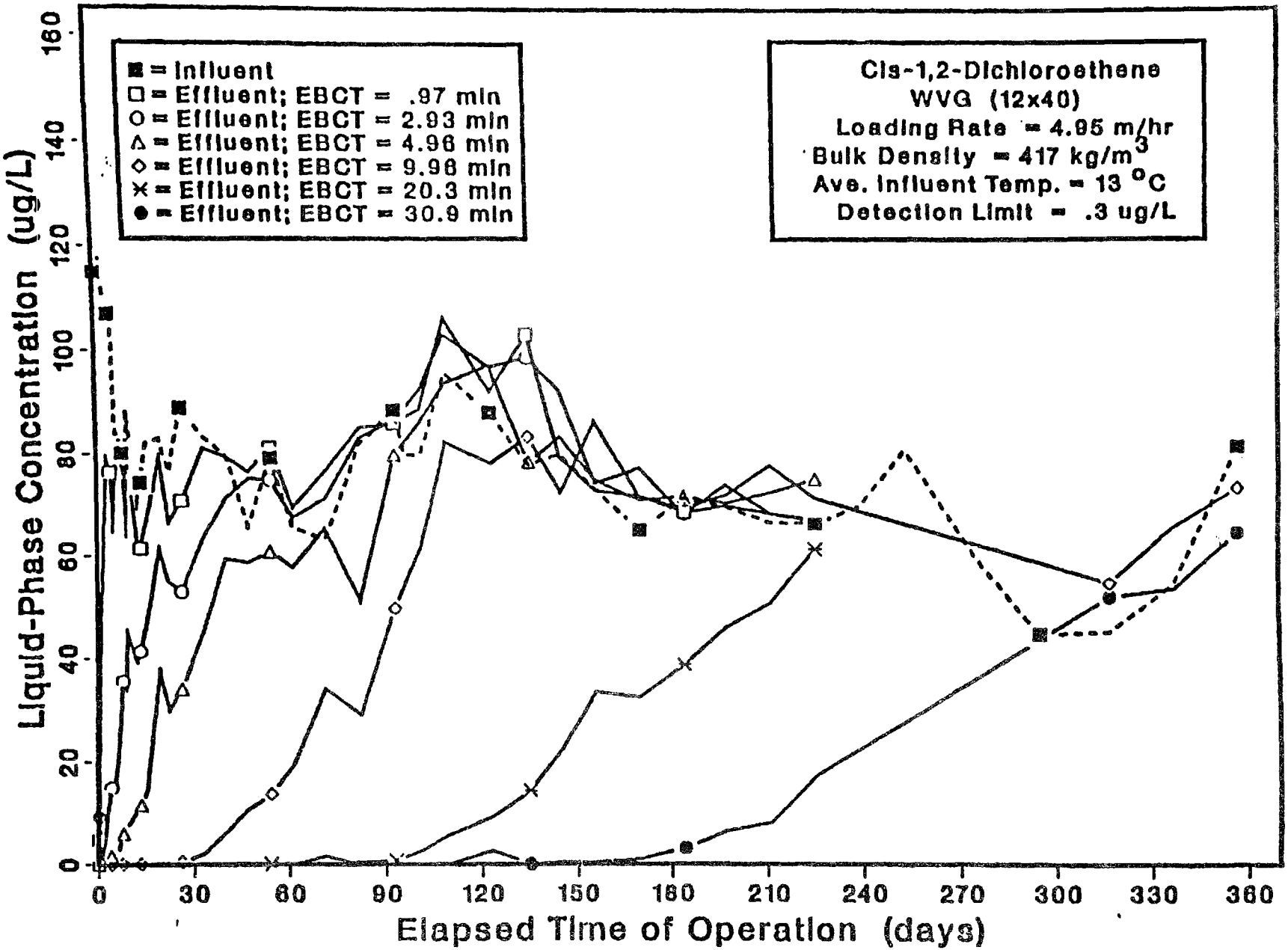

FIGURE 5. PILOT SCALE DATA FROM WAUSAU, WISCONSIN

Packed Tower Aeration

Aeration technology has proved to be especially effective for the removal of VOCs. However, the research at Wausau, Wisconsin (which also incorporates air stripping and off-gas control technology) indicates that aeration may in some cases be effective for removing compounds that have somewhat lower Henry's Law Constants than would normally be expected to be removed by this process. In this project, as with carbon facilities, modeling is being used to predict the performance of packed-tower aeration and results are promising. The off-gas control portion of the air stripping project at Wausau is being conducted in cooperation with the American Water Works Association Research Foundation.

DWRD also has another air-stripping research project currently underway at Baldwin Park, Calfifornia which is examinaing the removal of VOCs from a groundwater supply. As in Wausau, the Baldwin Park project is exmaining the problems of off-gas control technology.[6]

Another field-scale activity dealing with air-stripping has been concluded at Brewster, New York. In this project, modeling techniques and pilot-scale facilities were used to determine the scale-up relationships to be used for full-scale, air-stripping facilities. The purpose of the project was to develop a technique that could be used by consulting engineers to adequately predict the cost and performance of full-scale facilities using pilot aeration columns.

Conventional Treatment

Conventional treatment is unlikely to be used for removing organic contaminants from groundwater. However, field studies are being conducted at Tiffin, Ohio, where the river source contains high spikes of pesticides

because of local seasonal agricultrual applications. Powdered activated carbon, added to the water normally treated only by conventional treatment, appears to be quite effective for removing synthetic organic chemicals.

Secondary Discharge Problems

When evaluating treatment technology one has to be aware of the possibilities of creating secondary discharge problems. For example, while conducting GAC research on surface water supplies, it was discovered that dioxins were formed in the reactivation process. An extensive evaluation led to the installation of an afterburner, which was found to eliminate those dioxin byproducts when operating at a temperature of 2400°F.[7]

At Baldwin Park, California, the use of high-stack dispersion was investigated as a means of minimizing the impact of VOC removal from groundater. At Baldwin Park and at Wausau, Wisconsin, gas-phase carbon adsorption is being investigated for removal of both VOCs and SOC from air stripping waste gases.

The project with the Los Angeles Water and Power Company is intended to investigate the water-phase oxidation of VOCs and SOCs to CO_2 and H_2O using ozone in combination with ultraviolet light. Gas-phase oxidation of VOCs and SOCs by ozone and ultraviolet light also appears promising.

Future work will concentrate on residuals control from various unit processes such as reverse osmosis and ultrafiltration.

Inorganic Contaminants

Several field scale studies are being conducted for inorganics control. These technologies include: ion exchange and reverse osmosis. Specific

contaminants being removed include nitrates, radium and radon. Each of these technologies is discussed in the following paragraph.

Ion Exchange

Ion exchange technology has been field-tested for nitrate removal under a DWRD-supported cooperative agreement and has been pilot-tested for uranium removal at sites in the western part of the United States.[8,9]

The nitrate removal plant has been operating automatically for about 3 years. The 1-mgd (0.38 ML/d) demonstration plant is located in McFarland, CA and consists of three anion exchange vessels that are designed to reduce nitrate levels to below 10 mg NO_3-N/L, the EPA MCL and also the California requirement. Currently, about 500 gpm (32 L/S) of water is being treated and about 200 gpm (13 L/S) is bypassed and later blended with the treated water, resulting in a total product flow of 700 gpm (44 L/S). The blended water adequately meets the nitrate MCL and EPA's Secondary Regulation (Fed. Reg. 1979) for chloride and sulfate levels.[10]

Bench-scale studies were initally conducted at EPA-Cincinnati for uranium removal and later pilot-tested. The laboratory work showed that when drinking water containing 300 ug/L uranium was passed through anion exchange resin, more than 9,000 bed volumes were treated before breakthrough was observed. DWRD then evaluated the performance of twelve 1/4-cubic-foot (0.007 m^3) anion-exchange systems installed in New Mexico, Colorado, and Arizona at sites where uranium levels in the raw water exceeded 20 ug/L. Results confirmed the findings shown in the laboratory. Because of the high loading capacity of the anion resins for uranium, these units are well suited for point-of-use applications where on-site regeneration is not feasible. For centralized treatment, the resin may be regnerated and recycled by backwashing it with sodium chloride solution.

Reverse Osmosis

Groundwater sources in Illinois, Iowa, Florida, Texas, Wisconsin, and some Rocky Mountain states contain radium in excess of the 5 pCi/L MCL. RO treatment of radium-laden ground water was demonstrated in 1977 when DWRD and Sarasota County, FL water supply staff undertook a cooperative effort to study the operation of eight RO systems.[11] The systems were located in small communities serving a population from 39 to 15,000 and the design capacities varied from 800 gpd (3 kL/d) to 1 mgd (3.8 ML/d). Six different manufacturers of RO systems were represented and both the hollow fiber and spiral wound cellulose acetate membranes were used. The study showed from 82-96% Ra-226 removal for all systems, resulting in treated water that contained below the EPA MCL of 5 pCi/L.

RO technology has also been pilot tested for nitrate removal as part of DWRD cooperative agreements at three locations.[12,13,14] As mentioned previously, high nitrate levels exist in the well waters of Suffolk County, LI, NY, along with several SOCs.[12] This combination of organic and inorganic contaminants is the reason that RO was selected as one of the treatment technologies to be studied there. Seven commercially available membranes were evaluated for their rejection capabilities. Nitrate removals ranged from 75-95%, and research is continuing with one of the polyamide membranes that proved relatively efficient for both nitrate and SOC rejection. At Charlotte Harbor, FL both high pressure (265-359 psig) and low pressure (163-187 psig) RO systems were studied for the removal of several spiked inorganic contaminants, including nitrate, from a natural groundwater.[13] The investigation showed that the high pressure system was significantly more effective for removing all substances measured. The comparison for nitrate

removals, for example, was 80% vs. 6-24%. Before ion exchange was selected for full-scale evaluation at McFarland, CA, a 20,000 gpd (77 m^3/d) RO system was examined for nitrate removal.[14] Even though the system experienced frequent electrical and mechanical failures, nitrate rejection of about 65% was achieved.

Radium Removal Technologies

DWRD has sponsored research to study promising methods for radium removal.[15,16] The ion exchange process, with both weak acid resin and strong acid resin were investigated. Both resins effectively removed radium from water to well below the 5 pCi/L MCL and, in most cases, to <0.5 pCi/L, respresenting over 96% removal. The weak acid resin in the hydrogen form also removed hardness, which was not the case for the strong acid resin in the calcium form. The maximum capacity of the weak-acid resin was about 2.3 times that of strong acid resin and much less spent regenerate per unit volume of water treated was produced from the weak-acid column than from the strong-acid column. Another part of this project was to determine the feasibility of Dow Chemical Company's Radium-Selective Complexer (RSC) for removing radium from brines compared with typical groundwaters. The RSC is a synthetic resin that has a high affinity for radium. The capacity of RSC was observed to have been about 200 times greater in 450 mg/L TDS water than in 40,000 mg/L TDS brine (51,000 pCi/dry g vs. 300 pCi/dry g). However, the effect of other parameters, including calcium, sodium, and other ions, in addition to EBCT, needs to be determined. The application of the RSC for treatment of radium from brines is presently being studied at a small community in Colorado under a research cooperative agreement with DWRD.

Radon Removal Technologies

In response to the Agency's recent emphasis on radon in the environment, DWRD has funded a project to evaluate several treatment techniques for the removal of radon from community water supplies. Three treatment methods, packed tower aeration, diffused bubble aeration and granular activated carbon (GAC) will be evaluated for the removal of radon from two community water supplies in New Hampshire. The study will compare the methods for effectiveness, costs, operation, maintenance and other related factors. To accomplish the objectives, the three treatment systems will be constructed and operated at each of the two sites. The two sites selected are trailer parks, one whose water supply serves 40 homes with an average daily flow of 4.6 gpm and an average radon concentration of 155,000 pCi/L. The other location has 56 homes, the average daily water usage is 6.3 gpm, and the average radon concentration is 40,000 pCi/L. After construction of the treatment systems, they will be operated for 6-12 months. At the end of this project, a report will be developed as a guideline to help State Agencies and small communities select an appropriate technology for radon gas treatment in public water supplies.

Summary of Technologies Studied

Table 5 summarizes the treatment technoliges that DWRD is evaluating for removal of VOCs, synthetic organic chemicls (SOCs), nitrates, and radionuclides from water supplies. The table indicates carbon adsorption is effective for removing both VOCs and SOCs. Packed tower and diffused aeration are best suited for removing VOCs. Ion exchange has been field-tested to show effective removal of nitrates and pilot-tested for uranium removal Reverse osmosis (RO) has proven to be effective in the field for radium

removal and pilot-tested for nitrate removals. Of the technologies that show promise and are being tested at the bench- and pilot-scale, conventional treatment with powdered activated carbon (PAC) is effective for removing a few of the SOCs, ozone oxidation is effective for removing certain classes of VOCs and SOCs, and certain reverse osmosis membranes and ultraviolet treatment are also potentially effective against VOCs and SOCs. Aeration and carbon adsorption are being examined for their radon removal capabilities.

Table 6 summarizes the various technologies examined for contaminant removal, and based on data gathered to date, it attempts to characterize their relative performances for both Phase I and Phase II organics.

TABLE 5. TREATMENT TECHNOLOGIES EVALUATED BY DWRD FOR REMOVING VOCs, SOCs, NITRATES, AND RADIONUCLIDES FROM DRINKING WATER

Technology Status	Technology	Contaminant Class or Specific Contaminant Removed
Field-tested	1. Carbon Adsorption	1. VOCs, SOCs
	2. Packed Tower and Diffused-Air Aeration	2. VOCs
	3. Ion Exchange	3. Nitrates
	4. Reverse Osmosis	4. Radium
Pilot-tested	1. Reverse Osmosis	1. Nitrates, Uranium
	2. Ion Exchange	2. Uranium
Promising Technologies	1. Conventional Treatment with Powdered Activated Carbon	1. SOCs
	2. Ozone Oxidation	2. VOCs, SOCs
	3. Reverse Osmosis	3. VOCs, SOCs
	4. Ultraviolet Treatment	4. VOCs, SOCs
	5. Ion Exchange	5. Radium
	6. Selective Complexer	6. Radium
	7. Aeration	7. Radon
	8. Carbon Adsorption	8. Radon

TABLE 6. PERFORMANCE SUMMARY FOR ORGANIC TECHNOLOGIES EXAMINED

Regulatory Phase	Organic Compounds	REMOVAL EFFICIENCY† Granular Activated Carbon Adsorption Filtrasorb 400[a]	Packed Tower Aeration	Reverse Osmosis Thin Film Composite	Ozone Oxidation (2-6 ppm)	Conventional Treatment
VOLATILE ORGANIC CONTAMINANTS						
	Alkanes					
I	Carbon Tetrachloride	++	++	++	0	0
I	1,2-Dichloroethane	++	++	+	0	0
I	1,1,1-Trichloroethane	++	++	++	0	0
II	1,2-Dichloropropane	++	++	++	0	0
II	Ethylene Dibromide	++	++	++	0	0
II	Dibromochloropropane	++	+	NA	0	0
	Alkenes					
I	Vinyl Chloride	++	++	NA	++	0
II	Styrene	NA	NA	NA	++	0
I	1,1-Dichloroethylene	++	++	NA	++	0
II	cis-1,2-Dichloroethylene	++	++	0	++	0
II	trans-1,2-Dichloroethylene	++	++	NA	++	0
I	Trichloroethylene	++	++	++	+	0
	Aromatics					
I	Benzene	++	++	0	++	0
II	Toluene	++	++	NA	++	0
II	Xylenes	++	++	NA	++	0
II	Ethylbenzene	++	++	0	++	0
II	Chlorobenzene	++	++	++	+	0
II	o-Dichlorobenzene	++	++	+	+	0
I	p-Dichlorobenzene	++	++	NA	+	0
PESTICIDES						
II	Pentachlorophenol	++	0	NA	++	NA
II	2,4-D	++	0	NA	+	0
II	Alachlor	++	++	++	++	0
II	Aldicarb	NA	0	NA	NA	NA
II	Carbofuran	++	0	++	++	0
II	Lindane	++	0	NA	0	0
II	Toxaphene	++	++	NA	NA	0
II	Heptachlor	++	++	NA	++	NA
II	Chlordane	++	0	NA	NA	NA
II	2,4,5-TP	++	NA	NA	+	NA
II	Methoxychlor	++	NA	NA	NA	NA

(See footnotes at end of table)

(Continued)

TABLE 6. PERFORMANCE SUMMARY FOR ORGANIC TECHNOLOGIES EXAMINED (Contd.)

Regulatory Phase	Organic Compounds	REMOVAL EFFICIENCY† Granular Activated Carbon Adsorption Filtrasorb 400[a]	Packed Tower Aeration	Reverse Osmosis Thin Film Composite	Ozone Oxidation (2-6 ppm)	Conventional Treatment
	OTHER					
II	Acrylamide	NA	0	NA	NA	NA
II	Epichlorohydrin	NA	0	NA	0	NA
II	PCB's	++	++	NA	NA	NA

†++ = Excellent 70% - 100%
+ = Average Removal 30% - 69%
0 = Poor 0% - 29%
NA = Data not available or compound has not been tested by EPA Drinking Water Research Division
a = Excellent removal category for carbon indicates compound has been demonstrated to be adsorbable onto GAC, in full- or pilot-scale applications, or in the laboratory with characteristics suggesting GAC can be a cost-effective technology.

Although Table 6 only provides a general guideline for removal of compounds, several interesting trends are noted. Carbon adsorption appears to provide removal for a wide range of organics whereas conventional treatment is revealed as a poor treatment for those compounds listed in the table. Packed tower aeration manifests itself as an excellent technology for volatile organic compounds and may have application for a limited number of pesticides. Ozone oxidation appears to be a good treatment technology for certain classes of organics such as simple alkenes and aromatics, as well as certain similar, but more complex organic structures. Although only a few organics have been subjected to long-term testing via reverse osmosis, promising removals for several low molecular weight organics can be seen.

Table 7 shows that ion exchange and reverse osmosis each result in excellent contaminant removals.

TABLE 7. PERFORMANCE SUMMARY FOR INORGANIC TECHNOLOGIES EXAMINED

Regulatory Phase	Inorganic Compound	Removal Efficiency			
		Reverse Osmosis	Ion Exchange	Aeration	Carbon Adsorption
II	Nitrate	++	++		
III	Radium	++	++		
III	Uranium	++	++		
III	Radon			*	*

++ = Excellent 70%-100%
* = Research being conducted by DWRD

Tables 6 and 7 were generated using a variety of sources, including EPA-DWRD pilot- and field-scale studies, Henry's Law Constants for prediction of removal of some of the pesticides, as well as the use of oxidative

trends for predicting the removal of complex pesticides. These tables, therefore, carry the caveat that the cited removals should not be used for design purposes, but that each technology must be tested on compounds, under field conditions, before the EPA-DWRD will advocate a technology's use.

SURFACE WATER FILTRATION/MANDATORY DISINFECTION

DWRD's primary activities in this area are the studies related to Giardia and viral inactivation. Current studies on Giardia inactivation are being conducted at Ohio State. Hepatitus A and phage inactivation studies are being conducted at the University of North Carolina. Field studies related to inactivation of Giardia are being planned. A major result of these studies are the calculation of CT values for various organisms at different levels of temperature, pH and disinfectant dose. The following projects are ongoing in this area:

- Reports on concentration and time values for Hepatitis A and coliphage inactivation by:

  Chlorine and Chloramines
  Chlorine dioxide and ultraviolet light

- Laboratory - scale studies on the inactivation of Giardia Muris by chlorine, chlorine dioxide, and chloramines.

- Pilot scale study at Harrisburg, PA on inactivation of virus and Giardia by chlorine and chloramines.

- Laboratory study on inactivation of Cryptosporidium by chlorine and chloramines.

- Evaluating treatment plants and distribution systems for Legionella.

PROHIBITION OF LEAD MATERIALS

The amendments to the SDWA prohibit the use of lead in any material in contact with potable water. DWRD's major current project dealing with lead solder is being conducted with the South Huntington Water District on Long Island, New York.

Ninety sites were identified and selected for this study. Ten homes were selected in each of nine age groups from zero to over 20 years old. These sites have been sampled three times at different pH levels: less than 6.2, 7.2 and 8.2. The homes were randomly slected to obtain a geographic distribution in the 19.4-square-mile service area of the District. The type of existing solder was verified in each home through scraping of an exposed solder joint and testing by an atomic absorption spectrophotometer. Of 95 homes tested, only one had less than 0.5 percent lead in the solder; 67.3 percent of the homes had lead content ranging from 55 to 65 percent in the solder.

First-draw samples were tested for copper and cadmium in addition to lead. An additional sample was drawn for determination of various water quality parameters including pH. Copper values above the 1 milligram per liter (mg/L) secondary Maximum Contaminant Level (up to 7.77 mg/L at 6.9 pH) were found. These sites were checked for stray electric currents in the water service pipe to determine whether or not the high copper values were caused through grounding of electric systems to the water plumbing system.

During low pH sampling of 64 first-draw tests for cadmium, only one sample at 42 ug/L was above the drinking water standard. Since the second sample at 10 seconds contained only 3 ug/L cadmium, it is assumed the presence of cadmium was caused by the faucet.

On the first-draw lead samples taken, 61.8 percent were above the drinking water standard. The results ranged from a low of 2.0 ug/L in a 1968 home at pH = 5.9, to values ranging from 500 to 1,200 ug/L (pH ranges from 5.6 to 6.9) at homes constructed between 1981 and 1983. However, the highest lead value (1,300 ug/L) was obtained at pH = 5.9 in a 1968 home.

There appears to be a correlation between the age of the lead solder and its ability to leach lead into the drinking water. Ignoring the first zero-second flush and allowing the first 300 milliliters (mL) of flush for the faucet's leaching of lead, the second sample at 10 seconds were compared for 75 homes. For homes constructed in 1980, 1981, 1982, and 1983, the second 125 mL sample (taken in March and April, 1984) indicated that 23 homes, or 70 percent, exceeded the 50 mg/L drinking water standard, and 10 homes were less than this maximum contaminant level. For homes constructed between 1955 and 1979, only seven, or 17 percent, exceeded the drinking water standard at a low pH with 35, or 85 percent, less than the maximum contaminant level. Table 8 summarizes some of the first draw results.

TABLE 8. RESULTS FROM HOUSEHOLD LEAD STUDY FIRST DRAW SAMPLES

pH	% of Homes Exceeding 50 ug/L
< 6.2	58.7
6.2 - 8.2	26.6
78.2	24.4

Leaching of metallic solders, particulary lead solder, appears to be affected by the following factors:

- pH of water
- Plumbing workmanship,
- Hardness of water
- Time since last use of water
- Percentage of lead in solder.

Where these conditions are conducive to lead leaching, large numbers of consumers may be exposed to high-lead, first-draw water.

Several interesting results have come from this ongoing study that may provide information on leaching from various kinds of solder from special pipe loops. Tables 9 and 10 provide some useful summary data from the project. As can be seen there is lead in the various alternative solders being tested. In addition all four pipe loops have experienced copper leaching at very high levels.

TABLE 9. LEAD SOLDER PROJECT

Solder Type	Highest Lead Value	pH	Standing Time
Tin/Silver	0.015 mg/L	5.3	4 hrs
Tin/Silver	0.042 mg/L	5.4	4 hrs
Tin/Silver	0.057 mg/L	5.3	4 hrs

TABLE 10. COPPER LEACHING IN FOUR PIPE LOOPS

pH	Solder	Copper (mg/L)
5.5	Tin/Silver	3.80
5.5	Tin/Antimony	4.28
5.5	Tin/Copper	4.50
5.5	Tin/Lead	4.28

Tables 11, 12 and 13 illustrate some of the problems to be encountered when trying to meet the presently discussed 20 ug/L lead level in households. These data are from other ongoing research projects. As can be seen at lower pHs for short sampling periods in new homes it will be very difficult to meet the proposed standard. At higher pH's for longer sampling periods and for increasing age of test site the proposed standard can be met although it is only met consistently in older homes.

TABLE 11. PERCENTAGE OF TEST SITES WITH LEAD IN DRINKING WATER GREATER THAN 20 ug/L AT LOW pH (6.4 & LESS)

AGE OF TEST SITE (Years)	FIRST DRAW	10 SEC	20 SEC	30 SEC	45 SEC	60 SEC	90 SEC	120 SEC
0 - 1	100%	100%	100%	100%	100%	86%	86%	88%
1 - 2	100%	71%	86%	57%	57%	29%	43%	14%
2 - 3	86%	86%	57%	57%	43%	43%	43%	29%
3 - 4	100%	86%	100%	71%	71%	71%	29%	29%
4 - 5	86%	57%	29%	43%	43%	43%	14%	0%
6 - 7	78%	44%	33%	33%	11%	11%	11%	0%
9 - 10	71%	29%	14%	14%	14%	14%	0%	0%
15 - 16	57%	14%	14%	14%	14%	14%	14%	14%
20 & Older	86%	27%	29%	0%	14%	0%	14%	0%

TABLE 12. PERCENTAGE OF TEST SITES WITH LEAD IN DRINKING WATER GREATER THAN 20 ug/L AT MEDIUM pH (7.0 - 7.4)

AGE OF TEST SITE (Years)	FIRST DRAW	10 SEC	20 SEC	30 SEC	45 SEC	60 SEC	90 SEC	120 SEC
0 - 1	100%	90%	90%	60%	30%	20%	10%	10%
1 - 2	80%	60%	30%	10%	20%	0%	10%	0%
2 - 3	40%	20%	10%	10%	10%	0%	0%	0%
3 - 4	50%	20%	20%	30%	20%	30%	30%	20%
4 - 5	30%	10%	10%	0%	10%	0%	0%	0%
6 - 7	10%	0%	0%	0%	0%	0%	0%	0%
9 - 10	20%	0%	0%	0%	0%	0%	0%	0%
15 - 16	40%	20%	20%	10%	0%	0%	0%	0%
20 & Older	20%	0%	0%	0%	10%	0%	0%	0%

TABLE 13. PERCENTAGE OF TEST SITES WITH LEAD IN DRINKING WATER GREATER THAN 20 ug/L AT HIGH pH (8.0 & GREATER)

AGE OF TEST SITE (Years)	FIRST DRAW	10 SEC	20 SEC	30 SEC	45 SEC	60 SEC	90 SEC	120 SEC
0 - 1	100%	100%	60%	10%	20%	10%	20%	0%
1 - 2	67%	22%	11%	11%	11%	0%	11%	0%
2 - 3	30%	10%	10%	0%	0%	0%	0%	0%
3 - 4	25%	0%	0%	0%	0%	0%	0%	13%
4 - 5	30%	10%	0%	0%	0%	0%	0%	0%
6 - 7	20%	0%	0%	0%	0%	0%	0%	0%
9 - 10	10%	0%	10%	0%	0%	10%	0%	10%
15 - 16	33%	22%	11%	11%	0%	0%	0%	0%
20 & Older	20%	0%	0%	0%	0%	0%	0%	0%

DETERIORATION OF WATER QUALITY

DWRD is and has been conducting extensive studies into the deterioration of water quality in distribution systems. Methodology is being developed for

calculating the AOC associated with treated and distributed water. Work is being conducted into the identification of legionella and other organisms that may exist in distribution systems. The following general areas are being studied:

1. Microbial Contamination of Distribtuion Systems

Research has focused on corrosion inhibitors and the possibility of their acting to promote microbial growth in water mains. Other research (2 projects) are examining protection of bacteria by higher organisms as a mechanism for bacteria to be transported into the distribution system in a viable state. Still another project has been funded to learn about protection and transport of bacteria by GAC fines. Present work includes testing of sampling concepts to detect coliform bacteria and research on the assimilable organic carbon (AOC) in water and its relationship to bacterial growth and proliferation in mains. Inhouse and extramural work on AOC started in FY'86 and will continue into FY'88. Additional work related to biological stability of treated water will be needed, especailly if ozone is to be used more extensively in water treatment.

2. General Corrison Control Studies

In addition to the lead study mentioned previously, field studies on corrosion control methods for lead, galvanized steel and copper pipes continue to take place at various communities in the State of Washington. The project emphasizes the practicality of providing realistic assistance to utilities to implement corrosion control measures. Finally, bench-scale studies on the chemistry of silicates and phosphates for corrosion control has been completed at the University of Missouri.

3. Modeling and Cost Research

Extramural and inhouse research efforts have focused on the following four aspects of water main distribution system deterioration: (1) Computer models for mainframe and microcomputers to predict water quality and cost have been developed. This model, for example, estimates TTHM levels throughout the distribtuion system based on time-of-travel and mixing of water from wells of varying quality. Cooperative work dealing with the efforts of hydraulic behavior on the propagation of contamination in distribution systems has been initiated with members of a French-U.S. bilateral team; (2) Case studies have collected main break data and applied statistical techniques to identify system characteristics, environmental factors and installation practices that contribute to abnormally high break rates that can impair water quality; (3) Case studies have also analyzed repair, replacement and renovation costs and have to incorparate data base collection and analysis into a decision making strategy for utilities to minimize costs and insure hydraulic integrity and reliability; and (4) A study is underway to develop standardized distribution system costs and includes new construction, repair and rehabilitation.

SUMMARY AND CONCLUSIONS

DWRD is active in conducting treatability and technology studies to assist in development of maximum contaminant levels under the Safe Drinking Water Act. The Division is also involved in giving technical advice to states, EPA Regional Offices, water utilities and professional organizations. An organization of major interest to EPA is the Association of State Drinking

Water Administrators. In many ways the State Drinking Water Administrators are the first line of implementation of the SDWA. It is the purpose of this paper to help provide information to the State Adminstrators and to provide a point of contact for future information concerning the evaluation of various kinds of technologies for meeting SDWA maximum contaminant levels.

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Barriers to Implementing New Technologies

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PROJECT REPORT

Overcoming Barriers to the Introduction of New Technologies

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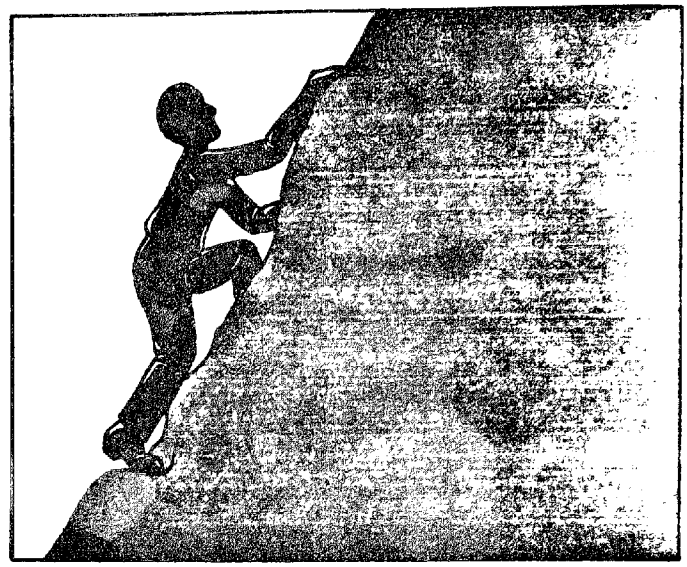
In June 1984, Wade Miller Associates, Inc., and the Utah Bureau of Public Water Supplies initiated a project to identify barriers to the introduction of new technologies into the drinking water field and to determine how some or all of these barriers can be eliminated. Sponsored by the AWWA Research Foundation, this project focused on the roles and interactions of equipment suppliers, state plan review engineers, consulting engineers, and utilities in the process of designing and constructing water treatment facilities and appurtenances. The project was designed to identify solutions since it was known that barriers to new technologies exist.

If the results of the study could be distilled into one statement, it would be that there are no heroes or villains responsible for introducing or blocking new technology in the potable water supply industry. Each of the involved parties operates from a different perspective and also has a different set of concerns. These concerns often are either not appreciated or fully understood by the other parties. These perceptions and concerns impact specific actions taken or not taken. All parties are sincerely interested in seeing that water systems have well-designed, cost-effective technologies. The failure to achieve this goal is rooted in the basic decision structure in which all the major participants operate.

The rate of introducing new technologies into water supply, and in fact into all facets of local government, has historically been slower than it has been in many other sectors of the economy. There are several reasons why this is true.

- Several types of organizational entities are engaged in the process, and their interactions often lead to miscommunications and breakdowns in the system.
- The water industry itself is a mature industry; the emphasis is on reliability and use of proven treatment techniques and products. Although there is innovation and change in some aspects of water supply, the rate of change is considerably slower than in the field of microcomputers or telecommunications, for example.



- Because of public health concerns and the emphasis on proven techniques, the number of new products being introduced is low relative to other industries. Some products that are considered new, such as ozone and reverse osmosis, have actually been used in water treatment plants since 1906 and 1967, respectively.

Organizational Entities

The five major organizational entities that interact continuously in the course of water plant design, construction, and operation, are: state drinking water officials who review and approve plans and specifications, consulting engineers who design the facility, equipment suppliers, the general contractor, and the utility.

State regulatory agencies. State drinking water administrators are public health officials charged with the primary responsibility for protecting the public health by ensuring that utilities deliver a potable, safe supply of water to the consumer. They view their role as one of primary oversight of designers, equipment suppliers, and water utility owners and operators. In this role, they often must evaluate complex technologies and rule on the use of substances whose chemistry is not always well understood. Long after the engineer and contractor have completed their work and the warranty on the equipment has expired, state drinking water officials must monitor drinking water quality and work with problem systems.

As a group, state regulators perceive themselves as understaffed and less than well equipped in terms of resources and access to knowledge needed for the review process. Consequently, there is a strong predisposition to favor "tried and true" technologies. The principal concern is system operation; cost is

relegated to a secondary consideration. Thus, state regulators tend to favor old-line technologies with conservative design parameters. By requiring unit processes to be lightly loaded and/or to have very long detention times, it is believed that the operator will have more time to respond to problems. Because of their lack of resources and their commitment to protection of the public health, state regulators often appear to be arbitrary and conservative in their judgments.

Consulting engineers. Design engineers are concerned with designing a water treatment plant that will function efficiently. This generally means that equipment selected is tried and proven. The engineer has little incentive to specify new, often unproven technology. In fact, the engineer has a disincentive; if the plant does not function properly, liability claims and/or damage to the firm's reputation can be significant.

The consulting engineer is the lead professional in most water supply system projects. He is responsible for determining the client's needs and designing and overseeing the installation of a water treatment system that will meet those needs within the regulatory and public health framework. In effect, he is the primary procurer of products and technologies.

The survey of 20 consulting engineers conducted in this study served to confirm that designers are highly conservative in their philosophy and not inclined to take a leading role in advocating new technologies and products. The key factor that drives consulting engineers to rely on well-established older technologies is liability. The engineering firm generally holds virtually all of the liability associated with the design of a treatment plant. State regulatory personnel have no liability. Equipment supplier liability is limited to product warranties. So long as the plant is constructed properly, the contractor is not liable for its performance. As a result of this situation, engineering firms must carry expensive liability insurance; insurance carriers are quick to cancel or raise fees to exorbitant levels if a claim is filed. Hence, the engineer has a substantial amount to lose if a new technology fails to perform. Since many of the smaller water systems are designed by small engineering firms, a major problem can force the firm to close down.

Equipment suppliers and general contractors. The most elegant plans and specifications will not treat a single drop of water until they are converted into the physical structure of the treatment plant. The contractor and the equipment supplier, working with the engineer, create the actual system from the paper abstraction. General contractors are the favorite target of criticism by those who conveniently ignore the highly competitive, low-bid environment in which general contractors must work.

The equipment supplier is the primary source of innovation and forward movement in water treatment technology. The supplier's environment stimulates change and innovation since the company's survival and prosperity depend to a large part on its ability to improve on the state of the art and thereby create a salable advantage over competitors in a highly competitive and price-driven environment. The supplier performs many valuable services, including research and development (R&D), pilot testing, training and supporting design engineers, and providing supplies and services to operators. Much of the funding for professional activities, publications, and exhibitions comes directly or indirectly from suppliers seeking to advertise their products.

Equipment suppliers are concerned primarily with selling a product that satisfies the demands of the marketplace. The supplier is profit motivated. However, his profits are often invested in research or product development that ultimately benefits the industry.

Utilities. Utilities are often the forgotten organizational entity. Water utilities are usually as conservative as their state counterparts. Like the consulting engineers, they have little incentive to try new products or process equipment. When they do opt for installation of an innovative process or treatment technique, the incentive is the promise of a significant reduction in costs—capital costs, operation and maintenance costs, or both.

Others. The role of the U.S. Environmental Protection Agency (USEPA) in product introduction should be mentioned briefly. Although the USEPA is the primary developer of drinking water regulations, it specifically does not get involved in product testing or endorsement and is not directly involved in the "decision loop" of states, consulting engineers, utilities, and equipment suppliers. It does get involved in the approval-acceptance of direct and indirect additives to drinking water, but only on an advisory basis. The USEPA's advisory opinions on treatment chemicals and paints and coatings have never been mandatory. The state regulatory agencies have primary authority and responsibility in this area. Many choose to rely primarily on USEPA's advisory rulings, making them mandatory for approval. Since the USEPA limits its work to issuing advisory opinions on new products that are essentially identical in chemical formulation to previous products, states that limit their own approvals to products that have been "approved" by the USEPA basically bar the introduction of any new products of this type in their states.

Specific Barriers

Certainly one of the principal barriers to introduction of new technologies is the methodology by which

(continued on page 8)

(continued from page 7)

water treatment systems are designed, purchased, and operated. It has been called the "great American low-bid process," the "eternal triangle" of the consulting engineer who designs the plant, the general contractor who builds it (using equipment from the supplier), and the owner who operates it. While having no direct fiduciary interest, the state drinking water administrator, as the principal guardian of the public health, is also very much involved.

When something goes wrong, an all too frequent occurrence, the situation quickly dissolves into a triangle of "finger pointing," each party trying to shift the responsibility to the other. The entire system is full of loopholes: the contractor may substitute cheaper, inferior equipment that local or federal procurement regulations force the engineer or owner to accept; the engineer fails to "do his homework," resulting in less-than-efficient processes and hardware. The owner may take the best designed and constructed plant in the world and produce poor quality water by using unqualified, untrained operators.

This process does not establish a clear, single source of responsibility that can efficiently design, construct, and operate a plant. The net effect of the system is to drive the technology and equipment quality to the lowest common denominator, and drive the costs up, to the benefit of no one.

Another barrier is the lack of a uniform set of guidelines for reviewing new or old technologies. Consequently, the supplier finds that he must meet widely divergent standards for treating waters of similar composition that simply happen to be located in different geographical and/or political areas. This serves to drive up the cost of equipment and to complicate system design.

State regulatory agencies that do not periodically review and update their standards may appear to have little technical basis for existing standards. In some extreme cases, an entire policy having major economic impact on the state's water utilities may be rooted in the personal prejudices of a long-term senior employee who has not kept abreast of technical evolution. Policies in states operating on this basis may be characterized by abrupt changes that correspond to the retirement or reassignment of key personnel.

About one-half of the states rely on the "Ten States Standards" (TSS) for all or a major part of their basic criteria. Those states that are not a part of the TSS committee that generates these guidelines tend to interpret the standards in a much more rigid manner than was intended by the authors. This has led to the phenomenon of new technologies being approved by TSS committee states, while the same are rejected by an outside state citing the TSS as the reason. Use of the TSS by so many states reflects a strong desire among state officials for greater commonality of basic standards. The problem with the TSS is that they have institutionalized some basic criteria that are not based on best available technology. For example, even though modern filters provide effective treatment at rates far in excess of the two-gallons-per-minute-per-square-foot guideline listed in the TSS, this requirement remains in the standards long after it has been rendered obsolete.

The combination of the low-bid environment and the lack of serious prequalification of suppliers has placed severe profit constraints on the equipment supply industry. Suppliers have responded by cutting back on services, reducing warranties, substituting cheaper designs and materials in products, and reducing product R&D efforts. The first cost of the product may be lower; however, the service life cost and maintenance headaches associated with cheap equipment may dwarf any up-front savings.

The great lack of communication between equipment suppliers and state regulatory officials contributes to an atmosphere of distrust and misunderstanding between them. Survey responses and conversations with members of both groups during this study clearly established that each party suffers from considerable misconceptions about the other and these misconceptions are allowed to interfere in the working relationship to the detriment of both parties.

Conclusions and Recommendations

Even though there are clearly several barriers to the introduction of new products, the system does work. As noted earlier, most water treatment professionals—state administrators, consulting engineers, equipment suppliers, and utility managers—have a common goal of providing a high quality product to the consumer.

The procurement system, as currently structured, is inefficient and unwieldy, however. Virtually no incentives exist for risk taking, either by the consulting engineers or the state plan review engineers. Utilities sometimes can benefit from risk taking in the form of lower costs of an innovative technology. For the most part, however, the water treatment equipment supplier is selling to a conservative constituency that places a high premium on reliability and, under most state laws, low-bid prices.

Of all the key actors surveyed during this study, only the consulting engineers appear to accept the current system used for procurement, design, and construction of water treatment facilities. The state drinking water administrators recognize that they are perceived as "barriers to innovation" and would like to take actions to ensure that they are not barriers. The more progressive utilities may be frustrated by conservative state guidelines and would like to see

changes. Most equipment suppliers are frustrated by the present way of doing business, but are relatively powerless to change the status quo.

In addition to the inefficiency of the procurement process, the industry is plagued by a clear lack of communication. This lack of communication cuts across all groups. The states, until the recent formation of the Association of State Drinking Water Administrators (ASDWA), have not had a forum for sharing information with each other. Equipment suppliers often appear to develop new products without consideration for the concern of state administrators. They market their products to the consulting engineer and typically consider the engineer, and not the utility, to be the client. Consulting engineers are criticized by states and equipment suppliers alike for not being willing to "take more chances." Engineers are especially criticized for not sticking by a specification once written.

Principal recommendations for actions that can break down some of the existing barriers are as follows:

1. Consideration should be given to the development of a uniform set of national guidelines that can be used by all states in the plan review process. The feasibility of such a set of standards is a controversial topic; however, the states appear to want and need the consistency that would result from this action. It is exceedingly important that any such guidelines or standards be kept as current as possible. Continued use of outdated design parameters based on outmoded technology can be a major barrier to the introduction of new technologies if such parameters are incorporated into national guidelines or standards.

2. There is a clear consensus among the majority of state agencies and most of the other participants for a national "clearinghouse" that would support direct communication between state regulators, equipment suppliers, consulting engineers, and water system operators. The clearinghouse could serve as a vehicle for disseminating new product information and test data, and generally foster the spread of design, product, and operational information within the industry.

3. The current practice of low-bid purchasing inhibits the introduction of new technologies by causing credible suppliers to expend unnecessary resources while watching low-bid suppliers win procurements on the basis of the first cost, not service life costs. The process makes it more difficult for state officials to approve new technologies, particularly packaged treatment systems, for fear of inferior substitutions to approved products at the time of bidding. Numerous examples of successful equipment and service procurement on a negotiated or prequalified bid basis exist in the municipal sector overseas (i.e., as in France where two large, vertically integrated companies dominate the water industry), and in the municipal privatization and industrial sectors in the United States.

Feasible alternatives to the current practice should be defined, and steps should be taken to educate municipal buyers and consulting engineers in a more effective procurement approach. The lead role would have to be taken by USEPA, the American Water Works Association (AWWA), and ASDWA since consulting engineers seem to accept the current procurement process.

4. In the current environment, exhorting the consulting engineer to "take more risks" on new technology will have no significant impact unless some mechanism for reducing his liability in the event of failure is also developed. A definitive analysis of the current liability situation and development of alternative models that would share liability among the principal participants (i.e., designers, equipment suppliers, contractors, system owners, and states) should be undertaken by AWWA, ASDWA, or other interested parties.

5. State regulatory agencies need to look closely at their decision making to assure that it is consensus-based and not dominated by one, or several, strong-willed staff members who have not kept pace with the development of water treatment technology. States should emphasize, even require, participation in professional educational activities by those staff members who are reviewing plans and specifications and who are responsible for design criteria. Resources should be made available for site visits to treatment plants that use new technologies, for participation in pilot studies, for sharing information and exchanging ideas with plan review engineers in other states, and for travel to regional or national conferences or seminars dealing with new technologies.

6. Equipment suppliers need to recognize the importance of state drinking water officials and make a concerted effort to work with and understand their constraints and perspectives. In particular, manufacturers need to understand the public health implications that drive the regulatory process and address those issues in their product submittals and research efforts. Also, new product development should include input from key state officials as early as possible, so that health and operational concerns can be recognized and incorporated.

7. One of the most important and immediate actions that should be taken is sponsorship of a workshop (or a series of workshops) that would bring equipment suppliers, states, and consulting engineers together in a forum conducive to constructive dialogue. USEPA's Office of Drinking Water in conjunction with the Drinking Water Research Division should provide funding for such workshops, which should be conducted by ASDWA alone or with the AWWA Research Foundation.

Technical Session: Filtration

Sigurd P. Hansen, *Senior Engineer, CWC-HDR, Inc., Cameron Park, CA*

Material not enclosed -- see separate handout.

Technical Session: Disinfection/By-Products
Rip G. Rice, *President, Rice International Consulting Enterprises, Ashton, MD*

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EMERGING TECHNOLOGIES FOR COMPLIANCE WITH DISINFECTION AND DISINFECTION BY-PRODUCTS REGULATIONS

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I. INTRODUCTION

The Safe Drinking Water Act Amendments of 1986 as related to Disinfection and Disinfection By-Products will require all community and non-community water supplies to disinfect their drinking water supplies. However, this must be accomplished in such a manner as to minimize or eliminate the formation of by-products of the disinfection process. Since some of the disinfectants employed in drinking water treatment (e.g., chlorine, chlorine dioxide, and ozone) also are used for oxidative purposes other than disinfection, the same by-products can be produced during such non-disinfection applications.

Historically, chlorine has been the primary disinfectant utilized by American water utilities. Its use has produced (and continues to produce) excellent results in terms of killing and/or inactivating pathogenic microorganisms, and also has provided many additional water treatment benefits (e.g., iron and manganese removal, color removal, sometimes taste and odor control, etc.).

On the other hand, chlorine also is an excellent chlorinating agent, producing trihalomethanes (THMs) and other halogenated organic materials during water treatment. Consequently, other disinfectants are being studied and utilized (chlorine dioxide, monochloramine, ozone) as well as combinations of oxidants/disinfectants (i.e., ozone followed by chlorine, chlorine dioxide, or monochloramine) to "replace" chlorination, or at least to lower the amounts of chlorine applied rather cavalierly in the past without regard to the chemical by-products produced by such practice.

Analogously, each of these alternate disinfectants or combinations thereof can be expected to produce its own set of oxidation/disinfection by-products. Therefore, EPA's major problem with respect to this subject area is to study the efficacy of each potentially promising alternative water treatment scheme, identify the by-products which can be or are produced, and determine their health effects.

Disinfection By-Products currently are discussed by some as a topic related solely to the "disinfection" step, without considering that the identical by-products can be produced during non-disinfection applications of the same oxidant/disinfectant. When breakpoint chlorination is employed for ammonia removal early in the treatment process, the same types of halogenated by-

products can be produced as when chlorine is added for disinfection after filtration, given the presence of the same types and concentrations of organic materials, and the same water parameters.

Ozone and potassium permanganate ($KMnO_4$) are prime candidates for coping with many Synthetic Organic Chemicals (SOCs) to be regulated under the SDWA by oxidation early in the water treatment process. As a result of adding ozone to raw water supplies (for turbidity, color, and/or taste and odor control, microflocculation, oxidation of THM precursors, or iron and manganese oxidation, for example), oxidation by-products will be produced which are of the same general types as when ozone is employed late in the water treatment process as the primary disinfectant.

Similarly, when potassium permanganate, rarely used, if ever, as a disinfectant, is applied for oxidative purposes (iron, manganese, color removal, taste and odor control), many of the same oxidation products are produced as when ozone, chlorine dioxide, or even chlorine are employed as disinfectants or oxidants (see Rice & Gomez-Taylor, 1986, and references cited therein).

II. DEFINITIONS

A. **DISINFECTION** -- The killing or inactivation of (pathogenic) microorganisms.

Attainment of the desired degree of disinfection is a function of the concentration of the disinfecting agent (in mg/L) times the contact time (in minutes) (**the "CT" value**, in mg/L-min). For example, with chlorine at a concentration of 2 mg/L and a contact time of 30 minutes, the product of [concentration x contact time] is 60. On the other hand, with ozone applied under viral inactivation conditions (0.4 mg/L maintained over 4 minutes), the "CT" product is 1.6.

B. **PRIMARY DISINFECTION** -- The major disinfection step normally practiced after filtration in a surface water treatment plant employing conventional or direct filtration. In groundwater treatment plants, primary disinfection also can be applied post-filtration (if filtration is used). If filtration is not incorporated in groundwater treatment, primary disinfection is practiced in the treatment plant, prior to the water entering the distribution system.

Oxidants/disinfectants which are used currently for primary disinfection are: chlorine, ozone, ultraviolet radiation, chlorine dioxide, and monochloramine.

C. **SECONDARY DISINFECTANT (RESIDUAL DISINFECTANT)** -- A disinfectant added to finished water to maintain a disinfecting residual concentration throughout the water distribution system.

Current secondary (residual) disinfectants are: chlorine, chlorine dioxide, and monochloramine.

D. **POINT OF DISINFECTION** -- The point in the water treatment process at which disinfectant is added for the purpose of killing or inactivation of microorganisms.

E. **DISINFECTION/OXIDATION BY-PRODUCTS** -- Materials produced or formed whenever a disinfectant or oxidant is added to water.

These by-products can be materials formed by:

(a) Reduction or disproportionation of the disinfectant (or oxidant) itself, e.g., chlorite and chlorate ions from chlorine dioxide, dissolved oxygen from ozone, chloride ion from chlorine,

(b) Oxidation of organic materials present in the water, i.e., aldehydes, ketones, alcohols, and carboxylic acids from the reactions of humic acids with ozone, chlorine, chlorine dioxide, $KMnO_4$, or

(c) Halogenation of organic materials upon the addition of halogen-containing disinfectants, e.g., trihalomethanes and other halogenated organics during chlorination, organic chloramines produced by reaction of monochloramine with organonitrogen compounds, etc.

If bromide ion is present in the raw water, it can be oxidized by ozone or chlorine (not by chlorine dioxide or chloramine) to form hypobromous acid, which, in turn, can brominate many organic materials. Bromine-containing trihalomethanes, for example, are known to be formed by this reaction mechanism.

Until recent years, it had been considered that chlorine is added to drinking water supplies primarily to disinfect or to remove ammonia. When chlorine is added to raw water to remove ammonia by breakpoint chlorination, the oxidative function of chlorine is utilized. Although disinfection also is obtained when the chlorine is added, nevertheless the primary purpose of breakpoint chlorination early in the water treatment process is oxidative removal of nitrogen (ammonia). On the other hand, since the chlorine is added at the point of greatest concentration of organics capable of being chlorinated, the maximum concentration of halogenated oxidation products will be produced simultaneously under these circumstances.

Therefore, and in light of current, more complete understanding of the roles of various disinfectants as also being strong chemical oxidants, it should be recognized that anywhere in the water treatment process a strong oxidant is added for the purpose of oxidation, disinfection may occur simultaneously. The degree of disinfection obtained under these circumstances will depend upon a number of factors, including the types of organisms present, the specific oxidant/disinfectant added, the water temperature, and the time the

disinfectant is in contact with the microorganisms present (i.e., the "CT" value).

Consequently, the point(s) of disinfection today should be redefined as any point(s) in the water treatment process at which a specific oxidant/-disinfectant is added for any purpose. The same "disinfectant by-products" can and will be produced, given the presence of the same types and levels of "disinfectant by-product precursors", and the same water conditions (i.e., temperature, pH, ionic strength, alkalinity, hardness, etc.).

From a nomenclature point of view, therefore, it is more appropriate to refer to "Disinfectant/Oxidant By-Products" (DOBs), rather than merely as Disinfection By-Products (DBPs).

III. EPA DISINFECTION REGULATIONS

A. STATUTORY REQUIREMENTS

Section 1412(b)(8) of the Safe Drinking Water Act Amendments of 1986 (enacted June 19, 1986) requires the EPA Administrator to propose and promulgate national primary drinking water regulations requiring disinfection as a treatment technique for all public water systems within 36 months (by June 19, 1989). Simultaneously, the Administrator is required to promulgate a rule specifying criteria that will be used by EPA or delegated State authorities to grant variances from this requirement, according to the provisions of Section 1451(a)(1)(B) and 1415(a)(3). This disinfection requirement applies to all waters used for drinking purposes, including groundwaters.

Section 1445(a) requires the EPA Administrator to promulgate regulations, not later than 18 months after enactment of the Safe Drinking Water Act Amendments of 1986 (by December 19, 1987), requiring every public water system to conduct a monitoring program for unregulated contaminants. These regulations shall require monitoring of drinking water supplied by the system, and shall vary the frequency and schedule of monitoring requirements for systems based on the number of persons served by the system, the source of supply, and the contaminants likely to be found. Each system shall be required to monitor once every five years after the effective date of the Administrator's regulations, unless the Administrator requires more frequent monitoring.

This monitoring requirement will apply to all disinfection and disinfection by-product regulations to be discussed in this presentation, as well as to compounds listed as Volatile and Synthetic Organic Chemicals (VOCs and SOCs).

1. Variances and Exemptions

A water utility will be required to disinfect unless it successfully applies to the state primacy agent for a variance. At this time, criteria for obtaining variances from disinfection requirements are not yet available. However, proof of microbiological safety during the variance period can be assumed to be a determining factor, and the State must find that in granting the variance, an unreasonable risk to the public health will not result.

The respective roles of variances and exemptions under the SDWA Amendments differ, but the logic is clear. Variances can be granted only on the basis that because of poor raw water quality, the MCLs cannot be met, even after application of Best Available Technology. There does not appear to be any endpoint for compliance under the variance provision, although the states must impose a compliance schedule as a condition of the variance [Section 1415].

In EPA's proposed Surface Water Treatment Rule (U.S. EPA, 1987a), EPA states:

> "... due to the acute and high risk associated with poor disinfection of surface waters, EPA is proposing that **no variances be allowed.**"

EPA also states that no variances will be allowed in the requirements for filtration of surface water supplies, in the same proposed Rule (U.S. EPA, 1987a). This position is taken under Section 1412(b)(7)(C)(ii) of the SDWA, which states that in lieu of the variance provisions, the EPA is to specify criteria by which States will determine which public water supplies will be required to filter.

Exemptions from any requirement respecting a maximum contaminant level or any treatment technique requirement, or from both, are allowed based on the inability to comply due to "compelling factors", which may include economic factors. As with variances, the state must find that the granting of an exemption shall not result in an unreasonable risk to health [Section 1416(a)-(1)]. However, the maximum length of time for an exemption is three years, and at the time the exemption is granted, the State must prescribe a schedule for compliance [Section 1416(b)(2)(B)]. For smaller connection systems (under 500), the exemption can be extended for several two-year periods [Section 1416(b)(2)(C)], if the system establishes that it is taking all practicable steps to meet the requirements of Section 1416(b)(2)(B).

In the proposed Surface Water Treatment Rule (U.S. EPA, 1987a), EPA is proposing that **no exemptions be allowed from the requirement of providing disinfection, but that exemptions be allowed for the degree of disinfection required and for meeting the filtration requirements.** For example, under certain conditions, an unfiltered system might obtain an exemption if it achieved a 99% inactivation of Giardia, but not the required 99.9% inactivation. Guidance for determining conditions under which an exemption might be granted is discussed in the Surface Water Treatment Rule Guidance Manual (U.S. EPA, 1987e).

Additional consequences of requiring disinfection also can be anticipated. For example, many groundwaters are not disinfected today. Those which contain iron and manganese will form insoluble oxides when a disinfectant/oxidant such as chlorine, chlorine dioxide, or ozone is added. In turn, this will require the addition of a filter for their removal. Thus the affected groundwater systems may also be forced to install filtration as a result of being required to disinfect.

Having installed filtration to cope with insoluble materials produced upon oxidation, the question now becomes, should primary disinfection also be practiced after filtration? If so, this will open the door to two-stage oxidation/disinfection. This is a prevalent treatment practice in many modern groundwater treatment plants.

EPA also may require redundancy of the necessary disinfectant feed equipment, along with an auxiliary power source, automatic start-up (and alarm) to ensure that continuous disinfection is provided. Many utilities fall short of having such facilities today.

2. Anticipated Timing of Disinfection Regulations

EPA anticipates promulgating the Surface Water Treatment Rule (SWTR) in mid-late 1988, which will include requirements for filtration and disinfection. Treatment processes (filtration and disinfection) will be discussed, individually and in combination, for removal of specific contaminants. Such processes will include the use of powerful oxidants (e.g., ozone, chlorine, and chlorine dioxide), which also can provide primary disinfection at their point(s) of addition.

In addition to the Surface Water Treatment Rule, EPA intends to promulgate additional regulations specifying disinfection requirements for systems using groundwater sources, and possibly more specific disinfection requirements for surface water systems. This Groundwater Treatment Rule currently is planned to be proposed early in 1991. It will include regulations for Disinfection By-Products (when health risks associated with disinfection by-products are adequately evaluated), revision of THM regulations, and proposed MCLs for the disinfectants themselves (e.g., chlorine, chlorine dioxide, chlorite/chlorate ions, and monochloramine).

In early 1988, the Environmental Protection Agency (U.S. EPA, 1988a) promulgated the First Drinking Water Priority List, which contains 53 substances or classes of substances that are candidates for regulation. These include the above disinfectants, ammonia, the four THMs currently regulated, ozone by-products, cryptosporidium, and many additional halogenated organic materials, some of which are by-products of chlorine disinfection.

At the same time (U.S. EPA, 1988a), EPA finalized the list of 83 substances mandated by the Safe Drinking Water Act Amendments to be regulated by June 1989. Many of these substances are at least partially reactive with chlorine dioxide, ozone and potassium permanganate. Consequently, they may be destroyed, or at least converted in chemical form by pretreatment with

strong oxidants, giving rise to byproducts. Such preoxidation will change the way these oxidized derivatives are removed in subsequent processing steps.

B. THE PROPOSED SURFACE WATER TREATMENT REGULATION (U.S. EPA, 1987a)

1. Applicability

This regulation will be applicable to all water treatment systems which use surface water, because all of these are at risk, at least to some degree, from contamination by Giardia lamblia, enteric viruses, and pathogenic bacteria. Surface water is defined as all water open to the atmosphere (e.g., rivers, lakes, streams, reservoirs, impoundments), and all springs, infiltration galleries, wells, or other collectors that are directly influenced by surface water.

"Directly influenced by surface water" means that the source is subject to pathogen contamination from surface waters. This determination is to be made on a case-by-case basis. The State will be responsible for determining which systems use surface water and, therefore, will be subject to the requirements of this rule.

EPA estimates that more than 90% of the systems which do not filter currently serve less than 10,000 people. Therefore, the impact of these proposed regulations will be maximum on small treatment systems.

2. Microorganisms to be Regulated

EPA plans to regulate the microorganisms listed in Table I, plus turbidity, which is included because it is an indicator of disinfectant performance. MCLGs for Giardia cysts and enteric viruses are given as "zero", not with respect to a specific water volume, but rather conceptually. EPA's intent is to approach the MCLG by requiring treatment technologies (e.g., filtration and disinfection).

Under the Surface Water Treatment Rule, all community and noncommunity public water systems using any public water source will be required to treat their surface water source(s) so as to achieve at least 99.9 percent removal and/or inactivation of Giardia cysts, and at least 99.99 percent removal and/or inactivation of enteric viruses. This can be accomplished by disinfection alone, or by a combination of filtration and disinfection. No variances or exemptions will be allowed for disinfection requirements.

At a minimum, treatment for any surface water will include disinfection. In addition, unless the system meets certain site-specific criteria, treatment also will include filtration. No variances from filtration will be allowed; but exemptions will be permitted.

TABLE I. MICROORGANISMS AND DISINFECTION GOALS

Parameter	Proposed[a] MCLG	Proposed[a] MCL
Total Coliforms	0/100 mL	b
Turbidity	-------	0.5 NTU[c]
Giardia[d]	zero	1,000 fold removal and/or inactivation
Pathogenic Viruses[d]	zero	10,000 fold removal and/or inactivation
Heterotrophic Plate Count (HPC)[e]	-------	compliance with filtration and disinfection criteria will ensure HPC control.
Legionella	zero	compliance with filtration and disinfection requirements will remove and/or inactivate.

a) U.S. EPA, 1987a.

b) Proposed MCL is based on presence or absence of coliforms in a sample, rather than on density. No more than 5 percent of the most recent 60 consecutive samples can be coliform-positive for systems analyzing fewer than 60 samples/year (3,300 persons or fewer), and no more than 5 percent of the total number of samples analyzed in the most recent 12-month period can be coliform-positive for systems analyzing at least 60 samples/year (3,300 persons or more). In addition, no more than one sample/month if less than 40 samples are collected per month, or 5% of the samples/month if 40 or more samples/month are collected, can be coliform-positive.

c) NTU = Nephelometric Turbidity Unit; filtered water turbidity. States may allow less stringent levels ($\leq$ 1 NTU) for systems using ozonation at CT values achieving 99.9 percent inactivation of Giardia cysts. All systems are expected to optimize treatment so as to achieve the lowest turbidities feasible at all times of the year.

d) Existing analytical methods are not considered to be technically and economically available for use in compliance monitoring. Consequently, a treatment technique regulation is proposed.

e) Former terminology - Total Plate Count

Systems with very clean and protected source waters (i.e., low total coliform or fecal coliform levels and low turbidity levels as specified in the Rule) would only be required to use disinfection to achieve the required degrees of inactivation of Giardia cysts and viruses. If such systems are continually

able to meet certain disinfectant "CT" requirements specified in the Rule, the water system can be assumed to be in compliance with the above inactivation requirements for Giardia and viruses without having to monitor for these organisms.

Systems with no potential sources of human enteric viruses within the watershed (at the discretion of the State) would not be subject to the requirement for 99.99 percent removal and/or inactivation of enteric viruses. It should be noted, however, that this provision will only benefit systems using chloramination for primary disinfection, since **other disinfectants (e.g., ozone, chlorine, chlorine dioxide), which achieve 99.9 percent inactivation of Giardia cysts also achieve much greater than 99.99 percent inactivation of enteric viruses at the same time.**

Systems required to filter could use a variety of technologies to meet the minimum 99.9 and 99.99 percent performance levels. To satisfy this requirement, systems would be required to meet certain turbidity removal and disinfection performance criteria, and comply with design and operating criteria specified by the State.

3. Appropriate Treatment Technologies

Conventional treatment (which includes coagulation, flocculation, sedimentation, rapid granular filtration, **and disinfection**) has been demonstrated to achieve at least 99.9 percent removal and/or inactivation of Giardia cysts and 99.99 percent removal and/or inactivation of enteric viruses, under appropriate design and operating conditions (U.S. EPA, 1987a). Filtration systems without disinfection, but with proper pretreatment (to produce water having turbidity levels $\leq$ 0.5 NTU), can be assumed to provide 99 to 99.9 percent inactivation of Giardia lamblia and 90 to 99.9 percent removal of viruses. Disinfection is needed to supplement filtration so that the overall treatment achieves greater than 99.9 percent removal and/or inactivation of Giardia cysts and 99.99 percent removal and/or inactivation of viruses.

EPA considers conventional treatment with disinfection to be the Best Available Technology (BAT) for most source waters in the United States because of the multiple barriers of protection that it provides.

Direct filtration (which includes coagulation), **slow sand filtration,** and **diatomaceous earth filtration, each with disinfection,** have been demonstrated to achieve at least 99.9 percent removal and/or inactivation of Giardia cysts and 99.99 percent removal and/or inactivation of viruses under appropriate design conditions (U.S. EPA, 1987b). The Surface Water Treatment Rule will allow their use under certain source water quality conditions as determined by the State.

The same comments about the effectiveness of the filtration step to remove Giardia cysts and viruses, and the need for supplemental disinfection, apply equally to direct filtration, slow sand filtration, and diatomaceous earth filtration.

Filtration technologies other than those specified above can be used if it is first demonstrated through pilot plant challenge studies, using Giardia cysts and viruses, or equivalent indicators, that the filtration technology, in combination with disinfection, can achieve at least 99.9 percent and 99.99 percent removal and/or inactivation of Giardia cysts and viruses, respectively.

4. Turbidity Limitations

For systems using conventional treatment or direct filtration, the proposed Surface Water Treatment Rule requires that filtered water turbidity be ≤ 0.5 NTU in 95% of the measurements taken every month. Other levels could be specified by the State after on-site demonstration that effective removal/inactivation of Giardia lamblia cysts, or effective removal of Giardia lamblia cyst-like particles can be obtained at other filtered water turbidity levels. For example, the State could allow less stringent turbidity performance criteria (up to 1.0 NTU) for systems demonstrating effective Giardia removal by pilot plant studies. However, in such cases, the proposed rule will require that the maximum filtered water turbidity level be ≤ 1 NTU in 95% of the measurements taken each month, and at no time exceed 5 NTU.

All systems will be expected to optimize their treatment so as to achieve the lowest turbidities feasible at all times of the year. This would promote optimal removal of Giardia cysts and other pathogens, and provide optimum conditions for disinfection.

For systems using slow sand filtration, the filtered water turbidity must be ≤ 1 NTU in 95% of the measurements taken each month, and at no time exceed 5 NTU. However, the State could allow a turbidity value greater than 1 NTU in 95% of the measurements if the filter effluent at the plant prior to disinfection consistently meets the long-term coliform MCL as required for the disinfection system (see footnote b, Table I).

For systems using diatomaceous earth filtration, the filtered water turbidity must be ≤ 1 NTU in 95% of the measurements taken each month, and at no time exceed 5 NTU.

For systems using other filtration technologies, the performance criteria would be the same as for conventional treatment and direct filtration. The State could allow a filtered water turbidity value greater than 0.5 NTU in 95% of the measurements taken (at no time exceeding 5 NTU) if the system demonstrates effective performance at such levels.

5. Minimum Disinfection Requirements

a. For Systems Which Do Not Filter

At a minimum, a surface water treatment system, or a groundwater treatment system "directly influenced by surface water" (to be determined by the

State), and **which does not filter** will be required to provide disinfection operational conditions which inactivate 99.9% inactivation of Giardia cysts and 99.99% inactivation of enteric viruses. Both of these levels of disinfection can be attained by application of chlorine, chlorine dioxide, and ozone, according to the "CT values" listed in Table IIA.

Table IIA. CT VALUES FOR ACHIEVING 99.9% INACTIVATION OF Giardia lamblia[a] (U.S. EPA, Nov. 3, 1987)

Disinfectant	pH	Temperature 0.5°C	5°C	10°C	15°C	20°C	25°C
Free Chlorine[b] (2 mg/L)	6	171	122	91	61	46	30
	7	261	186	140	93	70	47
	8	377	269	201	134	101	67
	9	521	371	279	186	139	93
Ozone	6-9	4.5	3	2.5	2	1.5	1.0
Chlorine Dioxide	6-9	81	54	40	27	21	14
Chloramines[c] (preformed)	6-9	3,800	2,200	1,850	1,500	1,100	750

a These CT values for free chlorine, chlorine dioxide, and ozone simultaneously will guarantee greater than 99.99% inactivation of enteric viruses.

b CT values will vary depending on concentration of free chlorine. Values indicated are for 2.0 mg/L of free chlorine. CT values for different free chlorine concentrations are specified in tables in the Guidance Document (U.S. EPA, 1987d).

c To obtain 99.99% inactivation of enteric viruses with preformed chloramines requires CT values > 5,000 at temperatures of 0.5, 5, 10, and 15°C.

To avoid the filtration requirement, EPA's proposed Surface Water Treatment Rule will require that a system practice disinfection and have backup disinfection capability provided by backup components, including an auxiliary power supply, with automatic startup (and alarm), to ensure that continuous disinfection is provided.

The unfiltered system also will be required to demonstrate by monitoring certain disinfection parameters that it is achieving disinfection operational conditions which inactivate 99.9 percent of Giardia cysts and 99.99 percent of enteric viruses on a daily basis. To make this demonstration without resorting to isolating and counting cysts and viruses, the system must monitor and report the disinfectant(s) used, disinfectant residual concentration(s), disinfection contact time(s), pH, and water temperature. The system

must apply these data to determine if their "CT" value exceeds that required by the Rule for the specific disinfectant or combination of disinfectants to determine if the minimum percent inactivations required are being achieved.

A subset of these "CT" values for the various disinfectants to provide 99.9 percent inactivation of Giardia lamblia cysts is shown in Table IIA. These values are based on laboratory studies, and include appropriate safety factors. Since Giardia cysts are much more resistant to free chlorine, ozone, and chlorine dioxide than are enteric viruses, it can be assumed that if a system achieves 99.9 percent inactivation of Giardia cysts using these disinfectants, it will achieve much greater than 99.99 percent inactivation of enteric viruses simultaneously.

On the other hand, enteric viruses are significantly more resistant to chloramine residuals than are Giardia cysts. Systems using chloramination for primary disinfection, therefore, will have to demonstrate that they are achieving 99.99 percent of inactivation of enteric viruses as well as 99.9 percent inactivation of Giardia cysts. On-site pilot plant challenge studies, using seeded organisms, will be needed to determine whether lower CT values for chloramines achieve the required levels of inactivation. Such studies require a high level of expertise to carry out, and specialized independent (commercial) laboratories or university research personnel to make such determinations.

For the purpose of calculating CT values, **disinfection contact time,** in minutes (for chlorine, chlorine dioxide, or monochloramine) is the time required for the water to move between the point of disinfection application and the first customer. For ozone, because of its short half-life in water, disinfection contact time must be defined as the time the water is exposed to a continuous ozone residual concentration during the water treatment process.

Residual disinfectant concentration (in mg/L) for chlorine, chlorine dioxide, or chloramine is the concentration of the disinfectant at a point in the distribution system before or at the first customer. Contact time in pipelines must be calculated based on "plug flow" (i.e., all water moves homogeneously in time between two points) by dividing the internal volume of the pipeline by the peak hourly flow through that pipeline. Contact time within mixing basins and storage reservoirs must be determined by tracer studies or an equivalent demonstration.

For ozone, the residual of disinfectant concentration probably will be defined as that ozone residual measured between two specific points in the treatment process. These two points of ozone residual measurement will also define the contact time for purposes of calculation of CT-values.

If disinfectants are applied at more than one point, only the percent inactivation of all disinfectant sequences prior to the first customer may be considered in the determination of total percent inactivation. In making this determination, the disinfectant residual of each disinfection sequence and corresponding contact time must be measured before subsequent disinfection application point(s).

If multiple disinfectants are used (e.g., primary disinfection with ozone, followed by later secondary disinfection with chloramines or chlorine), the percent inactivation achieved by each of the disinfectants is additive and would apply in determining the overall disinfection performance provided.

b. For Systems Which Filter

For systems which filter, and which produce a filtered water turbidity ≤ 0.5 NTU, it may be assumed that 99 to 99.9% removal of Giardia cysts and 90 to 99% removal of viruses is attained by the filtration system. EPA recommends that systems credit filtration systems with 2-logs of Giardia inactivation, but only one-log of virus inactivation. Therefore, disinfection will be required to provide an additional 90% inactivation (1-log inactivation) of Giardia cysts and 99.9% inactivation (3-logs inactivation) of viruses.

Table IIB lists CT values necessary to achieve 90 percent inactivation of Giardia lamblia cysts. With the exception of chloramines, where higher CT values than those indicated in Table IIB might be needed, these conditions will achieve greater than 99.99% inactivation of viruses simultaneously.

If multiple disinfectants are used, the percent inactivation achieved by each of the disinfectants is additive and will apply in determining the overall disinfection provided. The clarification/filtration processes used, the degree of fecal contamination in the water at the point(s) of primary disinfection, and the formation of disinfection by-products (currently trihalomethanes) will influence the type(s) of disinfectant used and the level of CT value(s).

Under the proposed SWTR, the entire treatment train must achieve a minimum overall removal and/or inactivation of 99.9% for Giardia cysts and 99.99% removal of enteric viruses, respectively.

If a water treatment system has demonstrated that filtration is achieving greater than a 2-log removal of Giardia cysts, the Primacy Agency may permit the disinfection requirement to be reduced to the Ct requirements for **0.5 log reduction of Giardia cysts -- but not for systems using direct filtration!**. CT values which provide 0.5-log reduction of levels of Giardia cysts simultaneously provide greater than 4-logs reduction in levels of viruses, but only with ozone, chlorine and chlorine dioxide. Table IIC lists CT values for attaining 0.5-log inactivation of Giardia cysts.

Based upon raw water total coliform levels at the point of disinfection, EPA recommends that for systems which filter, sufficient disinfection be provided, in addition to the 2-logs of inactivation of Giardia cysts and one-log of inactivation of viruses credited to the filtration system, the following levels of additional disinfection be provided :

Table IIB. CT VALUES FOR ACHIEVING 90% INACTIVATION OF *Giardia lamblia*[a] (U.S. EPA, 1987a,d)

Disinfectant	pH	Temperature 0.5°C	5°C	10°C	15°C	20°C	25°C
Free Chlorine[b] (2 mg/L)	6	60	40	30	20	15	10
	7	90	60	40	30	23	15
	8	130	90	60	50	34	22
	9	170	120	90	60	46	31
Ozone	6-9	1.5	1	0.8	0.7	0.5	0.3
Chlorine Dioxide	6-9	27	17	13	9	7	5
Chloramines[c] (preformed)	6-9	1,270	730	620	500	366	260

a These CT values for free chlorine, chlorine dioxide, and ozone simultaneously will guarantee greater than 99.99% inactivation of enteric viruses.

b CT values will vary depending on concentration of free chlorine. Values indicated are for 2.0 mg/L of free chlorine. CT values for different free chlorine concentrations are specified in tables in the Guidance Document (U.S. EPA, 1987d).

c To obtain 99.99% inactivation of enteric viruses with preformed chloramines requires CT values > 5,000 at temperatures of 0.5, 5, 10, and 15°C.

Raw Water Total Coliforms * (#/100 mL)	*Giardia* Cyst Inactivation (logs)	Enteric Virus Inactivation (logs)
< 100	1.0	3.0
< 500	1.5	3.5
< 1,000	2.0	4.0
< 5,000	2.5	4.5
< 10,000	3.0	5.0

* at the point of disinfection

Table IIC. CT VALUES FOR ACHIEVING 0.5-LOG INACTIVATION OF Giardia lamblia[a] (U.S. EPA, 1987d)

Disinfectant	pH	Temperature 0.5°C	5°C	10°C	15°C	20°C	25°C
Free Chlorine[b] (2 mg/L)	6	28	20	15	10	8	5
	7	43	31	23	15	12	8
	8	63	45	34	22	17	11
	9	87	62	46	31	23	15
Ozone	6-9	0.8	0.5	0.4	0.4	0.3	0.2
Chlorine Dioxide	6-9	13	9	7	4.5	3	2
Chloramines[c] (preformed)	6-9	690	363	337	250	181	130

a These CT values for free chlorine, chlorine dioxide, and ozone simultaneously will guarantee greater than 99.99% inactivation of enteric viruses.

b CT values will vary depending on concentration of free chlorine. Values indicated are for 2.0 mg/L of free chlorine. CT values for different free chlorine concentrations are specified in tables in the Guidance Document (U.S. EPA, 1987e).

c To obtain 99.99% inactivation of enteric viruses with preformed chloramines requires CT values > 5,000 at temperatures of 0.5, 5, 10, and 15°C.

IV. EPA DISINFECTION BY-PRODUCTS REGULATIONS

A. STATUTORY REQUIREMENTS

Section 1412(b)(3)(A) requires the EPA Administrator to publish Maximum Contaminant Level Goals (MCLGs) and promulgate national primary drinking water regulations for each contaminant which, in the opinion of the Administrator, may have any adverse effect on the health of persons, and which is known or anticipated to occur in public water systems. Not later than January 1, 1988, and at 3-year intervals thereafter, the Administrator must publish a list of contaminants which are known or anticipated to occur in public water systems and which may require regulation under this Act. It is this Section under which disinfection/oxidation by-products will be identified and regulated by the EPA, although the specific wording also includes synthetic organic chemicals (SOCs) which are not produced during the water disinfection process.

These regulations will be subject to the monitoring requirements of Section 1445(a) of the Safe Drinking Water Act Amendments, which have been discussed earlier.

B. CANDIDATE DISINFECTANT/OXIDANT BY-PRODUCTS TO BE REGULATED

At present, EPA is regulating only the four trihalomethanes as DOBs. The total concentration of these four compounds currently is regulated at 100 μg/L. Other compounds will be listed for regulation by EPA as their health effects become known.

In early 1988, the Environmental Protection Agency (U.S. EPA, 1988a) promulgated the First Drinking Water Priority List, which contains 53 substances or classes of substances that are candidates for regulation. These include the above disinfectants, ammonia, the four THMs currently regulated, ozone by-products, cryptosporidium, and many additional halogenated organic materials, some of which are by-products of chlorine disinfection. EPA currently is conducting research on health effects, analytical chemistry, and treatability for most of these compounds. Within three years of publication of this first Drinking Water Priority List (by January 22, 1991), EPA is required to promulgate regulations for 25 of the substances listed.

Ten operating water utilities were surveyed recently by EPA scientists (Stevens et al., 1987a,b,c). Some 200 discrete DOBs present in drinking water and produced by chlorination were isolated, and many have been identified. Although many of these DOBs are chlorinated, many are oxygenated with no chlorine atoms in their molecular structures.

Table IV lists the frequency of occurrence in the 10-utility survey of 22 chlorinated by-products of greatest current interest to EPA's Office of Drinking Water (Stevens et al., 1987a,b,c). Other disinfectants/oxidants can be expected to produce corresponding lists of compounds which may be proposed for regulation as DOBs in the future. Many of the compounds listed in Table IV have been proposed for possible regulation (see Table III).

Table V summarizes the currently known health effects associated with several types of chlorination by-products (Akin et al., 1987). Much of the information learned about disinfection by-products in drinking water has been inferred from studies of chlorination of naturally occurring organic materials present in source waters.

Studies on the toxicity of the readily identifiable compounds are continuing with the recognition that there is no reliable way to determine whether all substances found to possess some biological activity are being identified. Because the concentrations of disinfection by-products in drinking water are low, it may not be possible to detect any biological activity directly. Thus it is not possible to determine if efficient recovery of biologically active substances is being achieved by the standard or advanced isolation and identification methods that have been investigated for this purpose.

Table III. DISINFECTANTS AND DISINFECTANT BYPRODUCTS LISTED IN THE FIRST DWPL (U.S. EPA, 1988a)

Disinfectants:
Chlorine, Hypochlorite Ion, Chlorine Dioxide, Chlorite Ion, Chlorate Ion, Chloramine, and Ammonia
Four Trihalomethanes
Chloroform, Bromoform, Bromodichloromethane, Dichlorobromomethane,
Haloacetonitriles:
Bromochloroacetonitrile, Dichloroacetonitrile, Dibromoacetonitrile, Trichloroacetonitrile
Halogenated Acids, Alcohols, Aldehydes, Ketones, and Other Nitriles
Others:
Chloropicrin (trichloronitromethane), Cyanogen Chloride, Ozone Byproducts

However, after chlorination, mutagenic activity can be determined directly in solutions containing about 2 g/L of humic acid. Thus recovery of mutagenic activity during subsequent extraction and fractionation can be followed unambiguously. From these types of studies, it has been found that the total mutagenic activity of the compounds in those samples that could be identified by GC/MS and for which sufficient quantities were available for Ames testing, accounted for only a few percent of the total activity observed in the solution. Obviously some biologically active substances were produced that were not being extracted and characterized.

Extensive studies of the by-products of ozonation, chloramination, and treatment with chlorine dioxide have not yet been conducted (Akin, 1987). However, it is well-known that the by-products of ozonation, for example, are more highly oxygenated and polar in nature than the starting materials. However, even fewer of these by-products of ozonation have been identified than in the case of chlorination. Currently, studies are underway to determine if ozonized, concentrated humic acid solutions are mutagenic, or produce any effects in subchronic bioassays in rodents. These same solutions will have to be tested for biological activity after subsequent treatments with either chlorine, monochloramine, or chlorine dioxide, because in actual practice, ozonation applied as the primary disinfectant after filtration normally is followed by one of these secondary disinfectants to provide a bacteriostatic residual for the distribution system.

Table IV. OCCURRENCE OF CHLORINATED DISINFECTION BY-PRODUCTS AT 10 WATER UTILITIES (Stevens et al., 1987a,b,c)

Compound	Number of Locations	Range of Values (ug/L)
High Confidence		
Chloroform	10 of 10	2.6 to 594
Bromodichloromethane	10 of 10	2.6 to 77
Chlorodibromomethane	10 of 10	0.1 to 31
Bromoform	6 of 10	0.1 to 2.7
Dichloroacetonitrile	10 of 10	0.2 to 9.5
Dibromoacetonitrile	3 of 7	0.4 to 1.2
Bromochloroacetonitrile	7 of 7	0.2 to 4.0
Chloropicrin	8 of 10	0.2 to 5.6
Low Confidence		
Chloroacetic Acid	6 of 10	< 10
Dichloroacetic Acid	10 of 10	< 10 to > 100
Trichloroacetic Acid	6 of 10	10 to 100
Trichloroacetaldehyde (as Chloral Hydrate)	10 of 10	10 to 100
1,1,1-Trichloropropanone	10 of 10	10 to 100
2-Chlorophenol	0 of 10	----
2,4-Dichlorophenol	0 of 10	----
2,4,6-Trichlorophenol	0 of 10	----
Qualitative Only		
1,1-Dichloropropanone	0 of 8	----
1,1-Dichloro-2-butanone	0 of 8	----
3,3-Dichloro-2-butanone	1 of 8	----
1,1,1-Trichloro-2-butanone	0 of 8	----
Cyanogen Chloride	1 of 7	----
Dichloroacetaldehyde	0 of 10	----

C. ANTICIPATED TIMING OF REGULATIONS

Before DOBs can be proposed for regulation, they must be identified as being present in drinking water supplies and produced during the disinfection (or oxidation) process, isolated, and their health effects determined. At present, only the four THMs are being regulated as disinfection by-products. The current MCL for TTHMs is 100 μg/L. However, the National Academy of Sciences (1987) has recommended that this level be lowered. EPA regulators concur in this thinking, and plan to propose a new THM standard when the Groundwater Treatment Rule is proposed in late 1990 or early 1991 (U.S. EPA, 1987a; 1987d).

Table V. SUMMARY OF HEALTH EFFECTS ASSOCIATED WITH CHLORINATION BY-PRODUCTS (Akin et al., 1987)

Chemical Class	Example	Toxicological Effects*
Trihalomethanes	Chloroform	C, H, RT
	Dichlorobromomethane	H, RT
	Dibromochloromethane	H, RT
	Bromoform	H, RT
Haloacetonitriles	Chloroacetonitrile	G, D
	Dichloroacetonitrile	M, G, D
	Trichloroacetonitrile	G, D
	Bromochloroacetonitrile	M, G, D
	Dibromoacetonitrile	G, D
Haloacid Derivatives	Dichloroacetic Acid	MD, C, N, OL, A
	Trichloroacetic Acid	HPP
Chlorophenols	2-Chlorophenol	F, TP
	2,4-Dichlorophenol	F, TP
	2,4,6-Trichlorophenol	C
Chlorinated Ketones	1,1-Dichloropropanone	M
	1,1,1-Trichloropropanone	M
	1,1,3,3-Tetrachloropropanone	M
Chlorinated Furanones	MX	M, Cl
Chlorinated Aldehydes	2-Chloroacetaldehyde	G

* C = Carcinogenic; H = Hepatotoxic; RT = Renal Toxic; G = Genotoxic; D = Developmental; M = Mutagenic; MD = Metabolic Disturbance; N = Neurotoxic; OL = Ocular Lesions; A = Aspermatogenesis; HPP = Hepatic Peroxisome Proliferation; F = Fetotoxic; TP = Tumor Promoter; Cl = Clastogenic

From the number of halogenated compounds listed for possible regulation in the First Drinking Water Priority List (Table III), from the 22 chlorinated compounds listed in Table IV, and from the nearly 200 chlorination by-products identified in the 10-utility survey (Stevens et al., 1987a,b,c), it is apparent that most of EPA's current concerns are for by-products of chlorination.

V. BEST AVAILABLE TECHNOLOGIES AND TREATMENT TECHNIQUES

A. STATUTORY REQUIREMENTS

The SDWA Amendments require the EPA Administrator to specify MCLs for each contaminant to be regulated at a level which is as close to the MCLG as is feasible with the use of best available technology, treatment techniques, and other means which the Administrator finds, after examination for efficacy under field conditions, are available (taking cost into consideration) [Section 1412(b)(4)]. The Administrator also is required to list the Best Available Technologies (BAT) which are capable of meeting MCL regulations.

Granular Activated Carbon (GAC) technology is defined by the Safe Drinking Water Act Amendments of 1986 as being feasible for the control of synthetic organic chemicals, and any technology, treatment technique, or other means found to be best available for the control of synthetic organic chemicals must be at least as effective in controlling synthetic organic chemicals as GAC [Section 1412(b)(5)].

At first glance, this last paragraph may not appear to be applicable to this discussion of disinfectant/oxidant by-products. However, primary disinfection usually is practiced after all filtration steps, including after GAC adsorption. Many of the organic precursors of DOBs will be adsorbed by the GAC; thus when disinfection now is practiced, lower quantities of DOBs will be produced.

Conversely, the practice of preoxidation, using ozone, $KMnO_4$, ClO_2, or even chlorine, for the purposes of oxidation of color, iron and manganese, taste and odor materials, microflocculation, or of synthetic organic chemicals, will provide at least partial disinfection, according to the CT values cited in Tables IIA and IIB, and depending on the total coliform levels at the point of preoxidation/predisinfection. In some cases, particularly those involving ozone, chlorine dioxide, and chlorine at the lower pH value, it is possible that the primary disinfection requirement may be satisfied at this point in the water treatment process (prior to filtration). This is especially true in the case of ozone, for which the CT values necessary to provide 99.9% inactivation of Giardia cysts and greater than 99.99% enteric viruses range from 1 to 4.5 mg/L-min (see Table IIA).

If the water treatment process is modified to include the addition of strong oxidants/disinfectants ahead of filtration (including GAC filtration/adsorption), the chemical nature of many of the organic contaminants (VOCs and SOCs) may be altered, thus promoting their biodegradation in the filters and changing their GAC adsorption characteristics. At the very least, even partial oxidation of those easily oxidized VOCs and SOCs will decrease the adsorptive loading on the GAC filters advantageously.

The Administrator also is authorized [Section 1412(b)(7)(A)] to promulgate a national primary drinking water regulation that requires the use of a treatment technique in lieu of establishing an MCL, if the Administrator makes a finding that it is not economically or technologically feasible to

ascertain the level of the contaminant. In such case, the Administrator shall identify those treatment techniques which, in the Administrator's judgement, would prevent known or anticipated adverse effects on the health of persons to the extent feasible. Such regulations shall specify each treatment technique known to the Administrator which meets the requirements of this paragraph, but the Administrator may grant a variance from any specified treatment technique.

B. DEVELOPMENT OF CRITERIA FOR BEST AVAILABLE TECHNOLOGIES

EPA's overall approach to the development of BAT criteria currently includes the following five major steps (U.S. EPA, 1987c):

1. Identification of all candidate treatment technologies, or combinations of treatment technologies;

2. Initial screening of technologies;

3. Identification of available treatment technologies (or combinations of treatment technologies) for major contaminant categories and subcategories;

4. Evaluation of available technologies (or combinations of treatment technologies) in each category;

5. Determination of BAT for each major contaminant category or subcategory.

C. BAT FOR DISINFECTION

The following processes for removing or inactivating microbiological contaminants already have been identified by EPA during the initial screening of technologies:

1. Coagulation Sedimentation/Filtration
2. Direct Filtration
3. Pressure Diatomaceous Earth Filtration
4. Slow Sand Filtration
5. Cartridge Filtration
6. Disinfection/Oxidation
7. Ultraviolet Radiation

Evaluation of these technologies by EPA is proceeding with the objective of developing BAT Criteria Documents for each. UV radiation has been found to be ineffective for providing 99.9% inactivation of Giardia lamblia cysts (Rice & Hoff, 1981). Therefore its use as a primary disinfectant probably

will be limited to groundwaters which are not "directly influenced by surface waters".

Of the seven technologies listed, #1 (Conventional Treatment), #2, and #6 can be considered as well-known and in widespread practice. The other four can be considered as "Emerging Technologies", even though slow sand filters, for example, are utilized widely in other parts of the world. For example, the United Kingdom relies extensively on this technology in both small and large municipalities (Rachwal, et al., 1987).

D. BAT TECHNOLOGIES FOR DISINFECTION BY-PRODUCTS

At the present time, a BAT document exists only for THM removal (U.S. EPA, 1981). Available or Potentially Available Treatment Methods described in this 1981 document are grouped into the following three categories:

1. Best Generally Available Treatment Methods for Reducing (concentrations of) TTHMs;

2. Additional Treatment Methods for Reducing (Concentrations of) TTHMs;

3. Granular Activated Carbon (GAC) and Biological Activated Carbon (BAC).

Under category 1 are the following Best Generally Available Treatment Methods:

a. Use of chloramines as an alternate or supplemental disinfectant or oxidant,

b. Use of chlorine dioxide as an alternate or supplemental disinfectant or oxidant,

c. Improving existing clarification for THM precursor removal,

d. Moving the point of chlorination to reduce the amount of TTHM formation and, where necessary, substituting for the use of chlorine as a preoxidant, chloramines, chlorine dioxide, hydrogen peroxide, or potassium permanganate,

e. Use of powdered activated carbon for reduction of concentrations of THM precursors or TTHMs seasonally or intermittently at dosages not to exceed 10 mg/L on an annual average basis.

Under Category 2 are the following Additional Treatment Methods for Reducing (concentrations of) Trihalomethanes:

a. Off-Line Water Storage,

b. Aeration (after production of THMs),

c. Introduction of clarification where not currently practiced,

d. Alternate source of raw water,

e. Ozone as an alternate or supplemental disinfectant or oxidant.

At least items a, c, and d are technologies which are well-known. Only aeration and the use of ozone can be considered as "Emerging Technologies", even though the use of ozone in Europe has been extensive, particularly since World War II.

Finally, GAC and BAC technologies, because of their higher capital costs and lack of widespread adoption in the USA, both must be considered as "Emerging Technologies".

E. STRATEGIES FOR CONTROLLING DISINFECTION BY-PRODUCTS

Currently, EPA has identified three distinct strategies for controlling disinfection by-products:

1. Application of alternative disinfectants,

2. Removal of precursors prior to disinfection,

3. Removal of disinfection by-products once they are formed.

Initial screening of technologies has identified the following available treatment processes or unit process steps for controlling disinfection by-products, specifically chlorination by-products (THMs):

1. Oxidation
2. Coagulation, Sedimentation, Filtration
3. Direct Filtration
4. Lime Softening
5. GAC Adsorption (Precursor Removal)
6. PAC Adsorption
7. GAC Adsorption (By-Product Removal)
8. Packed Column Aeration
9. Diffused Aeration

Items #5, #7, and #8 are "Emerging Technologies", whereas the others generally are well-known.

However, it is logical to expect that EPA may expand this list to include combinations of treatment technologies for removing synthetic organic contaminants, including disinfectant/oxidant by-products, such as:

10. **Oxidation**, Coagulation, Sedimentation, Filtration (Conventional Treatment with Preoxidation)

11. **Oxidation**, Direct Filtration (Direct Filtration with Preoxidation)

12. **Oxidation**, Slow Sand Filtration

13. **Oxidation**, GAC Adsorption

In at least half of the more than 2,000 water treatment plants throughout the world using ozonation, for example (including more than some 35 of the 40 ozone plants currently operating in the U.S.A.), ozone oxidation is practiced prior to conventional treatment or direct filtration. Preozonation is practiced early in the treatment process for microflocculation, turbidity removal, taste and odor control, color removal, iron and manganese oxidation, oxidation of THM precursors, etc. In this manner, combinations of oxidation followed by conventional treatment or direct filtration reduces the concentrations of chlorine-demanding organic materials at the terminal chlorination (currently the primary disinfection) step.

Although these process combinations are well-known throughout Europe, they must be considered as "emerging" in the U.S. today.

In process combinations #12 and #13, the oxidation step is designed to convert normally biorefractory organic materials into more readily biodegradable materials. During the slow sand filtration or GAC adsorption steps which follow oxidation, considerable biochemical conversion of dissolved organic materials to CO_2 and water occurs.

In subsequent studies, EPA plans to evaluate the sensitivity of process design criteria as functions of treatment performance and cost.

VI. DISCUSSION OF DISINFECTANTS AND OXIDANTS

A. BASIC ISSUES

The current interest in regulating disinfectants and disinfectant/oxidant by-products has been instigated by the recognition that when chlorine is added for disinfection purposes, it also produces halogenated organic materials. Their formation is a function of a number of factors, in particular the concentration and types of organic materials present in the water when chlorine is added, and the chlorinating conditions (amount of chlorine dosed, pH, temperature, reaction time, etc).

Therefore, the salient objective of water treatment now is to reduce the amounts of halogenated materials formed anywhere during the treatment process. In turn, this has prompted the three strategies identified by EPA:

1. Remove the undesired compounds after they have been produced;

2. Change disinfectants to those which do not produce the undesired by-products;

3. Reduce the concentrations of organics in the water before chlorine is added.

Modifications of these same three strategies also can be considered as applicable to coping with SOCs and their disinfection/oxidation by-products.

Of the three approaches, the first two can be criticized as disregarding the problem and treating the symptom ... keep the water treatment process the same, but either incorporate additional processing to remove the undesired materials produced by water treatment, or switch to another disinfecting material which will not produce the undesired materials.

Only the third approach recognizes and treats the problem itself, that is, the concentration of organics in the water, and how to remove these "precursors" of undesired by-products or lower their concentrations before adding chlorine. If one assumes that technological logic will win the day over partial solutions which only treat the symptoms, it can be expected that most water utilities will opt to apply the third strategy, provided that it is affordable.

1. First Approach

Once the halogenated organics have been produced, they are very difficult and/or costly to remove from water. Oxidation is ineffective, even with ozone, for removal of THMs. Adsorption by GAC is effective only for short periods of time, and GAC reactivation costs are quite high. Adsorption by powdered activated carbon (PAC) is costly and increases the quantities of sludge for disposal. Air stripping of volatile organic chemicals (VOCs) is efficient, but GAC may be required to adsorb the compounds (to prevent transfer of the pollutant from water to air), and the same problems of reactivation are present. Besides, after removal from the water, the VOCs now must be disposed of, and most of them can be expected to be subject to RCRA compliance under the appropriate hazardous waste disposal regulations.

2. Second Approach

Switching to an "alternative disinfectant" to chlorine (used as the primary and secondary disinfectant) is a logical approach, provided that the alternative disinfectant will:

(a) not produce halogenated organics,

(b) not produce other undesired disinfection by-products,

(c) provide guarantees of microbial disinfection or inactivation at least equal to those provided by chlorine, and

(d) provide a stable residual disinfectant in the distribution system.

For economic reasons, most utilities also would like the alternative disinfectant to be no more expensive than chlorine. All of this, particularly the "same cost" requirement, is asking a great deal of any single candidate alternative disinfectant. Given the fact that chlorine has been applied as the disinfectant of choice throughout the world since the early 1900s, if a cheaper and better disinfectant were available, it should have been in commercial use by this time.

Candidate "alternative disinfectants" currently being considered by many water treatment specialists are: chlorine dioxide, monochloramine, ultraviolet radiation, and ozone. However, both ozone and UV radiation can be rejected as candidates because neither provides a stable residual level for distribution systems. Miller et al. (1978), after studying European and Canadian applications of ozone for disinfection, concluded that ozone can be used as the secondary, residual disinfectant, **but only if five conditions are met simultaneously:**

1. Water temperatures must be cool (to slow biological regrowths),

2. Water must be free of iron (to eliminate growth of iron-consuming bacteria),

3. Water must be free of ammonia (to eliminate growth of nitrobacter microorganisms),

4. TOC values must be less than 1 mg/L (to minimize its accumulation as food for microorganisms),

5. Residence time in the distribution system must be less than 12 hours (so that microbial regrowths will be minimal).

Even in France, where post-filtration ozonation for primary and some secondary disinfection has been practiced since the early 1900s, all five conditions were found by Miller et al. (1978) to coexist only rarely.

Chlorine dioxide can be used as the secondary disinfectant in distribution systems, and in the water treatment plant for the primary disinfection step. However, it must be realized that ClO_2 is reduced when it disinfects and/or oxidizes, producing some level of chlorite ion, ClO_2^-, from which chlorine dioxide is generated.

Chlorine dioxide produces hematological effects in both humans and laboratory animals (NAS, 1987, pp. 89-90). The mechanism of these effects is not known; however it is believed to be related to the oxidant properties of chlorine dioxide and its aqueous reaction products, chlorite and chlorate ions. In addition, thyroid and developmental neurological effects have been observed in laboratory animals. These thyroid effects are thought to be caused by its oxidation of dietary iodide ion in the gastrointestinal tract. The oxidized iodine then binds to either food or tissue, and is unavailable for absorption. The mechanisms of the neurological anomalies are unknown.

Because of this behavior, EPA currently recommends that the total oxidant levels ClO_2 usage (chlorine dioxide + chlorite ion + chlorate ion) should not exceed 1 mg/L. This means that usage of chlorine dioxide as the primary disinfectant must be limited to rather clean waters, requiring very low applied dosages, i.e., 1.2-1.4 mg/L.

In Germany, for example, ClO_2 is employed for distribution system residual at dosage levels not to exceed 0.3 mg/L (Miller et al, 1978). In Switzerland, restrictions on the use of ClO_2 are even more rigid, 0.15 mg/L being the maximum allowable dosage (Schalekamp, 1986).

In laboratory studies, Werdehoff and Singer (1986) have shown that the 1 mg/L total oxidants from chlorine dioxide will not be exceeded if the dosage of ClO_2 does not exceed 1.2 to 1.4 mg/L. This level has been confirmed in pilot plant and full-scale plant studies at Evansville, Indiana by Lykins and Griese (1986) (see Case History of Evansville, IN -- Section VIII.C.1).

By elimination, this appears to leave monochloramine as the only apparent candidate "ideal alternative disinfectant" to chlorine. On the other hand, monochloramine is a very much weaker disinfectant than chlorine (see Tables IIA, IIB, IIC, and Section VI.B on Technical Issues - Disinfection and Disinfectants). Because of the very high CT values of monochloramine for inactivating 99.9% of Giardia lamblia cysts and 99.99% inactivation of enteric viruses (see Table IIA), it is impractical to consider its use as a primary disinfectant for surface waters or groundwaters "directly influenced by surface water". Therefore, monochloramine should be considered only as the secondary disinfectant for these types of systems (U.S. EPA, 1987a,d).

3. Third Approach

Without much argument, except perhaps cost, the concept of reducing the concentration(s) of organics in water before chlorine is added will produce fewer halogenated organic DOBs. This approach addresses the basic problem of removal of organics. A more restrictive subset of this approach is to remove organics or lower their concentrations before any strong oxidant is added. This is because the organic oxidation products of disinfectants/-oxidants other than chlorine will not be well identified for some time, since more sensitive analytical procedures and health effects data continue to be developed.

A compromise approach is to employ non-chlorinous oxidants in the early stages of water treatment (e.g., ozone, potassium permanganate, hydrogen peroxide, before or during rapid mix, and/or prior to filtration) to assist in the removal of organic materials by partial oxidation of the organics, more efficient flocculation and filtration. In such cases, the non-chlorinous oxidants do not produce halogenated oxidation products, except for those waters which may contain substantial amounts of bromide ion (which can be oxidized by ozone -- as well as chlorine -- to hypobromous acid, which then may produce brominated organics, such as bromoform --- see Section VI.C, Technical Issues - Disinfection By-Products).

This third approach, although installed in many water treatment plants for the purpose of lowering the concentrations of disinfection/oxidation by-products, also is applicable to the simultaneous removal or reduction in concentration of many SOCs and VOCs.

B. TECHNICAL ISSUES -- DISINFECTION AND DISINFECTANTS

It is paramount that the disinfectant, applied for the purpose of disinfection (as opposed to being applied for oxidation) be capable of providing the required levels of microorganism kills or inactivations. In addition to reducing levels of total coliforms, heterotrophic plate count organisms, and legionella bacteria, disinfection currently is defined by EPA (U.S. EPA, 1987a) to mean a 99.9% reduction in Giardia lamblia cyst levels, and a 99.99% reduction in enteric virus concentrations.

1. For Systems Treating Surface Waters

a. The "CT" Value

Disinfection should be recognized as a [concentration x contact time] phenomenon (C x T product). That is, the weaker the disinfectant, the longer it must contact the water being disinfected. Therefore, one of the consequences of changing disinfectants will be the appropriate lengthening or shortening of the contact times, thus changing the sizes of disinfectant contact chambers.

In EPA's proposed Surface Water Treatment Rule (U.S. EPA, 1987a), several tables of CT values are provided as guidance for water treatment officials in coping with the microorganisms to be regulated (see Table I). Table IIA compares the CT values for the four major disinfectants over the pH range of 6 to 9 at 0.5°C to 25°C with respect to their abilities to achieve 99.9% inactivation of Giardia lamblia cysts: free chlorine (at 2 mg/L), ozone, chlorine dioxide, and preformed chloramines.

Several important conclusions can be drawn from Table IIA:

1. Ozone is by far the most efficient disinfectant of the four (CT values of 4.5 at 0.5°C to 1 at 25°C). This means that a 0.5 mg/L residual ozone concentration would have to be maintained over 9 minutes at 0.5°C ranging down to 2 minutes at 25°C in order to guarantee 99.9% inactivation of Giardia lamblia cysts and more than 99.99% inactivation of virus inactivation.

2. Chlorine dioxide over the pH range of 6-9 is at least twice as effective as free chlorine at pH 6 only. At pH 7, 8, and 9, free chlorine becomes progressively less effective than chlorine dioxide.

3. A residual chlorine dioxide level of 1 mg/L would have to be maintained for 81 minutes at 0.5°C ranging down to 14 minutes at 25°C in order to guarantee 99.9% inactivation of Giardia lamblia cysts.

4. A residual of 2 mg/L of free chlorine at pH 7 would have to be maintained for 130 minutes at 0.5°C ranging down to 23.5 minutes at 25°C in order to guarantee 99.9% inactivation of Giardia lamblia cysts. If the water being disinfected also contains high trihalomethane formation potentials, using chlorine as the primary disinfectant under these conditions will produce high THM and other halogenated organic (see Table IV) concentrations.

5. When CT values are attained with free chlorine, chlorine dioxide, and ozone to inactivate 99.9% Giardia lamblia cysts, simultaneous attainment of 99.99% inactivation of enteric viruses is assured.

6. Preformed chloramines are by far the weakest disinfectant of all. To achieve 99.9% inactivation of Giardia lamblia cysts with a 2 mg/L residual would require contact times of 1,650 minutes at 0.5°C ranging down to 375 minutes at 25°C.

7. Much longer contact times are required with preformed chloramines to attain 99.99% inactivation of enteric viruses (CT values > 5,000 at 0.5-15°C) than to attain 99.9% inactivation of Giardia lamblia cysts. This means that attainment of the required 99.9% inactivation of Giardia lamblia cysts with preformed monochloramines **does not assure 99.99% inactivation of enteric viruses.**

This has led EPA to the recommendation that surface water systems wishing to use monochloramine as their primary disinfectant will have to demonstrate efficacy by conducting pilot scale tests with challenge organisms (Giardia cysts and viruses) -- a costly and time-consuming process. Thus, from a practical and cost standpoint, monochloramine should not be considered as a primary disinfectant (U.S. EPA, 1987a;d).

b. Suggested No Adverse Response Levels (SNARLs)

For some substances not regulated as known or suspected carcinogens and for which there are adequate toxicity data available from prolonged ingestion studies in humans or animals, the Subcommittee on Disinfectants and Disinfectant By-Products of the Safe Drinking Water Committee of the National Academy of Sciences has calculated Suggested No-Adverse-Response-Levels (SNARLs). In a recent publication (National Academy of Sciences, 1987), SNARLs for adults and children are presented for chlorine dioxide, chlorite ion, chlorate ion, and monochloramine. These specific values are based on the assumption that 20% of the daily intake of these substances is by ingestion of drinking water, and are summarized in Table VI.

Also included in Table VI are recommended SNARLs for some of the halogenated disinfection by-products listed by the EPA in the first Drinking Water Priotiry List for possible regulation (U.S. EPA 1988a).

Table VI. NAS RECOMMENDED SNARLs FOR DISINFECTANTS AND DISINFECTANT BY-PRODUCTS (NAS, 1987)

Disinfectant/By-Product	for 70-kg adult	for 10-kg child
Chlorine Dioxide	0.21 mg/L	0.06 mg/L
Chlorite & Chlorate Ions	0.024 mg/L	0.007 mg/L
Monochloramine	0.581 mg/L	0.166 mg/L
Dichloroacetonitrile	0.056 mg/L *	-----
Dibromoacetonitrile	0.161 mg/L	0.046 mg/L

* The Subcommittee does not recommend this SNARL because of concern that DCAN may be carcinogenic.

c. Possible Regulatory Consequences

Values for SNARLs recommended in Table VI are quite significant, by themselves, but also when considered in light of the CT values for the disinfectants listed in Table IIA. Considered by themselves, they are indications of possible MCLs (or at least MCLGs) which EPA may propose and promulgate in the future (i.e., when the Groundwater Treatment Rule is proposed in 1991). If these SNARL values do become the basis for the corresponding MCLs, it is also probable that EPA will set the MCLG and/or MCL to protect the 70-kg adult, because exposure times would be calculated over a human lifetime.

In this event, a projected MCL of 0.21 mg/L for chlorine dioxide may eliminate this material from consideration as a primary disinfectant, except in very clean waters, and will reduce its utility as a secondary disinfectant (except in very clean waters).

At the same time, a projected MCL of 0.581 mg/L for monochloramine will virtually eliminate this material from consideration as a primary disinfectant because of the excessive contact times which would be required to attain 99.9% and 99.99% inactivations of Giardia lamblia cysts and enteric viruses, respectively, at this concentration. For example, at 0.5°C, a contact time of 5,690 minutes (94 hours = 3.95 days) would be required to assure 99.9% inactivation of Giardia lamblia cysts. At 25°C, a contact time of 1,293 minutes (21.6 hours) would be required. To attain 99.99% inactivation of enteric viruses at 0.5-15°C would require a contact time with monochloramine of > 8,620 minutes (> 143 hours = > 2.4 days).

The hypothesized 0.581 mg/L MCL for monochloramine would not eliminate this material from consideration as a secondary disinfectant, however, since EPA is likely to require only a "detectable residual" in the distribution system when the Surface Water Treatment Regulation is promulgated during 1988. Under these projected regulatory restrictions, the concept of a single

"alternative disinfectant" disappears, to be superseded by the concept of "alternative disinfecting systems". Such alternative disinfecting systems would involve the use of **combinations** of a primary disinfectant (e.g., ozone, ultraviolet radiation) to be followed by a secondary (residual) disinfectant (e.g., chlorine, chlorine dioxide, or chloramine) for the majority of cases.

For systems whose raw waters have very low THM formation potentials, or in which THMFP can be lowered appropriately prior to disinfection, then chlorine can continue to be both the primary and secondary disinfectant. However, the luxury of continued application of chlorine as the predisinfectant and as the primary and secondary disinfectant will be dictated by the future THM regulations, as well as future regulations for other halogenated organic by-products of chlorination (see next section).

1. EPA'S PERSPECTIVE ON RECOMMENDED NAS SNARLS

In the proposed SWTR (U.S. EPA, 1987a), EPA rejects the NAS assumption that only 20% of the daily exposure to chlorine dioxide and monochloramine comes from drinking water. EPA expects that exposure to these disinfectants from sources other than drinking water will be minimal. Therefore, assuming that nearly 100% of exposure comes from drinking water, the relative SNARLs might be estimated as 1 mg/L for chlorine dioxide (including its oxidation/reduction products, chlorite and chlorate ions) and 2.5 mg/L for chloramine. This is the current recommendation that concentrations of these two disinfectants do not exceed 1.0 and 2.5 mg/L, respectively. These levels were proposed by EPA earlier (U.S. EPA, 1979).

It is also possible that EPA might apply a different uncertainty factor (1,000) than used by the NAS (100) in calculating SNARLs (actually MCLs) for chlorine dioxide, chlorite and chlorate ions, and monochloramine. The significance of this possibility is illustrated in the following example SNARL calculation for monochloramine:

$$\frac{8.3 \text{ mg/kg bw/day} \times 70 \text{ kg} \times 0.2}{100 \times 2 \text{ liters}} = 0.581 \text{ mg/L, or } 581 \text{ ug/L}$$

where:

8.3 mg/kg bw/day = dosage in mg/kg of body weight per day

70 kg = average adult weight

0.2 = 20% of total daily intake

100 = uncertainty factor

2 liters = daily adult water consumption

It can be seen that changing the estimate of percent of total intake from 0.2 to 1.0 multiplies the calculated SNARL by a factor of five. On the other hand, changing the uncertainty factor from 100 to 1,000, decreases the calculated SNARL by an order of magnitude (a factor of 10).

For example, using an uncertainty factor of 1,000, the NAS SNARL for ClO_2 for adults becomes 0.021. When this figure is multiplied by 5 (to correct for 100% daily exposure rather than 20% exposure), the SNARL becomes 0.105 mg/L. Similar calculations for monochloramine gives a revised projected SNARL of 0.29 mg/L.
To put these potential regulatory limits into perspective, the three possibilities discussed above are summarized in Table VII for chlorine dioxide, chlorite and chlorate ions, and monochloramine.

From this table, the range of highest and lowest potential MCL levels can be projected, Variations A and B. In the proposed SWTR, EPA has rejected the NAS-proposed values and is proposing values close to the higher (Variation A) levels. However, further health effects studies are in progress, and these issues are to be revisited by EPA in about a year. At that time, it is possible that the current recommended maximum levels for chlorine dioxide and monochloramine may be lowered.

TABLE VII. PROJECTED MCLs FOR CHLORINE DIOXIDE AND CHLORAMINE

Disinfectant or By-Product	Projected MCLs Based on Variations in Adult SNARLs		
	June 87 NAS[a]	Variation A[b]	Variation B[c]
chlorine dioxide	0.21 mg/L	1.05 mg/L	0.105 mg/L
chlorite/chlorate ions	0.024 mg/L	0.12 mg/L	0.012 mg/L
monochloramine	0.581 mg/L	2.9 mg/L	0.29 mg/L

a 20% daily exposure; uncertainty factor = 100. The 20% daily exposure level number has been rejected by the EPA in favor of 100% (U.S. EPA, 1987a).

b 100% daily exposure; uncertainty factor = 100

c 100% daily exposure; uncertainty factor = 1,000

Therefore, the following possibilities appear with respect to chlorine dioxide and monochloramine:

1. If an MCL for chlorine dioxide is set at 0.10 mg/L (Variation B), chlorine dioxide would be eliminated as a primary and probably as a secondary disinfectant, except in very clean waters.

2. An MCL for chlorite/chlorate ions at either the highest or lowest value given may eliminate chlorine dioxide from consideration as a primary disinfectant.

3. For monochloramine, an MCL of 2.9 mg/L (Variation A) will allow this material to be applied both as a primary and secondary disinfectant. In fact, EPA's current proposal (U.S. EPA, 1987a;d) is to allow a maximum of 2.5 mg/L.

   On the other hand, an MCL of 0.29 mg/L (Variation B) would eliminate monochloramine from consideration as a primary disinfectant, but would not eliminate monochloramine as a secondary disinfectant.

Under these assumptions of total human exposure from drinking water, chlorine dioxide currently can be considered for primary and secondary disinfection, within the constraints of the appropriate "CT values", and monochloramine can be considered as a secondary disinfectant. However, there is a strong probability that EPA will propose MCLs by 1991 (Ground Water Treatment Rule) which will be lower than currently recommended levels, and which will reduce the practicality of both disinfectants as primary, and probably as secondary disinfectants as well.

2. For Systems Treating Groundwater

As pointed out earlier, many groundwater systems which do not now disinfect will be required so to do, but the Groundwater Treatment Rule will not be proposed by EPA until 1991. Since cysts normally are not present in groundwaters (except in those groundwaters "directly influenced by surface waters), requirements to inactivate these types of microorganisms are not expected. However the other microorganisms listed in Table I (total coliforms, pathogenic viruses, heterotrophic plate counts, and legionella organisms can be expected to be present, and therefore to be regulated. If viruses are regulated, the same 99.99% inactivation requirement can be expected.

a. "CT" Values and SNARLs

It can be anticipated that CT values similar to those given in the Surface Water Treatment Rule will apply to the various disinfectants, as well as the SNARLs and/or the resulting MCLs/MCLGs. Therefore, the same reasoning discussed above with respect to chlorine dioxide, chlorite and chlorate ions, and monochloramine should apply to eliminate or reduce the viability of these materials from consideration as primary and secondary disinfectants.

b. Possible Regulatory Consequences

This reasoning leads to the same conclusions regarding disinfection of groundwater systems as for surface water systems: in the majority of systems, the application of a primary disinfectant (e.g., ozone, UV radiation) will be necessary, followed by a secondary disinfectant (e.g., chlorine, chlorine dioxide, or chloramine) for the "detectable residual" to be carried throughout the distribution system.

As before, the ability to use chlorine as both the primary and secondary disinfectant will rest on the future MCLs for THMs and for other by-products of chlorination to be proposed by EPA in 1990 or 1991.

Ground water systems may face an additional complication, however, when they are required to disinfect. Those ground waters which contain significant levels of iron and manganese will produce insoluble iron and manganese oxides when treated with ozone or chlorine. This will necessitate the addition of filters to remove oxidized insoluble materials. In addition, both ozonation and chlorination also may cause flocculation of dissolved organics, and precipitate turbidity-causing particulates.

Formation of these types of insoluble materials will require secondary disinfection after filtration.

One major advantage of UV radiation as the primary disinfectant for groundwaters is that at appropriate applied energy levels, bacterial disinfection occurs readily, without extensive oxidation. Therefore, for groundwater systems with only traces of iron and manganese in their raw waters, use of UV radiation followed by secondary chlorination might be the least-cost alternative disinfecting system.

C. TECHNICAL ISSUES -- DISINFECTION/OXIDATION BY-PRODUCTS

Although to date, EPA is regulating only the four THMs as disinfection by-products, several additional halogenated organics have been listed in the first Drinking Water Priority List (U.S. EPA, 1988a) for possible regulation. Also included on the first DWPL are the three disinfectants themselves (chlorine, chlorine dioxide, chloramine), chlorite and chlorate ions, ammonia, and "ozone byproducts". This latter expression is intended as a catchall category. In the event that specific byproducts of ozonation are identified and shown to be detrimental to public health, they will be proposed for regulation individually.

Akin et al. (1987) describe the current EPA Health Effects Research Program dealing with compounds which have been identified as disinfection by-products and for which health effects data currently are being developed. All of those under current investigation are halogenated compounds which are listed in Tables IV and V.

The major technological issue in controlling current DOBs is how to reduce the concentrations of these halogenated organic materials without

compromising microbiological safety. Some will add, "...and without producing other by-products which are as potentially toxic (or of public health concern) as those produced from chlorine". Still others will add, "... and at no increase in costs".

1. Non-Halogenated DOBs

As has been concluded in an earlier discussion, only chlorine and ozone (possibly UV radiation for groundwater) appear to be the major primary disinfectants of the future for public water supplies. Ozone is known to produce oxygenated materials as oxidation products. High energy UV radiation also can produce oxidation products, provided that appropriate dissolved oxygen and peroxide levels are present. What types of non-halogenated oxidation products are produced by ozone and/or UV radiation, and what is known of their toxicities? Are similar types of non-halogenated oxidized organic materials produced from the use of chlorine?

a. From Ozonation (Rice & Gomez-Taylor, 1986)

Ozone generally is not reactive with saturated aliphatic hydrocarbon compounds. However, other types of aliphatic compounds, particularly olefins, are readily oxidized to unstable ozonides, peroxides, and hydroperoxide intermediates to form primarily aldehydes, ketones, and acids. A by-product of nearly all (if not all) organic oxidations with ozone is hydrogen peroxide. In the presence of additional ozone, however, the H_2O_2 is decomposed into hydroxyl free radicals, which are more powerful oxidizing agents than the ozone molecule itself. Hydroxyl radicals are rapidly destroyed by bicarbonate and carbonate ions, which comprise the natural alkalinity of raw waters.

Although ozone is capable of oxidizing many organic compounds completely to CO_2 and water, this conversion usually requires large doses of ozone (> 3 moles O_3/mole of organic compound) and long reaction times (sometimes hours). Under drinking water treatment plant ozonation conditions (1 to 5 mg/L applied ozone dosage; 5 to 20 minutes contact time), organic compounds usually are only partially oxidized. The oxidized organic materials are more polar, of lower molecular weight, more biodegradable, and usually more readily removed from solution by flocculation and filtration.

Oxalic acid (HOOC-COOH) is found commonly as a "final" oxidation product of many aliphatic, aromatic, and heterocyclic organic materials, because of its very slow rate of oxidation with ozone. Acetic acid is another "final" oxidation product which also is resistant to further oxidation, even with ozone, under drinking water treatment plant conditions.

Formic acid and formaldehyde also are formed during the later stages of ozone oxidation of many organic materials. However, these two by-products are readily oxidized to CO_2 and water, provided sufficient ozone is present in solution. Ozone oxidation rates of intermediate organic oxidation products usually are slower than the oxidation rates of the original compounds.

In a few instances, ozone oxidation products have been isolated which are more toxic than the original compounds. For example, ozonation of the pesticide heptachlor produces heptachlor epoxide, almost quantitatively. Heptachlor epoxide is quite stable to continued ozonation (Hoffman & Eichelsdörfer, 1971).

Parathion and malathion produce paraoxon and malaoxon, respectively, as initial oxidation products upon ozonation. Both of the oxons are at least as toxic than are the original thion pesticides. However, upon continued ozonation, the intermediate oxons continue to oxidize, producing innocuous final oxidation products (Laplanche et al., 1983).

Ozonation of phenol can produce resorcinol, which is a known THM precursor. This may explain the observations made by several groups that in following ozonation of some surface waters directly with chlorination, higher levels of THMs have been produced than by chlorination alone (Rice, 1980). In most cases, however, ozonation followed immediately by chlorination produces lower concentrations of THMs.

Infrequent finding of higher THM levels after ozonation and immediate chlorination has led to moving the initial ozonation point(s) to the rapid mix or before, and just sometimes just prior to filtration, to allow flocculation and even biodegradation of the more polar initial ozone oxidation products during filtration. Chlorination then follows at a later treatment stage. Under these conditions, lower THM levels always are found.

The National Academy of Sciences (1987) report (p. 67) notes that oxidation products of ozone (as well as non-chlorinated organic oxidation products from chlorine and chlorine dioxide) are similar to the organic compounds formed by natural oxidation processes. In other words, a surface water source such as a lake will be experiencing prebiological and chemical oxidative processes for months, perhaps longer, by processes which are similar in their chemistries to oxidation processes used in water treatment.

It is concluded by the National Academy of Sciences (1987, p. 195) that little is known about the types of by-products produced by ozonation of natural organics, and that well-conceived studies need to be conducted which will focus on the stable compounds expected from ozonation reactions with humic materials. Since saturated aldehydes (non-toxic) are well-known oxidation products of organic materials, it is suggested (NAS, 1987) that particular attention should be paid to the search for unsaturated aldehydes (some of which are known toxicants) and for hydroxyhydroperoxides.

However, unsaturated aldehydes, if formed during ozone oxidation, should oxidize rapidly at the double bond with ozone, thus destroying them.

Finally, the National Academy of Sciences (1987, p. 196) states:

> "Notwithstanding the fact that these studies need to be carried out, drinking water suppliers should not dismiss the possibility of using ozone as an alternative to chlorine and chloramines in water treatment. Ozone is an excellent disinfectant (although it must be

used in combination with a secondary disinfectant to maintain a residual in the distribution system); ozone is an excellent oxidant for the various needs of water treatment; it does not form chlorinated by-products; and the admittedly inadequate studies now available point to lower toxicities of ozonated water than of chlorinated water."

b. From Chlorination

From the aqueous chlorination of various humic materials, Stevens et al. (1985) identified 98 specific organic compounds, including 47 discrete compounds containing chlorine and 51 discrete compounds that did not contain chlorine. Christman et al. (1980) showed that the products of chlorination of aquatic humic materials generally fall into three broad structural categories: non-chlorinated substituted aromatics, chlorinated straight chain acids, and non-chlorinated straight chain aliphatic acids.

Seeger et al. (1984) showed that at low chlorine doses, which are typical of those conditions currently found in drinking water treatment plants and their distribution systems, many ring-chlorinated aromatic acids are obtained, in addition to the numerous nonchlorinated aromatic and aliphatic compounds identified by earlier investigators.

In reviewing the available literature on products isolated and identified from the treatment of humic and fulvic acids in aqueous solution with ozone, chlorine, chlorine dioxide, and potassium permanganate, Rice & Gomez-Taylor (1986) concluded that the non-chlorinated oxidation products formed by all four oxidizing agents are similar.

More recently, Stevens et al. (1987a,b,c) isolated nearly 200 discrete compounds from 10 operating water utilities practicing chlorine disinfection. Of those compounds which were positively identified, 31 are non-chlorinated, and are similar to those identified in other studies of ozonation of humic/fulvic acids.

Therefore, consideration of ozonation as a water treatment agent should not be postponed simply on the basis of the myriad of oxidation products which are formed. Many of the same compounds are formed during chlorination.

D. COMPARISON OF DISINFECTANTS - OXIDANTS

1. General Considerations

The capability of one substance to oxidize another is measured by its Oxidation Potential, normally expressed in volts of electrical energy (referenced to the hydrogen electrode). The oxidation potential is a measure of the relative ease by which a substance is able to lose electrons, thereby being converted to a higher state of oxidation. If the oxidation potential of substance A is higher than that of substance B, then substance B can be oxidized by substance A. Oxidation potentials of representative

oxidants/disinfectants commonly used or encountered in water treatment are listed in Table VIII.

Table VIII. OXIDATION POTENTIALS OF WATER TREATMENT OXIDANTS[a]

Species		Oxidation Potential, Volts
hydroxyl free radical	$(OH)\cdot$	2.80
* ozone	(O_3)	2.07
hydrogen peroxide	(H_2O_2)	1.76
permanganate ion	(MnO_4^-)	1.68
* hypochlorous acid	(HOCl)	1.49
* chlorine	(Cl_2)	1.36
* hypobromous acid	(HOBr)	1.33
* bromine	(Br_2)	1.07
hypoiodous acid	(HOI)	0.99
* chlorine dioxide	$(ClO_2)(aq)$	0.95
* iodine	(I_2)	0.54
oxygen	(O_2)	0.40

a Source: Handbook of Chemistry & Physics, CRC Press, Inc.

* excellent disinfecting agents

Although the relative position of an oxidant in Table VIII is indicative of its ability to oxidize other materials, its oxidation potential does not indicate how fast one material will be oxidized by another, nor how far toward completion the oxidation reaction will proceed. One cannot tell from oxidation potentials alone whether a specific organic compound will be oxidized completely (to CO_2 and water) or only to the first of several intermediate stages.

One significant fact can be learned from Table VIII, however, at this point. As has been discussed in earlier sections of this report, it is rare that organic compounds treated with an oxidant even as powerful as ozone will be converted totally to CO_2 and water, under conditions normally encountered in water treatment plants. Therefore, no other commonly employed and less

powerful water treatment oxidant (such as chlorine, bromine, chlorine dioxide, etc.), all of which have lower oxidation potentials than ozone, will oxidize an organic material completely to CO_2 and water if ozone will not.

All oxidants weaker than ozone will be less effective than ozone in converting organic compounds to carbon dioxide and water, and thus may produce higher quantities of partially oxidized organic materials under water treatment plant conditions. It is important, therefore, for the water treatment professional to understand the chemistry of the organic components of the particular water supply when considering the use of any oxidant in the processing.

When oxidizing agents are added to water supplies containing specific organic compounds as impurities, it is not sufficient simply to follow the reduction in concentration of that compound. Other parameters, specifically the total organic carbon (TOC), provide needed information. With chlorine, the TOX (total organic halogen) also is a necessary parameter. In terms of the newer halogenated compounds to be regulated by EPA, TOX Formation Potential (TOXFP) will become important, particularly the non-purgeable TOXFP (the NPTOXFP). This is a measure of the non-volatile TOXFP in the water.

It is also desirable to know the products of oxidation of the organic impurities which are being treated by the oxidizing agent. When a discrete organic compound is oxidized, it may be totally destroyed by oxidation, but without a decrease in TOC content, In this instance, the concentrations of oxidation products may be as significant as the concentration of the original impurity.

It is also important not to attempt to relate the disinfection capability of a specific oxidant to its oxidation potential. Ozone is the most powerful oxidant listed in Table VIII, and it is also the best disinfectant (i.e., its CT values are less than for any other disinfectant for a given species of microorganism). However hydrogen peroxide and potassium permanganate, which follow ozone in Table VIII, are known to be poor disinfectants, while iodine and chlorine dioxide, which have oxidation potentials less than half that of ozone, are very good disinfectants.

Table VIII is useful to the water treatment specialist in understanding the degree of chemical transformation which can be expected when various oxidizing agents are used at various stages of the water treatment process.

Table IX lists data for the various disinfectants, comparing the dosages and contact times required for 99% inactivation of Escherichia Coli. Table X lists similar data for 99% inactivation of Poliovirus Type I.

2. Chlorine

This material is an excellent disinfectant, an excellent chemical oxidant, but unfortunately also is an excellent chlorinating agent. Its production of THMs is well-known, but it also produces a wide variety of additional

halogenated compounds (TOX). In addition, chlorine is known to produce significant quantities of non-halogenated oxidation products. Some of these, from humic and fulvic acids for example, are identical to those produced by potassium permanganate, ozone, and chlorine dioxide (Christman, et al., 1980).

TABLE IX. COMPARISON OF DISINFECTION PERFORMANCE TO E. COLI [a]

Disinfecting Agent	Concentration mg/L	Contact Time, min	CxT[b]	Temperature pH	°C
HOCl	0.1	0.4	0.04	6.0	5
$(OCl)^-$	1.0	0.92	0.92	10.0	5
NH_2Cl	1.0	175.0	175.0	9.0	5
ozone	0.04	0.50	0.02	7.2	1
ozone	0.0125	0.33	0.004	7.0	12
ClO_2	0.30	1.8	0.54	7.0	5
ClO_2	0.80	0.35	0.28	7.0	25
iodine	1.3	1	1.3	6.5	2-5
iodine	0.30	2	0.60	9.1	20-25
H_2O_2	90	~360	32,400	6.5	ambient
$KMnO_4$	1	45	45	5.9	0
$KMnO_4$	16	25	400	9.2	20

a From Drinking Water and Health, Vol. 2 (Washington, DC: National Academy Press, 1980), Chapter 2.

b Concentration of disinfectant times contact time.

On the positive side, chlorine provides a stable residual for the water distribution system, provided that the water is free of chlorine-demanding ammonia and organic materials.

3. Chlorine Dioxide

This chemical is a powerful oxidant and disinfectant. Because of its instability, it must be generated on-site, which can be considered a disadvantage. In its pure state, ClO_2 does not produce trihalomethanes in the presence of organic materials which do produce THMs with chlorine.

Some procedures for synthesizing chlorine dioxide from sodium chlorite and elemental chlorine involve the use of excess chlorine. Thus, in these

instances, some free chlorine is present in the water, resulting in the production of some THMs. The more that ClO_2 can be synthesized without the need for excess chlorine, the lower the concentrations of THMs which will be produced by the excess chlorine. One procedure for generating ClO_2 free of excess chlorine is by addition of mineral acid to solutions of sodium chlorite.

TABLE X. COMPARISON OF DISINFECTION PERFORMANCE TO POLIOVIRUS TYPE I [a]

Disinfecting Agent	Concentration mg/L	Contact Time, min	CxT[b]	pH	Temperature, °C
HOCl	0.5	2.1	1.05	6.0	5
HOCl	1.0	2.1	2.1	6.0	5
$(OCl)^-$	0.5	21	10.5	10.0	5
$(OCl)^-$	1.0	3.5	3.5	10.0	15
NH_2Cl	10	90	900	9.0	15
NH_2Cl	10	32	320	9.0	25
ozone	0.042	10	0.42	7.0	25
ozone	<0.3	0.13	<0.04	7.0	5
ClO_2	0.3	16.6	5.0	7.0	5
ClO_2	0.8	1.5	1.2	7.0	25
iodine	1.25	39	49	6.0	25-27
iodine	20	1.5	30	7.0	25-27

a From Drinking Water and Health, Vol. 2 (Washington, DC: National Academy Press, 1980), Chapter 2.

b Concentration of disinfectant times contact time.

Although chlorine dioxide does not produce the variety of chlorinated organic materials as does chlorine, nevertheless, some organic compounds do form chlorinated oxidation products, although in much smaller quantities than from chlorine (Rice & Gomez-Taylor, 1986). Mostly, however, ClO_2 oxidation products of organic materials are non-chlorinated.

A major disadvantage of chlorine dioxide is that as it performs its oxidation or disinfection work, about half of it reverts back to the chlorite ion. Although not all of the toxicological parameters of chlorite ion are as yet known, it does produce hematological effects (Condie, 1986). Consequently, EPA currently recommends that the total residual concentration of chlorine dioxide, chlorite ion and chlorate ion not exceed 1 mg/L in finished water

because of concerns about hematopoietic and possibly thyroid effects (Cotruvo and Vogt, 1985).

On the other hand, chlorine dioxide is not known to oxidize bromide ion in water to produce hypobromous acid (as does chlorine and ozone), which can form bromine-containing organic materials.

4. Monochloramine

This material is synthesized at the water treatment plant by the reaction of elemental chlorine with ammonia in equimolar quantities by one of three procedures:

1. Ammonia can be added to water already containing chlorine,
2. Chlorine can be added to water already containing ammonia,
3. A preformed solution of monochloramine can be added to the process water.

Procedure #1:

If chlorine is first added to the water to be treated to attain disinfection over a specific period of time, a CT contribution toward disinfection from free chlorine will be attained. However, the longer the free chlorine residual is sustained, the more halogenated organic materials which are not desired will be produced during the disinfection contact time. Thus there will not be major benefit to the use of chloramine, in that instantaneous halogenated organic levels will be the same. However, addition of ammonia will insure that THMs will not continue to be generated after monochloramine has been formed. In this manner, TTHM levels can be held to their initial levels.

Procedure #2:

If ammonia is first added to the water, then chlorine, provided that very good mixing is available, none of the water should be exposed to significant concentrations of free chlorine. This will lower concentrations of halogenated materials, but not necessarily guarantee disinfection since monochloramine now is the disinfectant.

In certain cases, however, this approach may be even less effective. When chlorine is added to waters which contain organic nitrogen materials, such as proteins and aminoacids, the chlorine reacts much more rapidly with the organo-nitrogen compounds to form organic N-chloramines than with free ammonia to form the inorganic monochloramine (Weil & Morris, 1949; Morris, 1967). In turn, the organic N-chloramines are even weaker disinfectants than is monochloramine.

Even worse, standard methods of analysis for monochloramine based on iodometry (i.e., DPD) do not distinguish between inorganic monochloramine and organic chloramines, because both oxidize iodide ion to iodine in the determination of "combined residual" chlorine (NAS, 1987, pp. 62-63).

Thus, a water utility with raw water containing organic nitrogenous materials which adds ammonia, then chlorine to produce "monochloramine" for primary disinfection may be seriously overestimating the ability of its treatment system to provide the desired degree of disinfection.

Procedure #3:

To be assured of producing the minimum quantities of chlorinated organics, the chlorine and ammonia can be mixed in organic-free water, and the monochloramine solution can be added to the water being treated. This approach "preforms" the chloramine. However, this approach produces minimal disinfection and also is subject to the same competition with organic nitrogen compounds as discussed above. The organo-nitrogen compounds still present can steal chlorine from the inorganic monochloramine, producing the much less effective organic chloramines, which are not distinguishable from inorganic chloramines by field iodometric analytical procedures.

a. Chloramine Summation

Because chloramine is a much weaker disinfectant than is free chlorine, or any of the other disinfectants, the contact time required to assure disinfection of any particular organism will be longer than with chlorine, chlorine dioxide, or with ozone.

In some cases, such as with patients who are on kidney dialysis machines, the ingestion of chloramine-containing water can be fatal. In municipalities using $ClNH_2$ as the terminal disinfectant, the utility generally advises local hospitals and health maintenance centers of the presence of monochloramine in their tap waters, and advises these institutions to employ distilled water for their dialysis patients.

As with chlorine dioxide, the use of monochloramine as a bacteriostat can follow post-filtration disinfection by means of ozone, for example, to provide minimum production of halogenated organics. Monochloramine is a very poor chemical oxidizing agent. However, it is known to dissociate slowly in water to produce small quantities of hypochlorous acid, which in turn produce traces of halogenated organic materials (Rice & Gomez-Taylor, 1986).

In assessing all currently known facts about monochloramine, the Subcommittee on Disinfectants and Disinfectant By-Products of the National Academy of Sciences' Safe Drinking Water Committee has stated recently (NAS, 1987, pp. 194-195):

> "Because it is a much weaker disinfectant than chlorine, chloramine must be used at higher concentrations and for longer periods of

contact to achieve sufficient disinfection. Even with extended contact time and higher concentrations, however, chloramination is not recommended as a primary disinfectant, especially where virus or parasitic cyst contamination is potentially present."

"Preformed monochloramine is undesirable as a primary disinfectant."

"The use of marginal chlorination as a method of introducing chloramines into a water supply system is specifically **not recommended** because, along with depletion of chlorine to produce inorganic monochloramine, organic chloramines that have even lower efficacy as disinfectants are formed. Organic chloramines have also been implicated as major contributors to the mutagenicity of chlorinated drinking and natural waters."

There are currently no suitable methods for fully quantifying the organic chloramine fraction in the presence of inorganic monochloramine. Until such methods are developed, utilities that handle water supplies containing high concentrations of organic nitrogen run the risk of overestimating the ability of their systems to maintain adequate disinfection."

"When free chlorine is used as the primary disinfectant, an amount should be used that is sufficient to produce a slight residual of free chlorine above that required to oxidize nitrogen, followed by addition of ammonia to form monochloramine and limit THM formation."

5. Ozone

a. General Considerations

This gas also must be generated on site, at the water treatment plant, because it is too unstable to be stored for significant periods of time in cylinders. Additionally, it is only partially soluble in water (about 13 times the solubility of oxygen). Therefore, one key to its successful use is proper gas/liquid contacting. If all of the ozone generated is not solubilized and reacted with water constituents, the excess ozone present after contacting must be reused or destroyed, in order to prevent unnecessary exposure of plant operating personnel to this material.

Because the generation, application, and handling of ozone is so foreign to the classical water treatment processor in the USA, and because of the relatively high capital cost of ozone generation and application equipment, the acceptance of ozone in North America has been slow to develop, even though it is used abundantly in other countries of the world (Miller et al., 1978).

On the positive side, ozone is the most powerful disinfectant and oxidizing material which is available to the water processor. It kills or inactivates all organisms tested in shorter periods of time than does any other disinfectant/oxidant available (see Tables IIA, IIB, IIC, VIII - X).

Ozone cannot produce any halogenated organic materials, other than indirectly, e.g., by oxidation of bromide ion (if that material is present in raw waters being treated) followed by bromination of organic precursors.

Being a powerful oxidizing agent, ozone used in very low applied dosages is able to neutralize charges on colloidal particles, thus causing them to precipitate. In higher applied dosages, ozone is quick to oxidize organic materials, but usually only partially. In rare cases, organic matter can be converted quickly to CO_2 and water by ozone. However, under normal water treatment conditions (i.e., dosages of 1-5 mg/L of ozone and contact/reaction times of 5-15 minutes), most of the organic materials contained in water are only partially oxidized.

b. Disinfection With Ozone

For purposes of disinfection, it is necessary to generate ozone, on-site, and apply the gas (normally air + 1-5% ozone) to the water to be disinfected (using an appropriate gas/liquid contacting device) for a length of time appropriate to provide the CT values given in Table IIA for 99.9% inactivation of Giardia lamblia cysts. In practice, dissolved ozone levels of approximately 0.4 to 0.5 mg/L are attained and maintained during the disinfection process. Ozone contact times in currently operating water treatment plants using ozone for bacterial disinfection and viral inactivation are a minimum of 10 minutes, and range up to 15-20 minutes.

EPA's proposed Surface Water Treatment Rule requires attainment of 99.9% inactivation of Giardia lamblia cysts. From Table IIA, the highest CT value for ozone is 4.5 (for water temperatures of 0.5°C). This means that for a dissolved ozone concentration of 0.5 mg/L, a maximum contact time of 9 minutes would be required at 0.5°C to attain the CT value of 4.5. This length of contact time is easily within the design capabilities of the technology, and would not produce unique consequential problems of design and installation of ozonation systems.

As will be discussed in the following subsections, ozone has many applications in drinking water treatment which utilize its oxidation capability, and which are entirely unrelated to its disinfection capabilities. On the other hand, whenever ozone is used for oxidative purposes, it is possible to attain primary disinfection simultaneously, for most oxidative applications of ozone. The simplest method of attaining simultaneous primary disinfection is to extend the contact time appropriate to attain the necessary CT value at the particular water temperature.

However, knowledge of the dissolved ozone concentration during oxidation also is critical to attainment of the appropriate CT value. In certain oxidative applications, specifically ozone oxidation of waters containing high levels of iron and manganese (groundwaters), and preozonation for microflocculation and turbidity control (surface waters), measurement of a dissolved ozone residual is inappropriate.

In the case or iron and manganese, the dark, precipitating oxides produced upon ozonation will interfere with measurement of dissolved ozone. In the case of microflocculation or turbidity control, the objective is to apply a very low dosage of ozone, which means that a measurable concentration of dissolved ozone may never be attained. In these cases, ozone disinfection would have to be provided as a separate treatment step, normally practiced just before or after filtration.

However, in all other oxidative applications, it is not only possible, but actually feasible to design the ozone dosage and contact time so as to produce the CT values required in Tables IIA, IIB, and IIC. In taking credit for ozone disinfection prior to filtration, attention must be paid to the total coliform levels at the point of primary disinfection. Successful attainment of both oxidation and primary disinfection before filtration means that only secondary disinfection will be required after filtration.

c. Microflocculation

Ozone oxidation of humic/fulvic materials can proceed to a variety of endpoints. With low applied ozone dosages, oxidation occurs primarily on the pendant groupings without cleaving the high molecular weight humic/fulvic polymer chains.

Partially oxidized organic materials contain a plurality of polar, oxygen-containing groupings, which now allow ready combination with cationic flocculating agents. Consequently, ozone can be effective in aiding in the removal of organics when used in or before the rapid mix step, provided that ozone oxidation is followed by coagulation then conventional or direct filtration.

On the other hand, when larger amounts of ozone are applied to solutions of humic/fulvic acids, not only does the oxidation of pendant groupings occur, but also oxidative scission of the high molecular weight humic/fulvic polymer chains. This produces low molecular weight, polar compounds, which are not as easily flocculated with cationic flocculating agents.

Thus, for optimum application as a flocculation aid, low applied ozone dosages should be employed. German experience in the use of ozone for microflocculation shows that the ratio of ozone applied to DOC (dissolved organic carbon) should be in the range of 0.1 (mg/L of applied ozone per mg/L of DOC) (Sontheimer, 1985).

d. Promotion of Biodegradability

These same partially oxidized organic materials also are more biodegradable, and advantage is taken of this behavior in many European water treatment plants. For example, slow sand filters remove organics from drinking water by operating in a biological mode. Preozonation of the water fed to the slow sand filters increases the biodegradability of organic materials, and

makes the combined oxidation/filtration step more effective (Rachwal, et al., 1987).

In a similar manner, if GAC adsorption is required for removal of refractory organic materials, and if some or all of the organic materials can be partially oxidized by ozonation, then preozonation prior to GAC filtration can promote biological removal of the partially oxidized organic materials in the GAC medium. The adsorptive capacity of such Biological Activated Carbon filters thus can be restricted to the ozone-refractory organics, while the ozone-sensitive organics (partially oxidized) are converted to carbon dioxide and water biologically.

The consequences of not providing a biological treatment step after ozonation in the water treatment plant are biological regrowths in the distribution system, unless a sufficient level of secondary disinfectant is present. If the secondary disinfectant is chlorine, then it is important that sufficient removal of organics has occurred before the chlorine is added. Otherwise, chlorinated organics still can be produced, sometimes in higher quantities than without ozonation (Rice, 1980).

e. By-Products of Ozonation

However, the partial oxidation of organic compounds has raised some concerns as to the possible toxicities of the intermediate oxidation products formed upon ozonation. In the majority of cases, these oxidation products are oxygen-containing derivatives of the original organic materials, mostly aldehydes, ketones, alcohols, and carboxylic acids. Ozone is quick to rupture many unsaturated linkages in organic molecules, producing aldehydes and ketones.

There are, however, a few organic compounds from which ozone has been shown to produce toxic oxidation products. For example, the pesticide heptachlor, although rapidly oxidized to "destruction" by ozone, produces heptachlorepoxide nearly quantitatively. This example illustrates the absolute necessity of knowing what specific compounds are present in the water being oxidized and/or disinfected, in order to determine appropriate pre- and/or post-treatment procedures to cope with these undesired oxidation products.

f. Catalytic Ozonation

For many organic compounds refractory even to so strong an oxidizing agent as ozone, the simultaneous application of ultraviolet radiation or hydrogen peroxide along with the ozone can accelerate otherwise sluggish reaction rates significantly. Acceleration is brought about by catalytic formation of hydroxyl free radicals, which are stronger oxidizing agents than ozone itself (see Table VIII).

g. Ozone Oxidation of Bromide Ion

Ozone does not form halogenated organic compounds, unless bromide ion is present in the raw water. If bromide ion is present, hypobromous acid will be produced, which can form brominated organic materials:

$$Br^- + O_3 \text{ -----> } (OBr)^-$$

$$(OBr)^- + H^+ \text{ -----> } HOBr$$

If bromide ion is present in sufficient quantity to result in the formation of bromine-containing organics in quantities which exceed current or projected MCLs, either the bromide ion should be removed, or chlorine dioxide should be considered as the primary disinfectant, followed by chloramination for secondary disinfection, or an alternate source of raw water should be utilized.

h. Summation for Ozone

Because it is such a powerful oxidizing agent and disinfectant (the strongest available for water treatment) and does not form halogenated by-products (except when bromide ion is present), ozone is the most versatile oxidant/disinfectant for water treatment.

As an oxidizing agent, ozone is useful added in very small quantities for turbidity control and microflocculation. In higher applied dosages, ozone oxidizes many troublesome inorganic materials (iron, manganese, sulfide, nitrite, arsenic), and destroys or alters the chemical structures of many organics responsible for tastes and odors, colors, THM formation, and other precursors of halogenated organics. Such alteration of chemical structures can make the oxidized organic materials readily removable from the treated water by flocculation/filtration, and/or by biological means. Many of the compounds listed as Synthetic Organic Chemicals by the EPA in the list of 83 compounds to be regulated by 1989 (U.S. EPA, 1988a) are at least partially oxidizable by ozone, although at varying reaction rates.

The more refractory, halogenated, organics which may be present in the raw water, which may not be oxidized with ozone at a practical rate, can be oxidized at greatly increased rates by combining ozone with UV radiation or with hydrogen peroxide.

The recent National Academy of Sciences Report (NAS, 1987, pp. 195-196) summarizes the latest thinking of the Subcommittee on Disinfectants and Disinfectant By-Products of the NAS Safe Drinking Water Committee with respect to water treatment and ozonation in particular as follows:

> "When possible, organic precursors should be removed prior to the disinfection process. This can be achieved by changing the order of the procedures of conventional treatment. A better approach, however, is to improve specific conventional treatment processes to remove organic compounds and to add processes such as carbon

adsorption **and preoxidation.** Initial removal of organic by-product precursors precludes the need for reducing (disinfectant) contact time, thus improving the efficacy of the disinfection processes and minimizing formation of organic chlorine by-products."

The use of alternative oxidants, especially ozone and chlorine dioxide, will increase in the United States in the coming decades. Little is known about the types of by-products produced by ozonation of natural organics. Well-conceived studies need to be conducted that will focus on the stable compounds expected from ozone reactions with humic material. ... Particular attention should be given to the search for unsaturated aldehydes and the hydroxy-hydroperoxides."

"Following these studies, further health effects studies are needed to determine whether ozone by-products are mutagenic or carcinogenic or produce other adverse effects. These studies should take into account variations that are likely to occur when the oxidation process is carried out in different matrices (pH, O_3/TOC ratio, alkalinity)."

"Notwithstanding the fact that these studies need to be carried out, drinking water suppliers should not dismiss the possibility of using ozone as an alternative to chlorine and chloramines in water treatment. Ozone is an excellent (primary) disinfectant (although it must be used in combination with a secondary disinfectant to maintain a residual in the distribution system); ozone is an excellent oxidant for the various needs of water treatment; it does not form chlorinated by-products; and the admittedly inadequate studies now available point to lower toxicities of ozonated water than of chlorinated water."

6. Ultraviolet Radiation for Groundwaters

The effectiveness of ultraviolet radiation as a bactericide and virucide has been well established (U.S. EPA, 1986), but is not appropriate for the inactivation of Giardia lamblia cysts (Rice & Hoff, 1981). It is a physical disinfecting agent compared to the other disinfecting agents being used, whose actions are chemical. Radiation at a wavelength of 254 nm penetrates the microorganism cell wall and is absorbed by the cellular nucleic acids. This can prevent replication (reproduction) and cause death of the cell. Since UV radiation is not a chemical agent, no potentially toxic residuals are produced. Although the structures of certain chemical compounds may be altered by the UV radiation, the energy levels used for disinfection are too low for this possibility to be a significant cause for concern.

UV radiation at a wavelength of 254 nm is readily available commercially in standard equipment from a number of suppliers. It was reported (Angehrn, 1984) that in 1984, some 2,000 communities in Western Europe now disinfect their drinking water supplies by means of UV radiation.

Major advantages of UV disinfection are its simplicity, lack of impact on the environment, and minimal space requirements. There is a negligible

likelihood of producing harmful chemicals in the water. Required contact times are very short, on the order of seconds rather than minutes. The equipment is simple to operate and maintain, but fouling of the quartz sleeves or Teflon tubes (housing the UV bulbs) must be dealt with on a regular basis. Fouling of these items normally is controlled by mechanical, sonic, or chemical cleaning.

On the other hand, waters containing high suspended solids concentrations, color, turbidity, and soluble organic matter can react with or absorb the UV radiation, thus reducing the disinfection performance. In addition, if the amount of radiation received by the organism is not a lethal dose, photo-enzymatic repair can occur, and the organism can become viable again. The phenomenon is termed "photoreactivation", and the enzymatic mechanism generally requires subsequent exposure to light at wavelengths between 300 and 500 nm (available in sunlight, incandescent, and fluorescent light sources).

The major operating costs are power consumption and annual replacement of the UV lamps. Increased popularity and lowered costs have occurred due to improvements in modern lamp and system designs, increased competition, and improved reliability and simplicity of operation.

The biocidal properties of UV radiation make it a candidate for use as a primary disinfectant, which must be followed by a secondary disinfectant since UV radiation provides no disinfecting residual. In addition, at biocidal wavelengths (254 nm) and energies, UV radiation does not produce much oxidation of organic materials. However, at higher energy intensities and low UV wavelengths (i.e., 184.9 nm), oxidation of organic materials can occur readily to produce CO_2 and water.

The UV light spectrum is broad enough to include wavelengths of unequal effects upon different organisms. Even for efficacious wavelengths, the influence of the UV radiation may differ. Also, the devices designed to discharge UV light are not all alike in the radiant energy they generate. Moreover, the UV emanations are susceptible to absorption by the molecules of the organismsuspending medium. Their germicidal influence may be reduced by the time they reach the microbe.

That UV radiation is of practical utility in controlling most organisms is beyond challenge. The devising of effective UV systems requires being engineered, however. More than an ultraviolet radiation source is needed. Finally, where the organisms are killed by the UV radiation, subsequent removal of the dead microbes may be required, as by filtration, when the presence of particles is undesired, or when their catabolic products may manifest total organic carbon (TOC) levels, or pyrogenic lipopolysaccharides.

VII. DISCUSSION OF TREATMENT TECHNOLOGIES FOR DISINFECTION AND TO MINIMIZE PRODUCTION OF DOBs

A. THE PROBLEM

In providing disinfection under the projected EPA drinking water regulations, water treatment systems will be faced with the challenge of how to disinfect surface and groundwaters to:

1. assure 99.9% and 99.99% inactivation of Giardia lamblia cysts and enteric viruses, respectively,

2. assure control of other microorganisms,

3. not impart toxicity to the disinfected water (mutagenicity, carcinogenicity, etc.),

4. minimize formation of chlorination and other undesired disinfection by-products, and

5. do all this without exceeding the projected MCL levels for the candidate disinfectants.

B. THE STRATEGIES

Before primary disinfection is practiced, the concentrations of organic materials should be as low as practicable, so as to minimize the production of oxidation and/or halogenation by-products. For secondary disinfection, the turbidity should be $\leq$ 0.5 NTU.

If the raw groundwater has the appropriate levels of turbidity and concentrations of dissolved organics, pretreatment can be eliminated. Otherwise, at least filtration must be applied.

Concentrations of dissolved organics can be reduced by applying conventional treatments of flocculation, perhaps sedimentation, then filtration. Newer techniques of coping with organics concentrations include oxidation (before filtration, with ozone, potassium permanganate) and adsorption (powdered or granular activated carbon).

An emerging oxidation technology is the use of ozone coupled simultaneously with UV radiation or with hydrogen peroxide. This technique generates hydroxyl free radicals, which are more powerful oxidizing agents than ozone alone.

C. DISINFECTION TECHNOLOGIES

According to the reasoning given earlier in this document, the use of chlorine for pretreatment and primary disinfection should be minimized. The current 100 μg/L MCL for THMs is expected to be lowered. In addition,

regulation of some of the halogenated by-products of chlorination listed in Table III may place even greater restrictions on the use of chlorine for some utilities.

Projected MCLs for chlorine dioxide and its decomposition products (chlorite and chlorate ions) effectively eliminate this material as a primary disinfectant, except for very clean waters and/or short distribution systems.

The known limited capability of monochloramine to achieve the mandated percent inactivations of Giardia lamblia and enteric viruses eliminate this material from the role of primary disinfectant.

Therefore, for surface water treatment, only two primary disinfectants remain: chlorine and ozone. For groundwater (unaffected by surface water), the same two primary disinfectants remain, plus UV radiation. For secondary (residual) disinfection, chlorine remains as the most viable, with occasional use of chlorine dioxide and monochloramine. The conditions of chloramination should be those recommended by the National Academy of Sciences (NAS, 1987): chlorination to the nitrogen breakpoint, followed by addition of ammonia.

Each disinfection approach will be discussed in this section. Much of this discussion is adapted from an earlier EPA publication (U.S. EPA, 1983) and supplemented by a more recent publication (U.S. EPA, 1986) which is a design manual for disinfection of wastewaters by means of chlorination, ozonation and UV radiation. Nearly all of the factors appropriate to disinfection of wastewaters is directly applicable to drinking water disinfection as well. Since most of the utilities which will be affected by the upcoming Surface Water and Groundwater Treatment Rules serve less than 10,000 persons, the emphasis of this discussion will be on the smaller utilities.

1. Primary Disinfectants

a. Chlorine

Chlorine, symbolized chemically as Cl_2, is the disinfectant most commonly used by U.S. water utilities. It is available in three forms:

Form	Formula	Name
gas	Cl_2	chlorine gas
solid	$Ca(OCl)_2$	calcium hypochlorite
aqueous solution	NaOCl	sodium hypochlorite

The gaseous form is used most frequently, especially by larger water utilities, because it is the lowest cost form of chlorine.

i. Chemistry of Chlorination

In the gaseous form, chlorine will react with water to form hydrochloric acid and hypochlorous acid:

$$Cl_2 + H_2O \quad <\text{-----}> \quad HCl + HOCl$$

chlorine	water		hydrochloric acid		hypochlorous acid

The hypochlorous acid then will react with the water by dissociation to an extent determined by the pH of the solution:

$$HOCl \quad <\text{-----}> \quad (OCl)^- + H^+$$

hypochlorous acid		hypochlorite ion		hydrogen ion

pH is a measure of the concentration of hydrogen ion in the water. The more hydrogen ion present, the lower is the pH. Conversely, the lower the hydrogen ion concentration, the higher will be the pH value.

At neutral pH (pH = 7.0), almost 80% of the chlorine is present in its most effective disinfecting form, hypochlorous acid; the remainder exists in the less effective hypochlorite ion form. As the pH increases, however, an increasing amount of HOCl will react with water to form more hypochlorite ion. At pH 8.0, for example, nearly 80% of the chlorine present exists as the hypochlorite ion, almost a complete reversal of the situation which exists at pH 7.

From the CT data given in Tables IIA, IIB, and IIC for chlorine inactivation of Giardia lamblia cysts, it can be seen that the CT values for a 2 mg/L concentration of chlorine increase rapidly for each temperature as the pH rises above 7.0. Consequently, effective pH control is essential in order to guarantee the amount of disinfection designed in chlorination systems. Figure 1 shows the relationship between pH and the concentration of hypochlorous acid, the desired chlorine species in aqueous solution at 0°C and 20°C.

When the chlorination step is conducted by adding either sodium hypochlorite or calcium hypochlorite, the chemical reactions which occur result in an alkaline (basic) product as compared to the acidic product obtained when using the gas:

$$NaOCl + H_2O \text{ -----> } HOCl + NaOH$$

sodium hypochlorite		water		hypochlorous acid		sodium hydroxide

$$Ca(OCl)_2 + H_2O \text{ ----> } 2HOCl + Ca(OH)_2$$

calcium hypochlorite	water	hypochlorous acid	calcium hydroxide

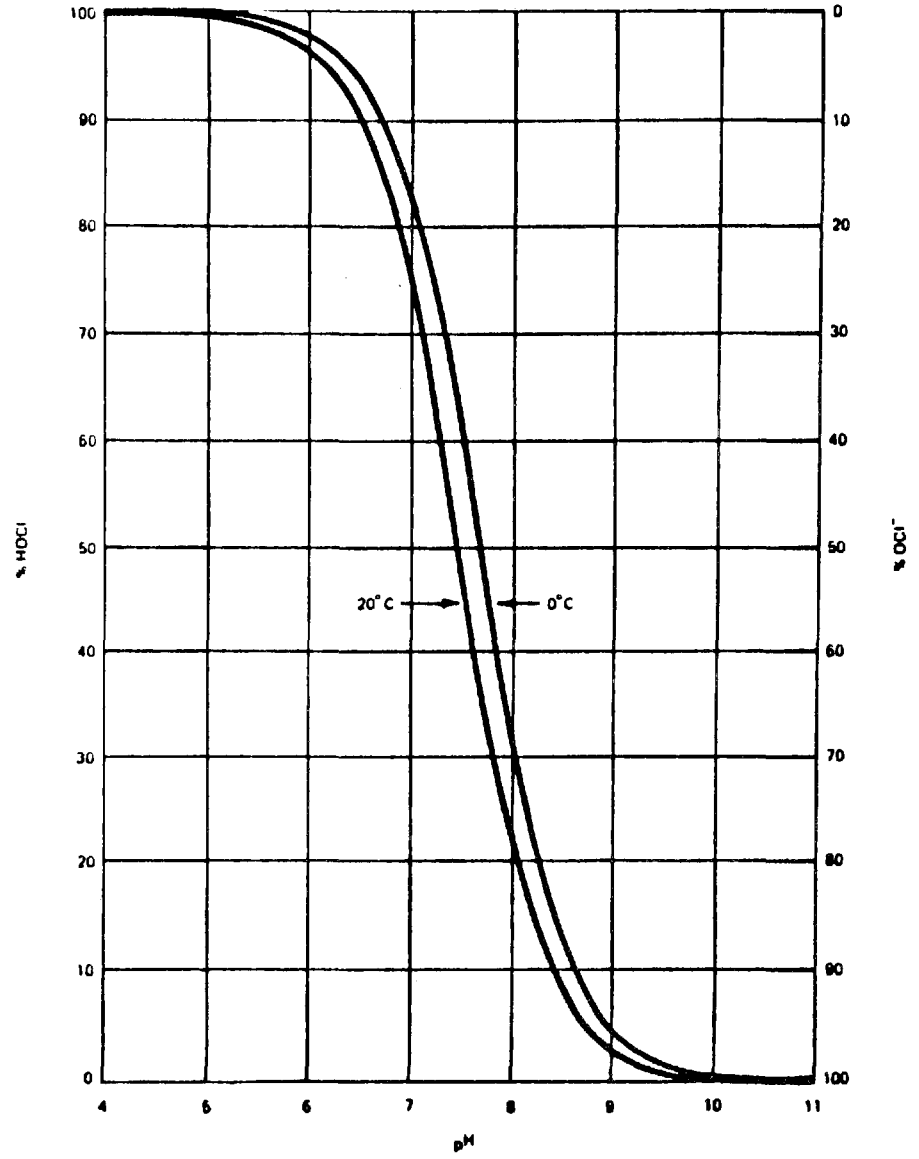

Figure 1. Distribution of hypochlorous acid and hypochlorite ions in water at different pH values and temperatures of 0°C and 20°C (AWWA, 1973).

The resulting hydroxides increase the pH values of the aqueous solutions. Since an increase in pH results in lower concentrations of HOCl, and therefore, poorer disinfection (requiring much longer contact times to

provide the appropriate CT value to guarantee 99.9% inactivation of Giardia lamblia cysts and 99.99% inactivation of enteric viruses), the ability to adjust and control pH becomes critically important when using the hypochlorite forms of chlorine.

ii. Establishing A Chlorine Residual

Hypochlorous acid is one of the most powerful oxidizing agents known. This means that it will react with many substances present in the water being disinfected, in addition to the target organisms. This fact is clear from the known production of trihalomethanes, and many of the halogenated compounds listed in Tables III and IV.

In order to achieve a concentration of chlorine sufficient to guarantee the required level of disinfection, it is necessary to add enough chlorine to react with all of the reactive substances which are likely to be present, and then provide the excess "residual" chlorine. These reactions consume chlorine and are collectively called the "chlorine demand" of the water. Thus the chlorine demand of a water must be satisfied before a residual of free chlorine can be provided and an adequate job of disinfection can be attained.

The concentration of chlorine determined by an analytical procedure is called the "available chlorine residual", and it means only that amount of chlorine originally added which remains available for disinfection. This residual may be either a free available residual, a combined available residual, or a combination of the two. Free available chlorine is essentially the sum of concentrations of hypochlorous acid and hypochlorite ions. Combined available chlorine is the sum of the concentrations of mono- and di-chloramines, plus nitrogen trichloride and organic nitrogen chlorine-containing compounds (see later discussion of Chloramines -- Section VII.C.2.b).

Intuitively, one would expect that each mg/L of chlorine added to water would be measurable as hypochlorous acid or hypochlorite ion. This is not the case, because chlorine reacts with many substances present in the water in complex manners. To understand some of these complex reactions better, Figure 2 shows what is called a "breakpoint curve". The amount of chlorine added is shown on the horizontal scale and the amount of available chlorine determined by an analytical procedure is shown on the vertical scale.

Assume that the chlorine is added slowly and that the water contains small amount of reduced substances such as sulfides, ferrous iron, organic materials, organic nitrogen materials (aminoacids and proteins), and some ammonia, all of which exert a chlorine demand. The initial amount of chlorine added will be taken up by reactions with the reduced substances, and the analysis for free available chlorine [HOCl + $(OCl)^-$] will show that none is present.

After the chlorine demands of the reduced substances have been satisfied, then the HOCl will react with ammonia, organic nitrogen materials, and some

of the organics present to yield chloramines and chlorinated organic compounds.

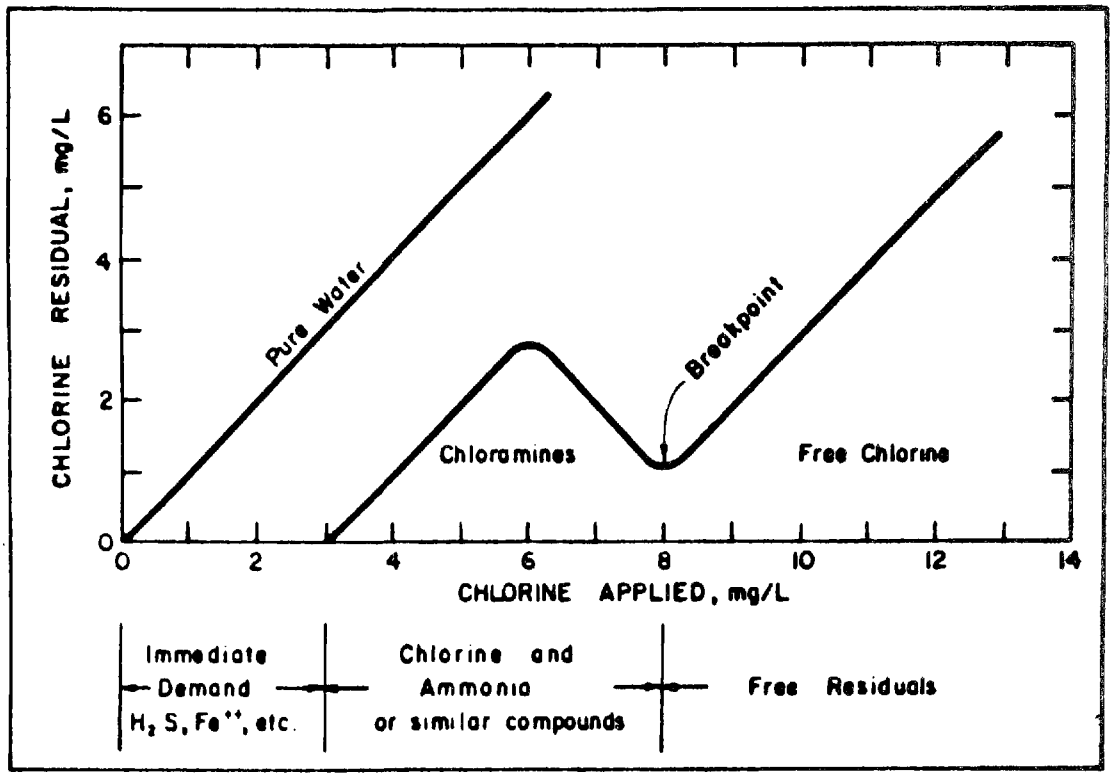

Figure 2. Graphical representation of the breakpoint chlorination reaction (U.S. EPA, 1983, p. III-10). The straight line at the left shows that chlorine residual is proportional to dosage in pure water. When impurities are present, they exert a chlorine demand.

When all of the ammonia and other chlorine-demanding organics have reacted with chlorine, the addition of more chlorine results in the hypochlorous acid oxidizing some of the same materials it just helped to create. The strange phenomenon observed is that the addition of more chlorine results in a decrease in the amount of residual (at this point a combined residual) indicated by the analytical procedure. When this oxidation is complete (called the breakpoint), then the addition of still more chlorine results in an increase in the amount of available chlorine measured. Note that the breakpoint must be surpassed before a free residual of chlorine can accumulate and persist.

It is important to be aware that the above illustration is considerably more complex than described, because the reactions taking place are time-dependent. For this reason, a breakpoint curve is difficult to recreate and predict. Individual tests must be run, seasonally, and the data plotted to define the breakpoint for each water.

iii. Factors Affecting Disinfection Efficiency of Chlorine

As indicated by the data of Tables IIA, IIB, and IIC, chlorine in the free state [HOCl + $(OCl)^-$] is quite an effective disinfectant. Rapid inactivation of most microorganisms can be obtained in a matter of minutes. However, effective disinfection with chlorine requires careful attention to:

1. **Concentration of free available chlorine** -- high enough in the plant so that it is always detectable at the farthest points in the distribution system (time basis),

2. **Maintaining the pH as close to 7.0 as is practical** or consistent with other water quality aspects, so as to maintain as much of the chlorine residual in the HOCl (hypochlorous acid) form,

3. **Time of contact long enough** to achieve the desired degree of microbial inactivation (i.e., to attain the CT value commensurate with the concentration of chlorine at the appropriate temperature).

4. **Mixing** -- baffle the chlorine contactor well to eliminate the possibility of short-circuiting of flow or provide an external mixing device.

Other factors also influence the chlorine disinfection process. Temperature has some effect on the ratio of HOCl to hypochlorite ion (see Figure 1) and has more effect on the disinfection rate (see Tables IIA, IIB, IIC, and Tables XI through XVI - taken from the October 10, 1987 Guidance Manual for the Proposed Surface Water Treatment Rule, U.S. EPA, 1987d), disinfection being faster at the higher temperatures. However, usually there is no means available to the operator to control temperature. Other tables are given in the Guidance Document (U.S. EPA, 1987d) relating residual chlorine levels to pH, concentration, and logs of Giardia inactivation.

iv. Disinfection With Chlorine Gas

Chlorine is a toxic, yellow-green gas at ordinary temperatures and pressures. It is supplied in high strength steel cylinders, under sufficient pressure to liquefy the chlorine. When chlorine is required, simply opening the gas valve allows rapid vaporization of the liquid. As the liquid evaporates, its temperature falls. This normally results in a slower rate of evaporation, thus requiring manifolding of containers or use of a vaporizer.

There are two basic types of gas chlorinators: (1) pressure operated, direct gas feed and (2) vacuum operated, solution feed. The former allows chlorine gas, under pressure, to be fed directly into the water to be disinfected. Solution feed units mix the gas with a side stream of water to form a solution of hypochlorous acid and hypochlorite ion, which then is mixed with the main stream.

TABLE XI. CT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 0.5°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
≤ 0.4	129	160	196	238	284	335	392
0.6	138	172	211	255	305	360	421
0.8	145	181	222	268	321	379	443
1.0	151	188	231	279	333	394	461
1.2	156	194	238	288	344	407	476
1.4	160	200	245	296	354	418	489
1.6	164	205	251	303	362	428	501
1.8	168	209	256	310	370	437	511
2.0	171	213	261	315	377	445	521
2.2	174	216	265	321	383	453	530
2.4	176	220	269	326	389	460	538
2.6	179	223	273	330	395	466	546
2.8	181	226	277	335	400	472	553
3.0	183	228	280	339	405	478	559

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

v. Disinfection With Sodium Hypochlorite Solution

Liquid chlorinators meter a previously prepared hypochlorite solution directly into the water to be disinfected. If the water supply system cannot afford the capital costs (see later sub-section) and requirements associated with storing and handling chlorine gas, solutions of sodium hypochlorite can be purchased. It must be remembered that sodium hypochlorite solutions are more costly per pound of available chlorine and do not contain the concentrations of chlorine available in cylinders of chlorine gas. Also, hypochlorite solutions decompose if stored for prolonged periods. Thus, small systems using sodium hypochlorite should plan to store no more than a one-month supply.

In recent years, methods for on-site electrolytic generation of aqueous solutions of hypochlorite ion have been developed. In a two-cell unit, a brine solution (salt in water) is electrolyzed, producing a solution of hypochlorous acid in one cell and a solution of caustic (sodium hydroxide) in the other:

$$Na^+ + Cl^- + 2H_2O + e^- \text{-----}>$$

sodium chloride water electron

$$HOCl + NaOH + H_2$$

hypochlorous acid sodium hydroxide hydrogen

TABLE XII.CT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 5°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
≤ 0.4	92	114	140	169	202	239	280
0.6	98	123	150	182	217	257	300
0.8	104	129	158	191	229	270	316
1.0	108	134	165	199	238	281	329
1.2	111	139	170	206	245	290	339
1.4	114	142	175	211	252	298	349
1.6	117	146	179	216	258	305	357
1.8	119	149	183	221	264	311	365
2.0	122	152	186	225	269	317	371
2.2	124	154	189	229	273	323	378
2.4	126	157	192	232	277	328	383
2.6	127	159	195	235	281	332	389
2.8	129	161	197	239	285	337	394
3.0	131	163	200	242	288	341	399

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

The advantages of this procedure are that purchasing and storing of gaseous chlorine and hypochlorite solutions are avoided. The primary technical disadvantages are the generation of hydrogen (which poses fire and explosion hazards), and the need to dispose of the caustic generated. In addition, the cost per pound, on a chlorine basis, typically is more than double for on-site electrolytic generation of hypochlorite ($0.30 to $0.35/lb) versus the cost of gaseous chlorine ($0.08 to $0.15/lb). However, site-specific considerations may make on-site hypochlorite generation the process of choice.

TABLE XIII. CT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 10°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
≤ 0.4	69	86	105	127	152	179	210
0.6	74	92	113	136	163	193	225
0.8	78	97	119	144	171	203	237
1.0	81	101	123	149	178	211	247
1.2	83	104	128	154	184	218	255
1.4	86	107	131	158	189	224	262
1.6	88	109	134	162	194	229	268
1.8	90	112	137	166	198	234	273
2.0	91	114	140	169	201	238	279
2.2	93	116	142	172	205	242	283
2.4	94	117	144	174	208	246	288
2.6	96	119	146	177	211	249	292
2.8	97	121	148	179	214	253	296
3.0	98	122	150	181	216	256	299

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

vi. **Disinfection With Solid Calcium Hypochlorite**

Solid calcium hypochlorite is stable when properly packaged and sealed. A water supply system can purchase its annual requirements in a single procurement. Simply mixing the proper amounts of solid and water to allow metering without clogging of pumps or metering valves is all that is required for use. Normally, an entire drum of calcium hypo-chlorite is made into solution. This avoids the partial use of a container, with attendant uncertainties of proper resealing and loss of strength.

vii. **Chlorination System Design**

Choice of the form of chlorination system to be used, whether gaseous chlorine, dry calcium hypochlorite, sodium hypochlorite solution or on-site generation, depends upon a number of factors which include the following:

- o availability of chlorine source chemical,
- o capital cost of the facility,
- o operation and maintenance costs for the equipment,

- o chemical costs,
- o location of the facility,
- o operator skills available,
- o safety.

TABLE XIVCT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 15°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
≤ 0.4	46	57	70	85	101	120	140
0.6	49	61	75	91	109	128	150
0.8	52	65	79	96	114	135	158
1.0	54	67	82	100	119	140	164
1.2	56	69	85	103	123	145	170
1.4	57	71	87	106	126	149	174
1.6	59	73	89	108	129	153	179
1.8	60	74	91	110	132	156	182
2.0	61	76	93	112	134	159	186
2.2	62	77	95	114	137	161	189
2.4	63	78	96	116	139	164	192
2.6	64	79	97	118	141	166	194
2.8	65	80	99	119	142	168	197
3.0	65	81	100	121	144	170	199

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

Each of the methods of chlorination will provide the same disinfecting power on a pound for pound basis of available chlorine when utilized at the same pH. However, each of the systems must be approached differently in terms of basic design and safety.

Sufficient chlorine must be provided to satisfy the chlorine demand of the water at the point of chlorine addition, plus an additional amount to maintain the required residual after a specified contact time (see CT values in Tables XI to XVI). The relative dosages of the various chemical sources of hypochlorite ion [$(OCl)^-$] in solution can be determined; these frequently will depend upon the point of chlorine application in the process.

The chlorine demand of raw water usually is far higher than that of finished water. In any case, a minimum contact time, commensurate with the CT

value, the pH of the water, and the temperature, must be maintained to assure the appropriate inactivation of Giardia lamblia and viruses.

TABLE XV.CT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 20°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
≤ 0.4	34	43	53	64	76	90	105
0.6	37	46	56	68	82	96	113
0.8	39	48	59	72	86	101	119
1.0	40	50	62	75	89	105	123
1.2	42	52	64	77	92	109	127
1.4	43	53	66	79	95	112	131
1.6	44	55	67	81	97	114	134
1.8	45	56	68	83	99	117	137
2.0	46	57	70	84	101	119	139
2.2	46	58	71	86	102	121	142
2.4	47	59	72	87	104	123	144
2.6	48	60	73	88	106	125	146
2.8	48	60	74	90	107	126	148
3.0	49	61	75	91	108	128	150

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

Chlorination With Gaseous Chlorine:

Chlorine is supplied in high strength steel cylinders with minimum chlorine capacities of 100 and 150 pounds, up to one ton, and in tank cars under sufficient pressure to liquefy the chlorine. Major manufacturers of gaseous chlorine are listed in Table XVII. However, the quantity consumed by small water systems normally would be purchased from local suppliers which are listed in the local telephone directory yellow pages under "Chemical Suppliers" or "Swimming Pool Suppliers".

Direct feed chlorinators add gas under pressure directly into the water to be disinfected. This type of unit normally is used only when electrical power is unavailable or insufficient water pressure differential to operate a solution feed unit. This is a site-specific application which will not be discussed further.

TABLE XVICT VALUES FOR 99.9% INACTIVATION OF Giardia CYSTS BY FREE CHLORINE AT 25°C *

Free Residual (mg/L)	pH						
	6.0	6.5	7.0	7.5	8.0	8.5	9.0
≤ 0.4	23	29	35	42	51	60	70
0.6	25	31	38	46	54	64	75
0.8	26	32	40	48	57	68	79
1.0	27	34	41	50	59	70	82
1.2	28	35	43	51	61	73	85
1.4	29	36	44	53	63	75	87
1.6	29	36	45	54	65	76	89
1.8	30	37	46	55	66	78	91
2.0	30	38	47	56	67	79	93
2.2	31	39	47	57	68	81	94
2.4	31	39	48	58	69	82	96
2.6	32	40	49	59	70	83	97
2.8	32	40	49	60	71	84	99
3.0	33	41	50	60	72	85	100

* These CT values achieve greater than a 99.99% inactivation of enteric viruses.

Solution feed units mix chlorine gas with a side stream of water to form a hypochlorous acid solution, which then is injected into the main stream. Solution feed chlorinators operate on a vacuum controlled basis, automatically shutting off if the side stream flow is interrupted. This type of unit, shown in Figure 3, is preferable for safety reasons over direct feed units.

The basic solution feed gas chlorinator includes the following components:

- o gas shut-off valve to interrupt gas flow;
- o vacuum regulator, or
- o gas flow indicator;
- o adjustable gas flow controller;
- o check valve;
- o venturi type gas injector.

The market for supply of gas chlorinators is quite competitive, as illustrated by Table XVIII, which provides a partial listing of suppliers of these types of units.

TABLE XVII. MANUFACTURERS OR PACKAGERS OF GASEOUS CHLORINE

Name	Address
Ashland Chemical Company Petrochemical Division	P.O. Box 2219, Columbus, OH 43216
Dow Chemical U.S.A.	2020 Dow Center, Midland, MI 48640
FMC Corp., Industrial Chemical Group	2000 Market Street, Philadelphia, PA 19103
Georgia-Pacific	P.O. Box 105605, Atlanta, GA 30348
Kaiser Aluminum & Chemical Corp. Industrial Chemical Division	300 Lakeside Drive, Oakland, CA 94643
Kaiser Chemicals Cleveland, OH 44124	30100 Chagrin Boulevard,
Kuehne Chemical Co., Inc. Kearny,	86 Hackensack Avenue, NJ 07032
Occidental Chemical Corp. Industrial & Specialty Chemicals	360 Rainbow Blvd. South, P.O. Box 728, Niagara Falls, NY 14302
Olin Corporation	120 Long Ridge Road, Stamford, CT 06904
Pennwalt Corporation Inorganic Chemicals Division	3 Parkway, Philadelphia, PA 19102
Stauffer Chemical Co.	Westport, CT 06881
Vulcan Materials Co., Chemicals Division	P.O. Box 7689, Birmingham, AL 35253

Well established standards for design of gas chlorination systems exist in standard waterworks industry literature (Great Lakes - Upper Mississippi River Board of State Sanitary Engineers, 1985; Am. Water Works Assoc., 1985). The following points are provided to highlight possible design questions:

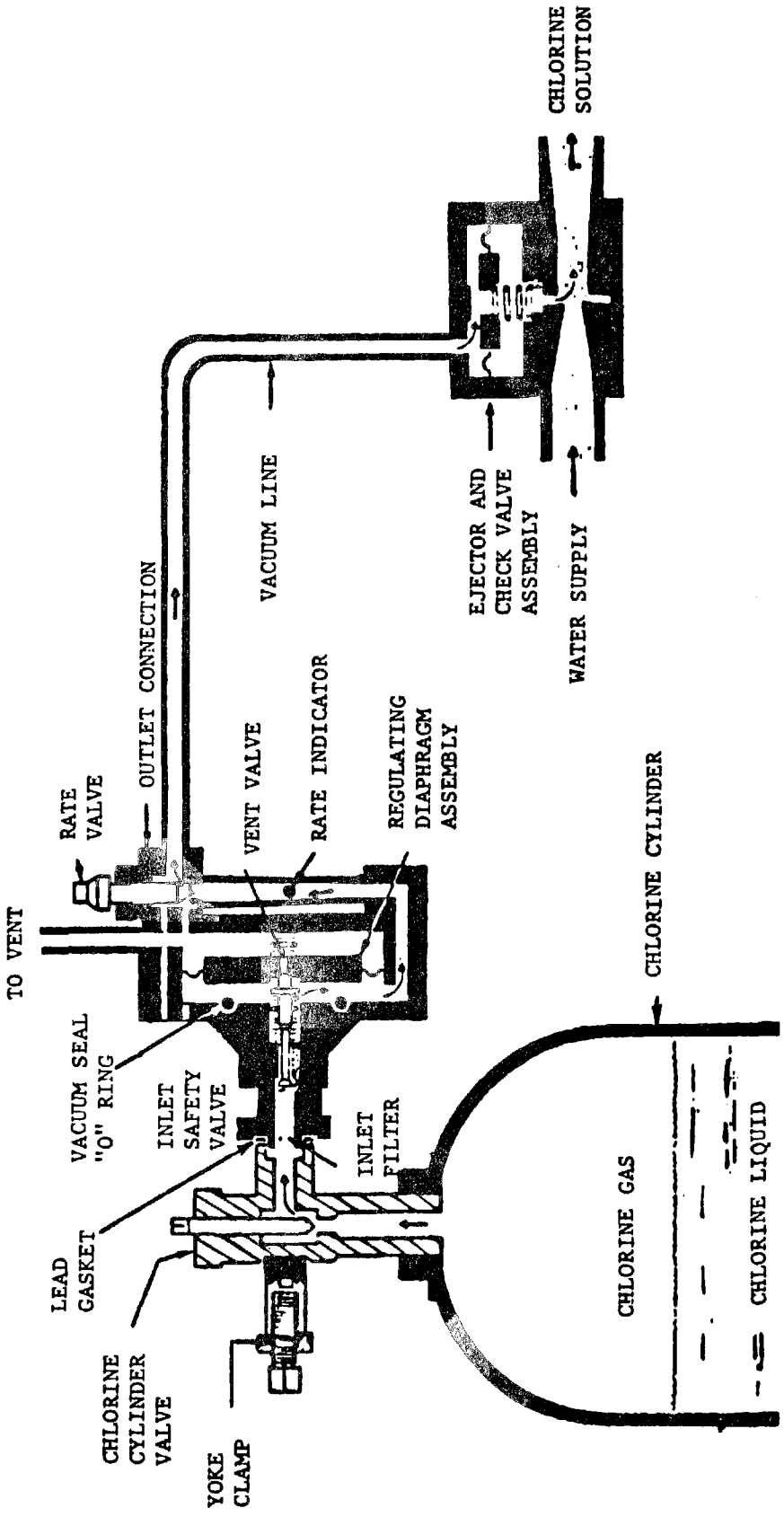

Figure 3. Solution feed gas chlorination system. (Courtesy of Capital Controls Co., Inc.)

TABLE XVIII. SOME GAS CHLORINATOR MANUFACTURERS

Name	Address
Capital Controls Co., Inc.	Box 211, Colmar, PA 18915
Chlorinators Inc.	733 NE Dixie Highway, Jensen Beach, FL 33457
Fischer & Porter Co.	County Line Rd., Warminster, PA 18974
Hydro Instruments Inc.	492 Richlandtown Pike, Box 615, Quakertown, PA 18951
Modern Process Systems Inc.	14834 Highland Road, Baton Rouge, LA 70810
Wallace & Tiernan, Division of Pennwalt Corp.	25 Main Street, Belleville, NJ 07109

Chlorination With Sodium Hypochlorite

Sodium hypochlorite, usually supplied in concentrations of 5 and 15% available chlorine, is available commercially only in solution. In this form, it is easier to handle than gaseous chlorine or calcium hypochlorite. However, sodium hypochlorite solutions will lose their disinfecting (oxidizing) power during storage, and should be stored in a cool, dark, dry area. The material is supplied in glass or plastic bottles, carboys, or lined drums ranging in size from 0.5 to 55 gal. Bulk shipment by tank truck also is a common form of transport. No more than a one-month supply of the chemical should be purchased, to prevent loss of available chlorine.

Chlorination With Calcium Hypochlorite

This material is supplied as a white solid which is quite corrosive, and gives off a strong chlorinous odor. It contains approximately 65% available chlorine, is readily soluble in water, and is available in granular, powdered, or tablet form. It is provided in 2, 5, 8, and 35 lb cans and in 100, 300, and 800 lb drums. The containers generally are resealable.

Calcium hypochlorite is hygroscopic (readily absorbs moisture), and reacts slowly with atmospheric moisture to form chlorine gas. Therefore, shipping containers must be emptied completely or carefully resealed. It is not feasible to handle this material in bulk handling systems.

The contents of a calcium hypochlorite container are emptied into a mixing tank where it is readily and completely dissolved in water. The resulting corrosive solution is stored in and fed from a stock solution vessel constructed of corrosion-resistant materials such as plastic, ceramic, glass,

or rubber-lined steel. Dosage of the solution at 1% or 2% available chlorine content is by a diaphragm type, chemical feed/metering pump.

viii. Chlorination Systems Costs (U.S. EPA, 1983)

In the following discussion, cost data are presented for the three types of chlorination systems discussed above, and as related to their use at small water treatment systems, sized to treat water volumes up to at least 1 mgd. The larger systems will have to change chlorine cylinders more frequently than will the smaller systems. For example, a 1 mgd water treatment plant using an average chlorine dosage of 5 mg/L will use nearly 42 lbs of chlorine per day. Thus, a 150-lb cylinder of chlorine will last between three and four days at this size plant.

Operating and maintenance costs presented do not include chemical costs. These will vary depending upon the volume of water treated and the dosage required.

Cost data were obtained primarily from two sources (Hansen et al., 1979; U.S. EPA, 1983), and updated by calling various vendors in mid-1987. However, a more recent publication by Gumerman et al. (1986) contains additional cost data developed specifically for small water systems. Cost curve figures from this later publication are included, as appropriate.

Solution-Feed Chlorination With Gaseous Chlorine

Equipment Costs

Table XIX shows a detailed cost breakdown obtained during May 1980 from three vendors of chlorination equipment. Data are presented in terms of a basic gas chlorination system, as well as costs for five increasingly complex systems. The basic system includes equipment to handle two 150-lb chlorine cylinders, two cylinder-mounted chlorine gas regulators, automatic changeover valve, and chlorine gas flow and rate valve ejector (with system backup). Alternate #1 adds two scales, a gas mask, and a diffuser corporation cock (to allow connection under water line pressure). Alternate #2 adds a flow-pacing chlorine addition system. Alternate #3 adds a flow meter. Alternate #4 adds a booster pump and piping. Alternate #5 adds a chlorine leak detector.

The cost comparisons in Table XIX present a basic-to-most-sophisticated comparison between the various system configurations in which gaseous chlorination systems can be purchased. Costs are comprised of equipment, installation, safety enclosure, contractor's overhead and profit, plus 10% engineering fee for the basic system estimates.

The basic (lowest cost) gaseous chlorination system costs about $9,350; with all options added, the most sophisticated gaseous chlorination system costs $16,050, in May 1980 dollars.

TABLE XIX. CAPITAL COSTS FOR GAS CHLORINATION (1980 Dollars*)

EQUIPMENT COSTS FOR A SYSTEM OF 100 lbs/day (2 kg/h) OR LESS

Basic System**	Average	$1,873
	High	2,300
	Low	1,320
Alternate #1 - add scales, mask diffuser, corporation cock	Average	770
Alternate #2 - add flow pacing - existing signal	Average	1,694
Alternate #3 - add flow meter & signal, 8 in. or less	Average	2,068
Alternate #4 - add booster pump & piping	Average	792
Alternate #5 - add Cl_2 gas detector	Average	1,382
INSTALLATION	Average	1,167
	High	1,500
	Low	1,000
SAFETY ENCLOSURE	Average	3,500
	High	6,000
	Low	2,000
CONTRACTOR'S OVERHEAD AND PROFIT (20%)		1,869
ENGINEERING FEES (10%)		934

TOTAL CAPITAL COST

Basic System	$9,343
Most Sophisticated (with Alternate #5)	$16,049

* May 1980 quotes (three vendors)

** Basic system includes two 150-lb chlorine cylinders, two cylinder-mounted regulators, automatic changeover valve, chlorine gas flow rate valve, and ejector (system with backup)

Construction Costs

Figure 4 shows construction cost curves for gas feed chlorination systems up to a maximum chlorine feed rate of 80 lbs/day (Gumerman et al., 1986).

Operation and Maintenance Costs

Hansen et al. (1979) state that in general, operation and maintenance costs for chlorination systems treating 2,500 gpd to 1 mgd are independent of flow. Process energy requirements are for the booster pump only, and are about 1,630 kWh/yr. Building energy requirements for a 25 ft^2 building to house the system would be 2,560 kWh/yr. Maintenance material requirements would be only for miscellaneous repair of valving, electrical switches, and other equipment, and would total about $40/yr. Labor requirements are for periodic checking of equipment, with an average requirement of 0.5 h/day, or 183 h/yr.

O&M costs of $2,457/yr are summarized in Table XX. Note that power costs were taken at $0.07/kWh and labor at $10.00/h. These were prevalent rates in 1982 and were used (U.S. EPA, 1983) to update the corresponding energy and labor costs made earlier by Hansen et al. (1979).

TABLE XX.O&M SUMMARY FOR SOLUTION-FEED GAS CHLORINATION

Item	Requirements*	Costs
ELECTRICAL ENERGY:		
Process	1,630 kWh/yr x $0.07 =	$ 114.10
Building	2,560 kWh/yr x $0.07 =	179.20
Total	4,190 kWh/yr x $0.07 =	$ 293.30
MAINTENANCE MATERIAL:	=	$ 40/yr
LABOR:	183 h/yr x $10/h =	$ 1,830
TOTAL ANNUAL O&M COST		$2,457

* Estimates of energy, maintenance, and labor made by Hansen et al. (1979).

O&M cost curves are depicted in Figure 5 (building energy, process energy, and maintenance material) and Figure 6 (labor and total O&M costs), both taken from Gumerman et al., 1986).

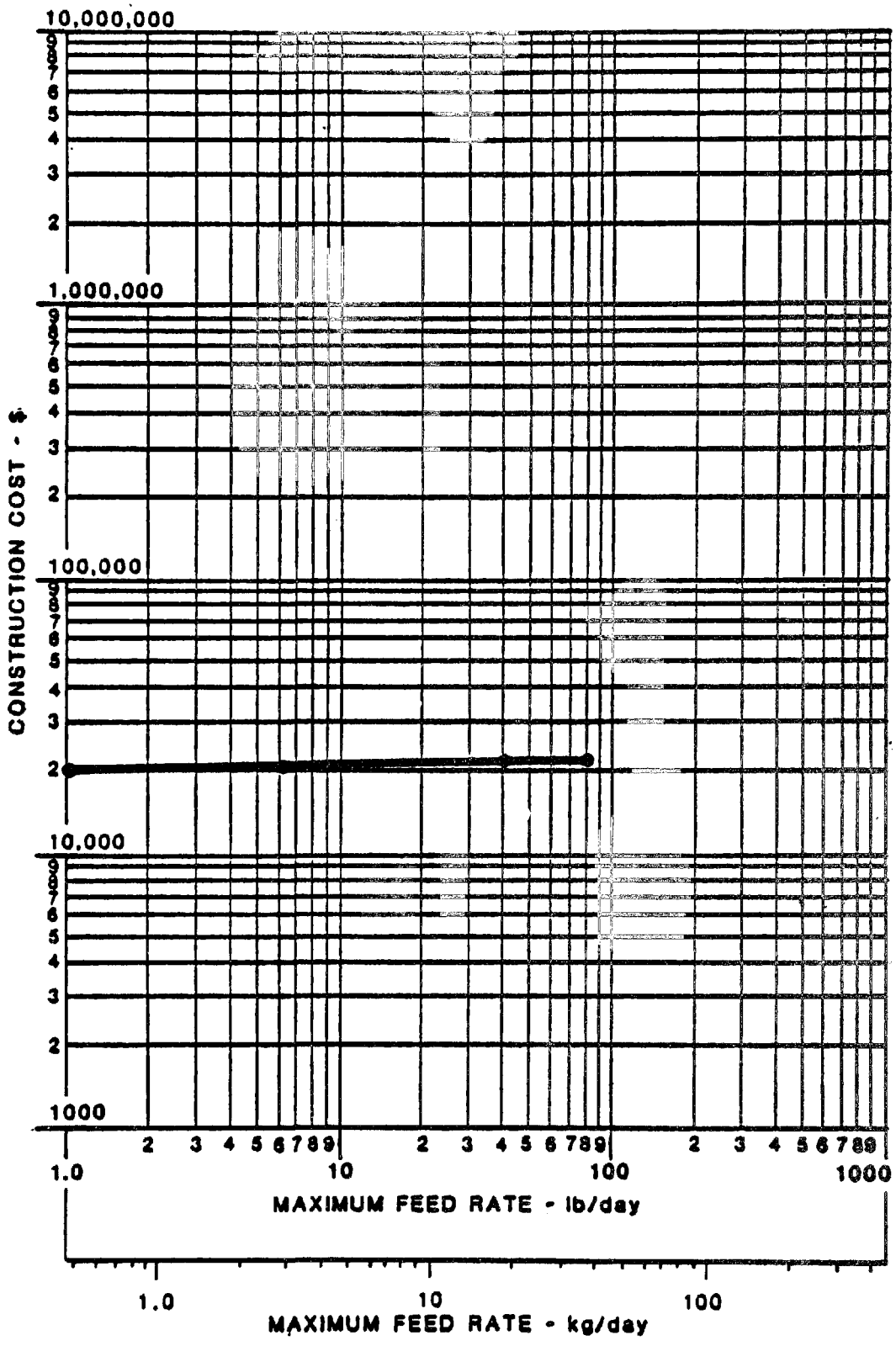

Figure 4. Construction cost for gas feed chlorination systems (Gumerman et al., 1986).

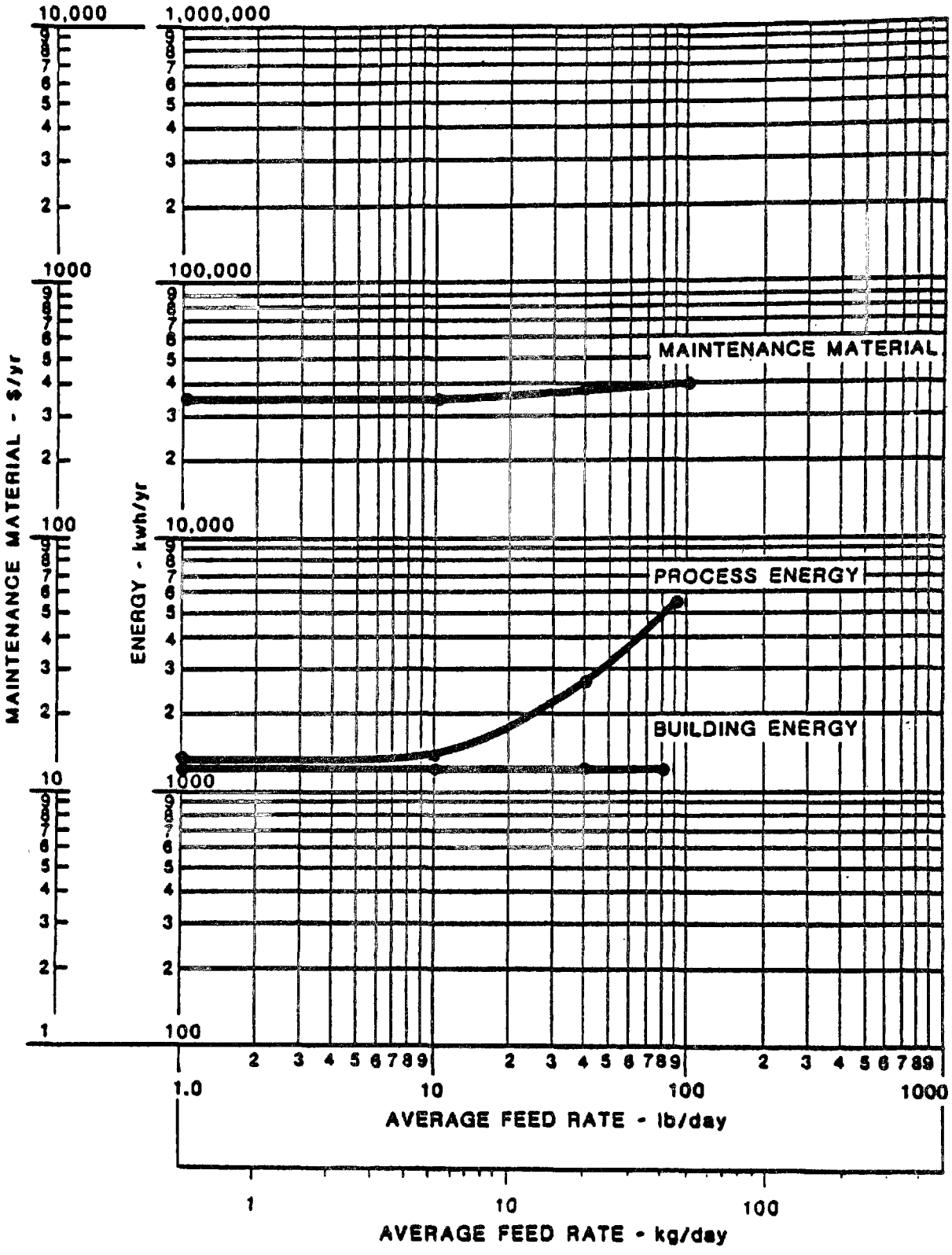

Figure 5. Operation and maintenance requirements for gas feed chlorination systems -- building energy, process energy, and maintenance material (Gumerman et al., 1986).

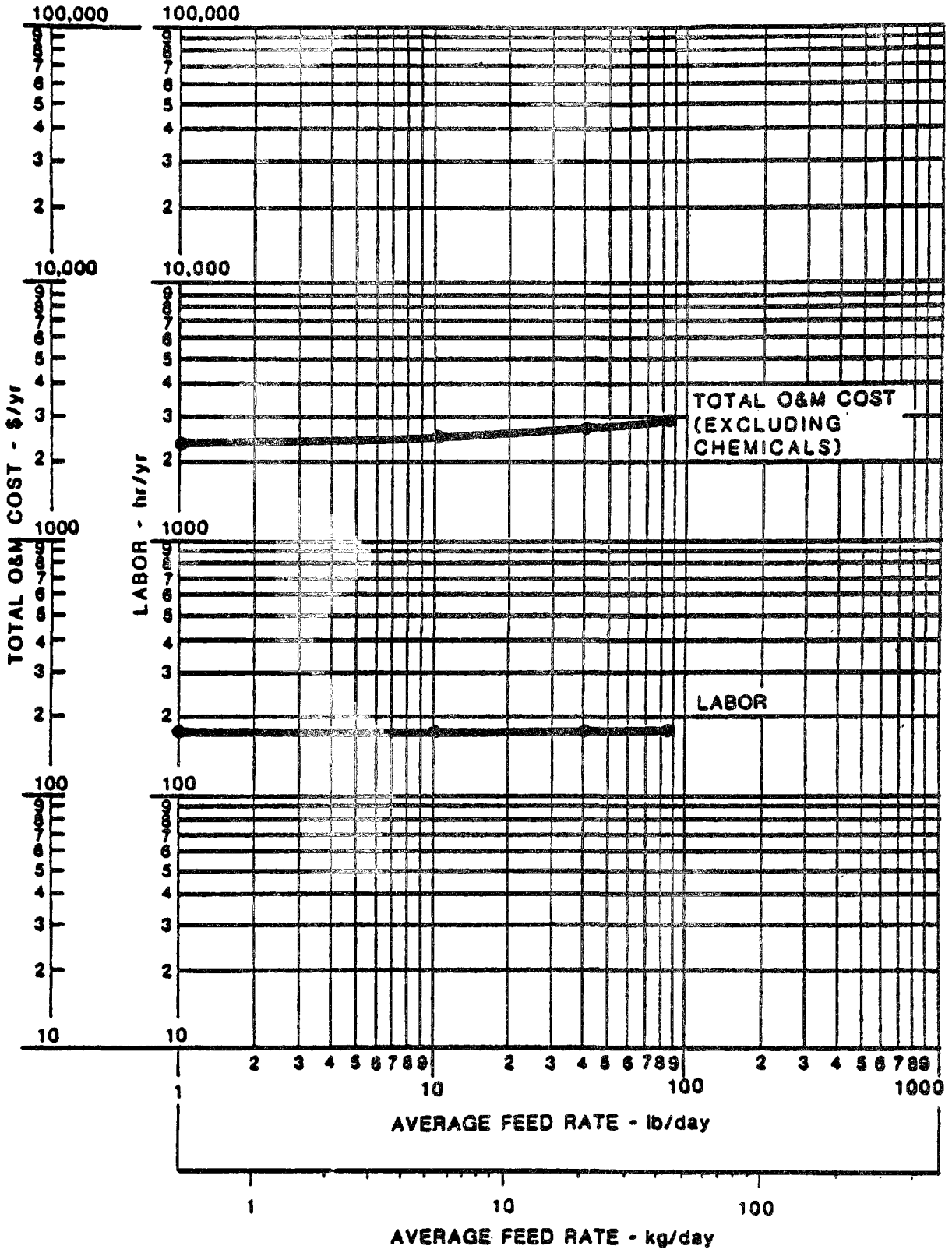

Figure 6. Operation and maintenance requirements for gas feed chlorination systems -- labor and total O&M cost (Gumerman et al., 1986).

Chemical Costs

In 150-lb cylinders, chlorine cost $0.47/lb in the Washington, DC/Baltimore area in January 1983. In 1987, the cost for gaseous chlorine in 150-lb cylinders is $0.37/lb, when purchased in ton quantities. For purposes of this discussion applicable to small water systems, the $0.47/lb will be considered as current.

Assuming a chlorine dosage of 5 mg/L, gaseous chlorine chemical costs would be about $18/yr to treat 2,500 gpd, and about $7,150/yr to treat 1 mgd.

To calculate costs for gaseous chlorine at lower or higher dosages, the following formula can be used:

$$\frac{\text{dosage (mg/L) x no. of L dosed/day x } Cl_2 \text{ cost/lb}}{\text{1000 (mg/g) x 454 g/lb)}} = Cl_2 \text{ cost/day}$$

Sodium Hypochlorite Solution Feed

Equipment Costs

Table XXI displays estimates obtained during May 1980 from two vendors of sodium hypochlorite chlorination equipment. Data are presented for the basic liquid hypochlorination system which includes two metering pumps (one serves as standby), solution tank, diffuser, and appropriate quantities of tubing. However, two types of basic system are costed, one activated electrically, the other activated hydraulically. The basic systems can be supplemented, and costs of four increasingly sophisticated alternatives also are presented in this table. Alternate #1 adds a diffuser corporation cock and anti-siphon backflow preventer. Alternate #2 adds a safety housing enclosure. Alternate #3 adds a flow-pacing system, and Alternate #4 adds a flow meter and signal.

The total capital costs for the basic and most sophisticated systems are:

	basic system	most sophisticated system
Electrically Activated	$3,643	$10,738
Hydraulically Activated	$5,023	$15,121

Construction Costs

Figure 7 is a cost curve (Gumerman et al., 1986) which shosw that the construction cost for hypochlorite solution chlorination systems is constant for systems feeding up to 100 lbs/day.

TABLE XXI. CAPITAL COSTS -- LIQUID CHLORINATORS*

EQUIPMENT COST (basic system**)		Electrically Activated	Hydraulically Activated
	Avg.	$ 1,800	$ 2,266
	High	2,300	2,782
	Low	1,300	1,750
INSTALLATION		500	1,000
SITE WORK		250	250
CONTRACTOR'S OVERHEAD & PROFIT (20%)		729	1,004
ENGINEERING FEES (10%)		364	503
Alternate #1: add diffuser corporation cock & anti-siphon backflow preventer		165	231
Alternate #2: add safety enclosure (housing)		6,930	6,930
Alternate #3: add flow pacing existing signal		---	1,485
Alternate #4: add flow meter signal, 8 in. or less		---	1,452
TOTAL CAPITAL COST:			
Basic System (Equipment + Installation + Site Work + Overhead & Profit + Engineering Fees		$3,643	$5,023
Most Sophisticated (with Alternate #2)		$10,738	---
(with Alternate #4)		---	$15,121

* May 1980 quotes (two vendors)

** Basic System includes two metering pumps (one standby), tubing, solution tank, and diffuser

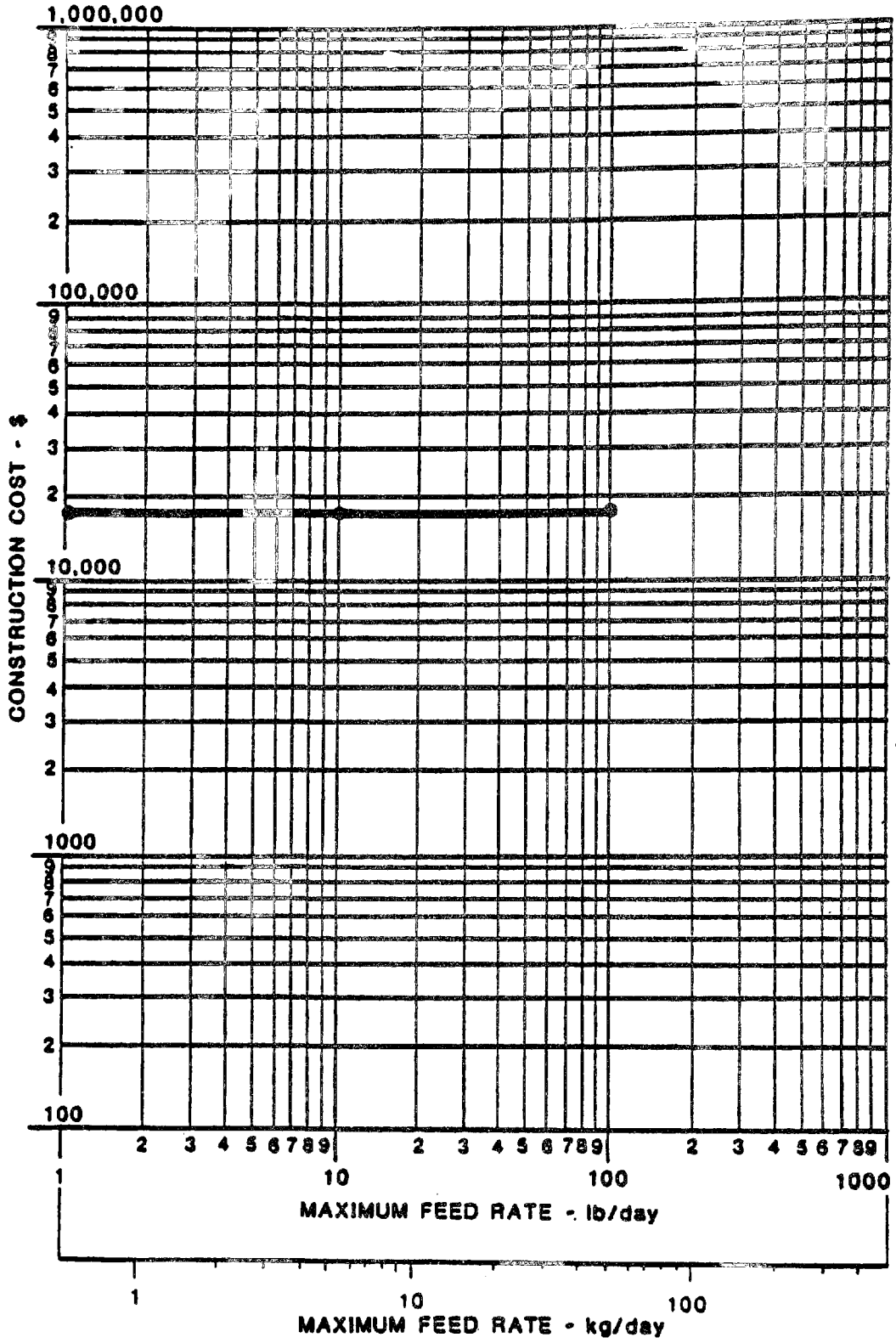

Figure 7. Construction cost for hypochlorite solution chlorination systems (Gumerman et al., 1986).

Operating and Maintenance Costs

As with solution-feed gas chlorinators, O&M requirements are independent of flow for plants treating 2,500 gpd to 1 mgd (Hansen et al., 1979). Process energy requirements are for the diaphragm metering pump and amount to 570 kWh/yr. Building energy requirements for a 25 ft^2 building would be 2,560 kWh/yr. Maintenance materials would be required only for minor component repair -- costs which are estimated at $20/yr.

Labor is required for periodic mixing of the sodium hypochlorite solution, as well as for checking of the equipment. Based on a requirement of 1 h/day, the annual labor requirement would be 365 h/yr.

Annual O&M costs of $4,108 are summarized in Table XXII. Note again that power costs are based on $0.07/kWh and labor costs of $10.00/h.

TABLE XXII. O&M COST SUMMARY FOR SODIUM HYPOCHLORITE SOLUTION FEED (U.S. EPA, 1983)

Item	Requirements*	Cost
ELECTRICAL ENERGY:		
Process	570 kWh/yr x $0.07 =	$ 39.90
Building	2,560 kWh/yr x $0.07 =	$ 179.20
Subtotal	3,130 kWh/yr x $0.07 =	$ 219.10
MAINTENANCE MATERIAL		$ 20/yr
LABOR	365 h/yr x $10/h =	$3,650
Total Annual O&M Cost		$4,108

* amounts estimated by Hansen et al. (1979)

Figure 8 shows constant O&M requirements for hypochlorite solution chlorination systems (building energy, process energy, and maintenance material) for systems feeding up to 100 lbs/day of chlorine. Figure 9 shows similar constant O&M maintenance requirements for hypochlorite solution chlorination systems (labor and total O&M costs). Both curves are from Gumerman et al. (1986).

Chemical Costs

Sodium hypochlorite customarily is sold as a 15% (by weight) solution. In July 1987, the cost of a 15% solution in 1,500 gal tanks in the Washington, DC/Baltimore area was $0.50/gal. A small water utility treating 2,500 gal/day with 5 mg/L of chlorine as sodium hypochlorite solution would require about 64 gal/yr. At $0.50/gal, this utility would spend about $32/yr.

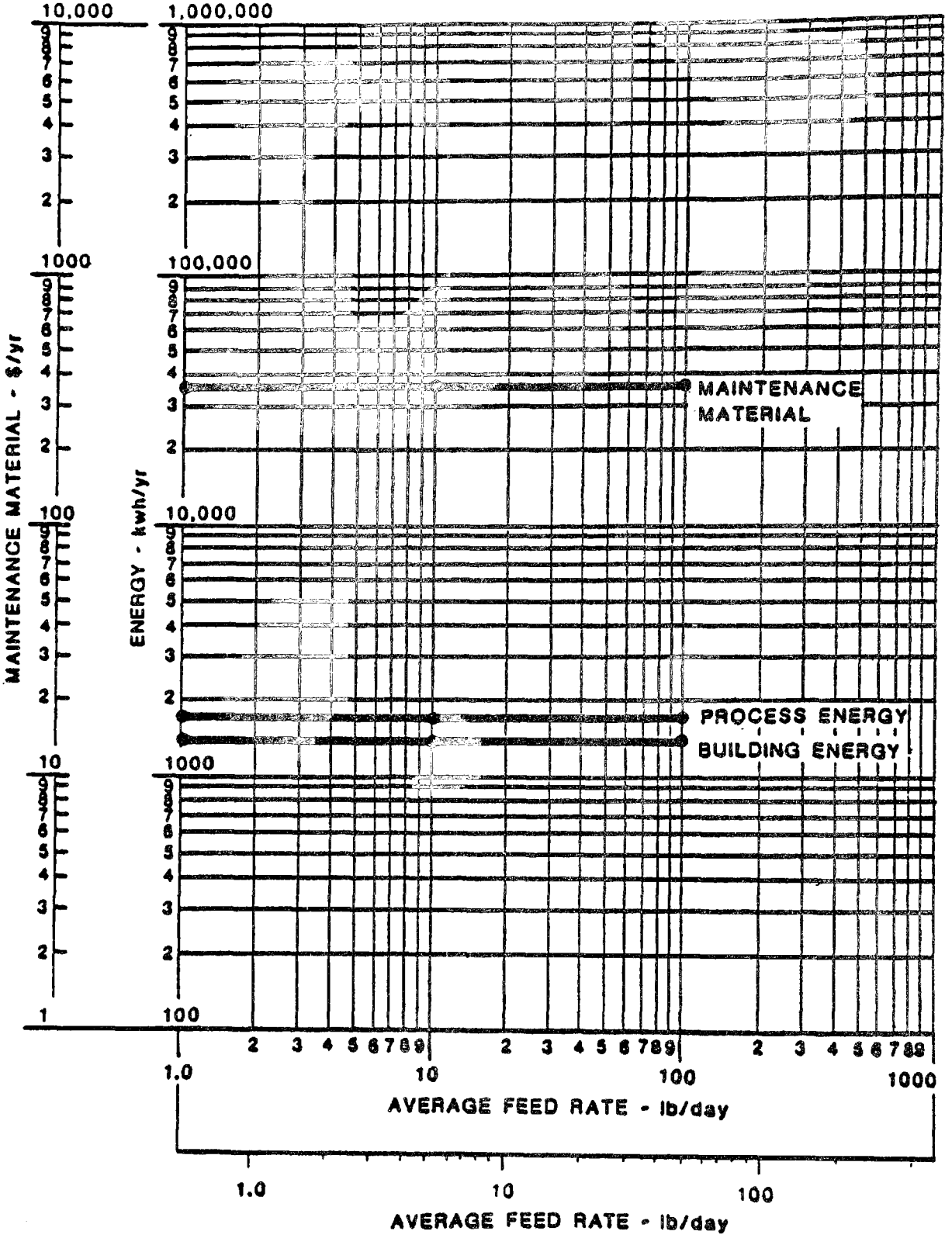

Figure 8. Operation and maintenance requirements for hypochlorite solution chlorination systems -- building energy, process energy, and maintenance material (Gumerman et al., 1986).

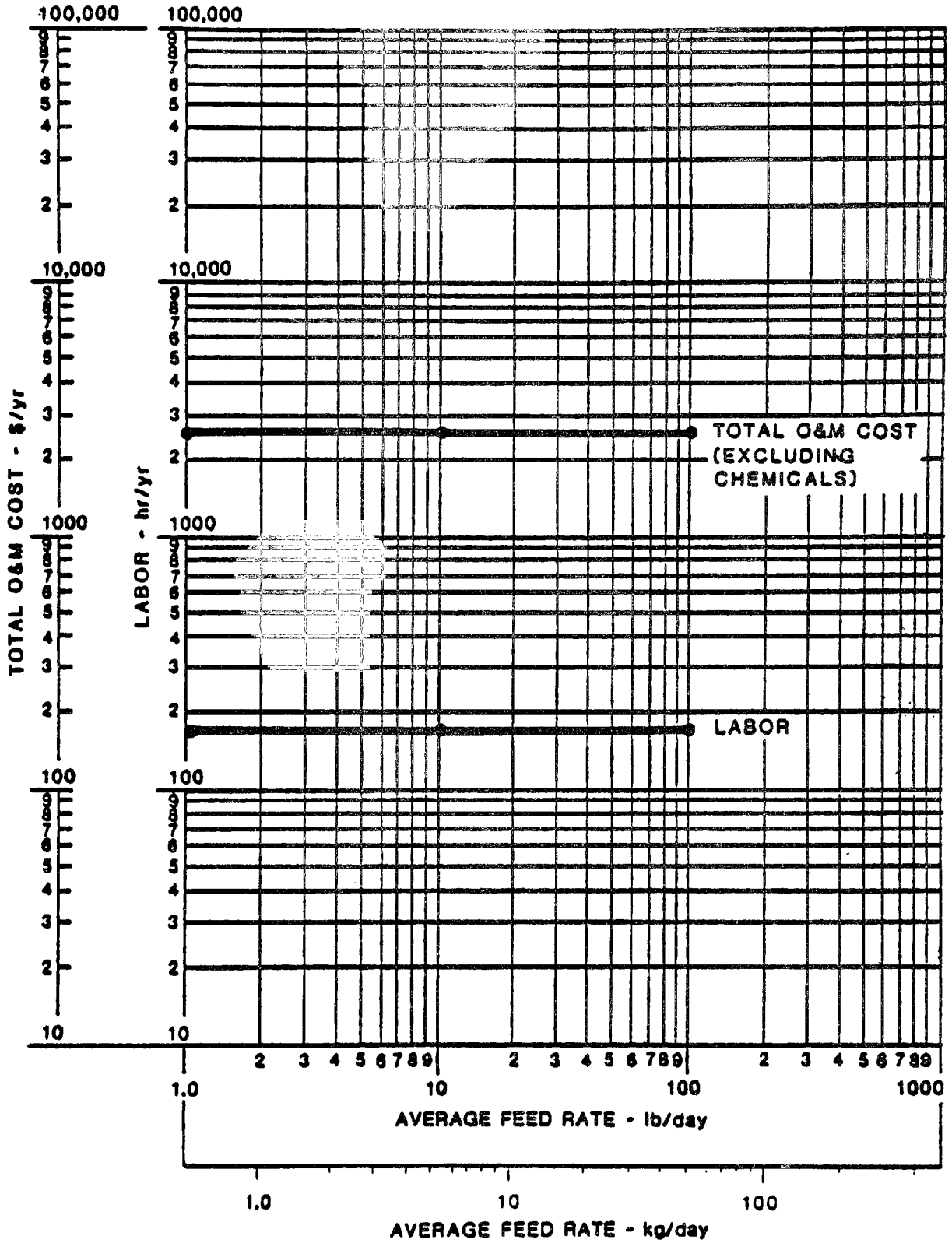

Figure 9. Operation and maintenance requirements for hypochlorite solution chlorination systems -- labor and total O&M cost (Gumerman et al., 1986).

A 1 mgd facility using 5 mg/L of chlorine would require 400 times more hypochlorite solution, and would spend $12,800/yr.

However, it should be realized that the cost for sodium hypochlorite solution is about three times the cost of gaseous chlorine in equivalent quantities, and that 0.9 lb of 15% NaOCl solution is equivalent in oxidation potential to one pound of gaseous chlorine. These ratios between the two forms of chlorine will assist in obtaining more accurate cost calculations.

Calcium Hypochlorite Solution Feed

Equipment costs and operating and maintenance costs for this method of disinfection should be very close to those for sodium hypochlorite feed systems. Solutions of calcium hypochlorite are prepared in a mixing tank, then transferred to a day tank (a tank which holds enough solution to last for one day), then injected into the water stream using a diaphragm metering pump.

Chemical Costs

Solid calcium hypochlorite, $Ca(OCl)_2$, contains 65% available chlorine. Therefore, one pound contains 65 lb of available chlorine. Since a 2,500 gal/day treatment plant requires 0.104 lb of chlorine per day (at an average dosage of 5 mg/L), 0.104/0.65 = 0.16 lb of $Ca(OCl)_2$ per day is required with which to prepare a solution for metering into the water to be treated.

During July 1987, calcium hypochlorite was selling for $0.95/lb in the Washington, DC/Baltimore area. Over a one year period, the 2,500 gal/day facility will require 0.16 lb x 365 days = 58.4 lbs of $Ca(OCl)_2$, x $0.95/lb = $55.48/yr. A 1 mgd facility, which uses 400 times the amount of chlorine, therefore will spend $22,192/yr for $Ca(OCl)_2$.

Pellet Feed Chlorinators

Figure 10 shows that construction costs for pellet feed chlorinators are constant for systems feeding up to 15 lbs/day. Figure 11 shows operation and maintenance requirements for pellet feed chlorinators (process energy and maintenance material); Figure 12 shows operation and maintenance requirements for labor and total O&M cost. These curves are taken from Gumerman et al. (1986).

Erosion Feed Chlorinators

Figure 13 shows constant construction costs for erosion feed chlorinators feeding up to six lbs/day of chlorine. Figure 14 shows operation and maintenance requirements for erosion feed chlorinators (process energy and maintenance material); Figure 15 shows O&M requirements for labor and total O&M cost. All three figures are taken from Gumerman et al., 1986.

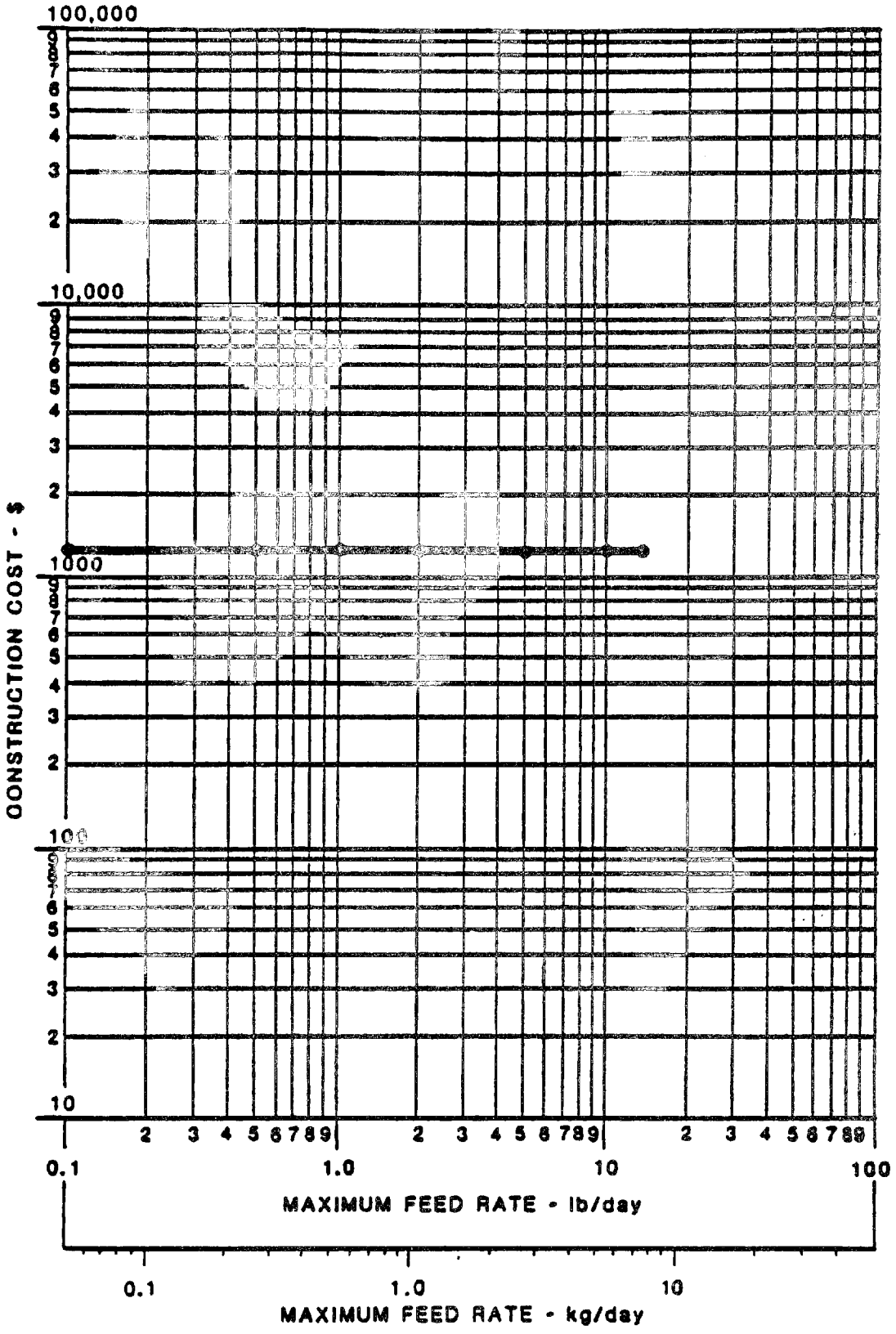

Figure 10. Construction cost for pellet feed chlorinators (Gumerman et al., 1986).

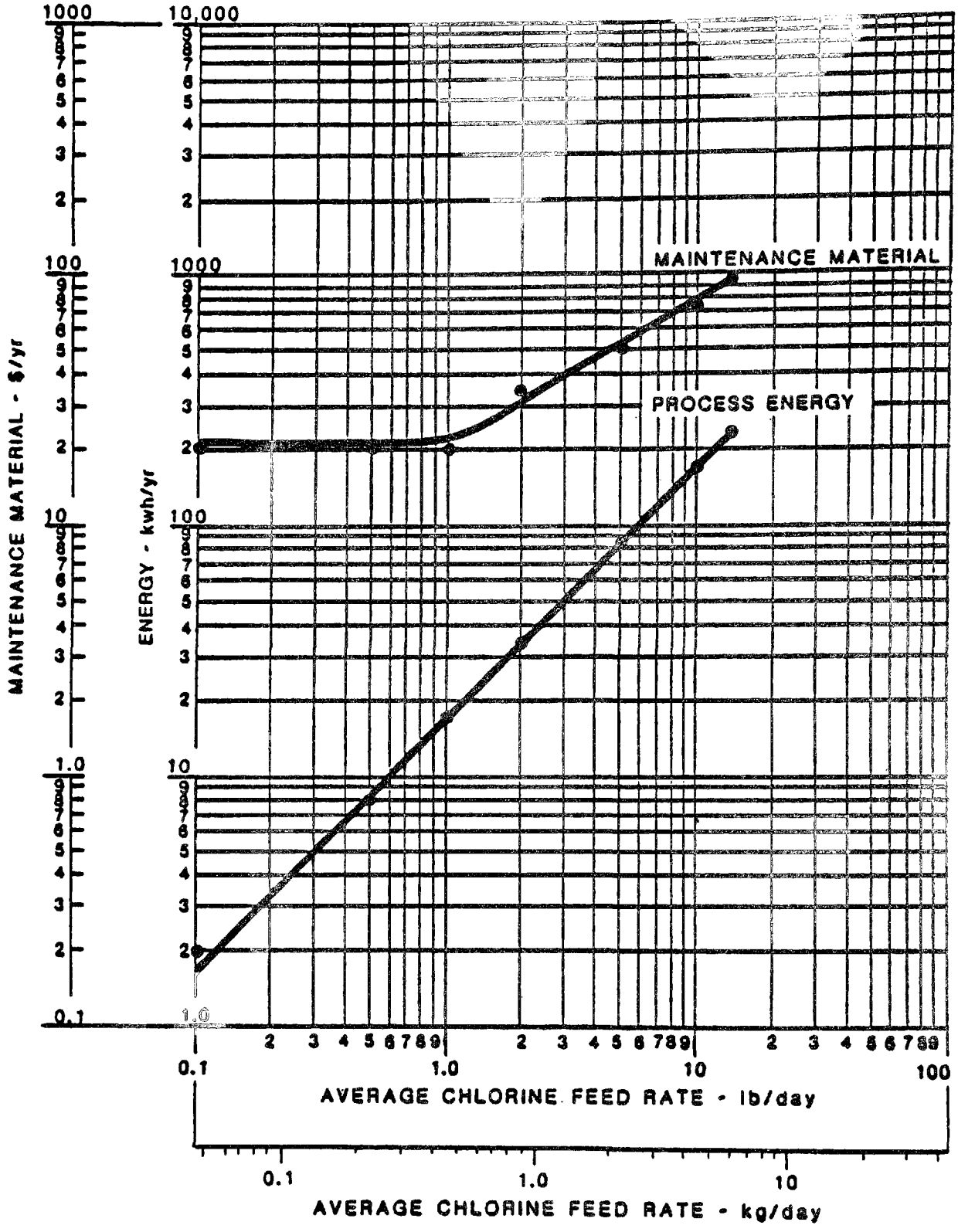

Figure 11. Operation and maintenance requirements for pellet feed chlorinators -- process energy and maintenance material (Gumerman et al., 1986).

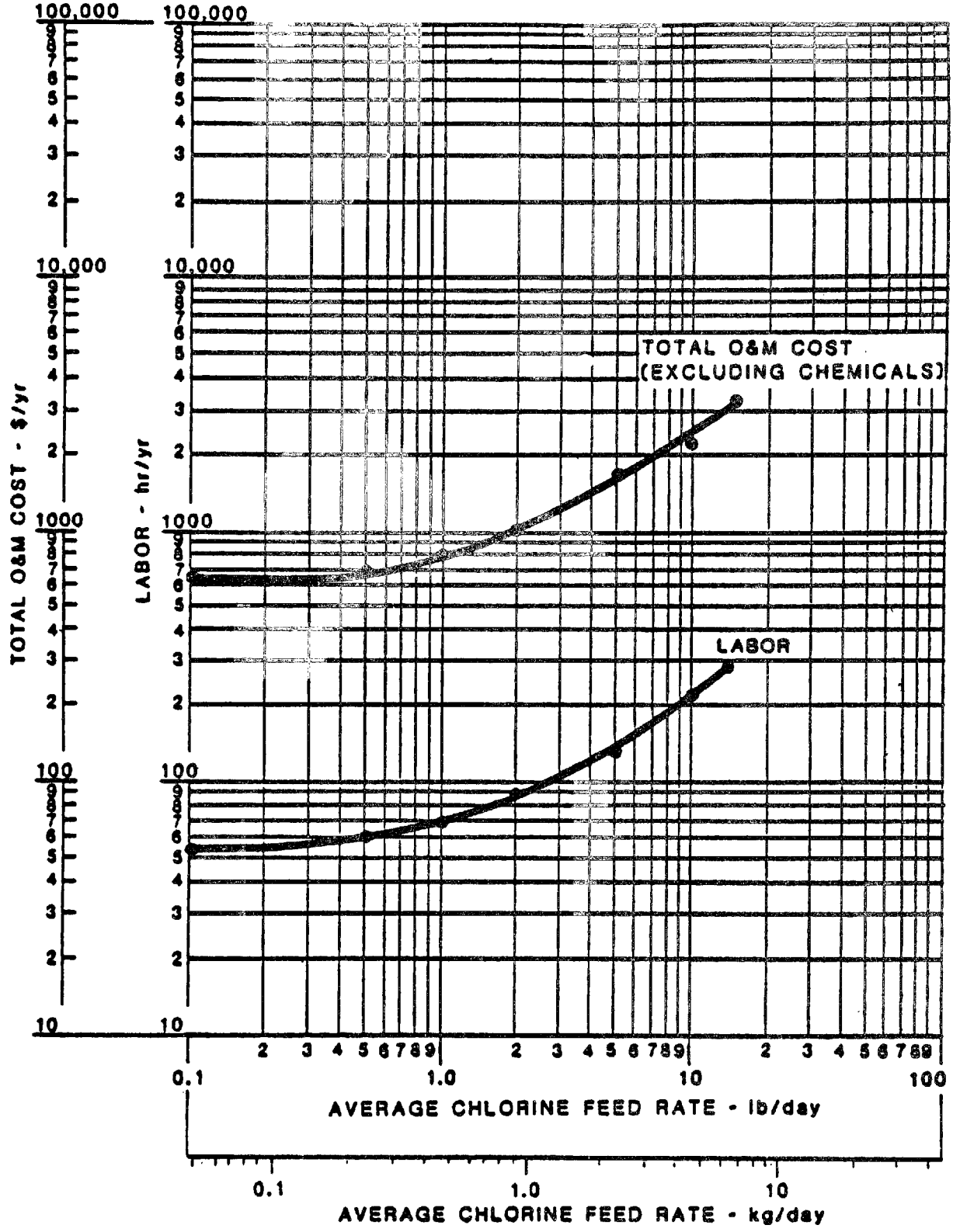

Figure 12. Operation and maintenance requirements for pellet feed chlorinators -- labor and total O&M cost (Gumerman et al., 1986).

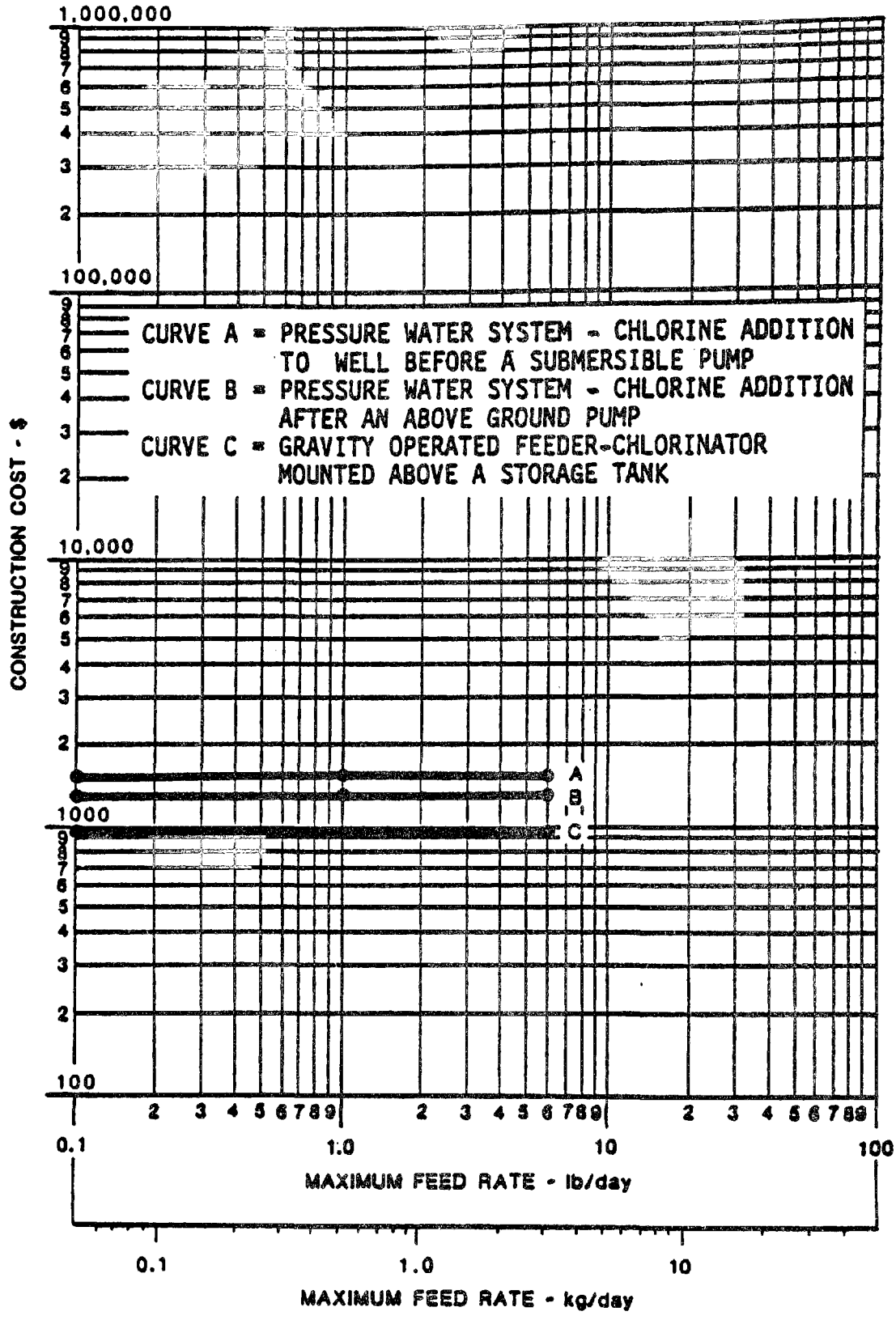

Figure 13. Construction cost for erosion feed chlorinators (Gumerman et al., 1986).

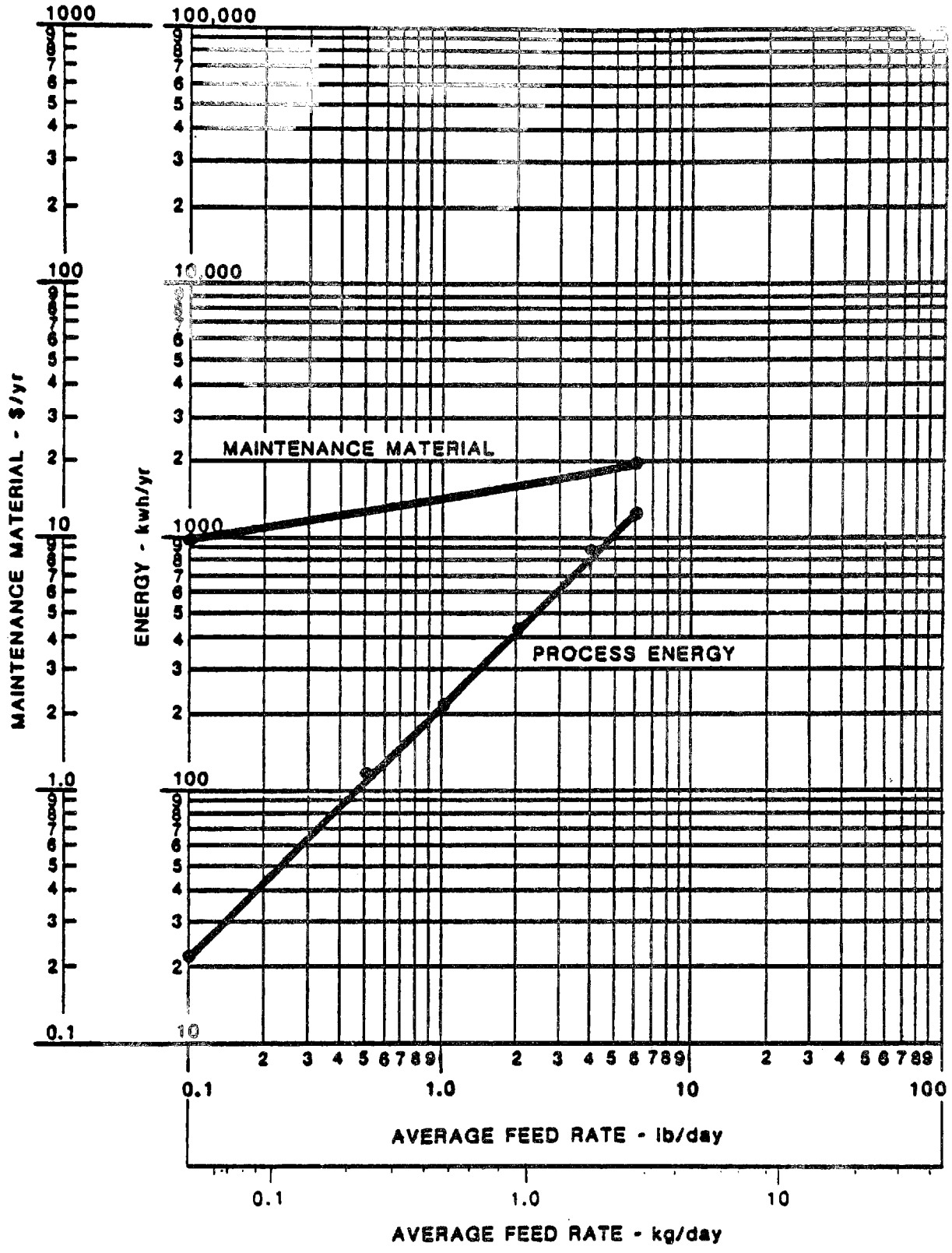

Figure 14. Operation and maintenance requirements for erosion feed chlorinators -- process energy and maintenance material (Gumerman et al., 1986).

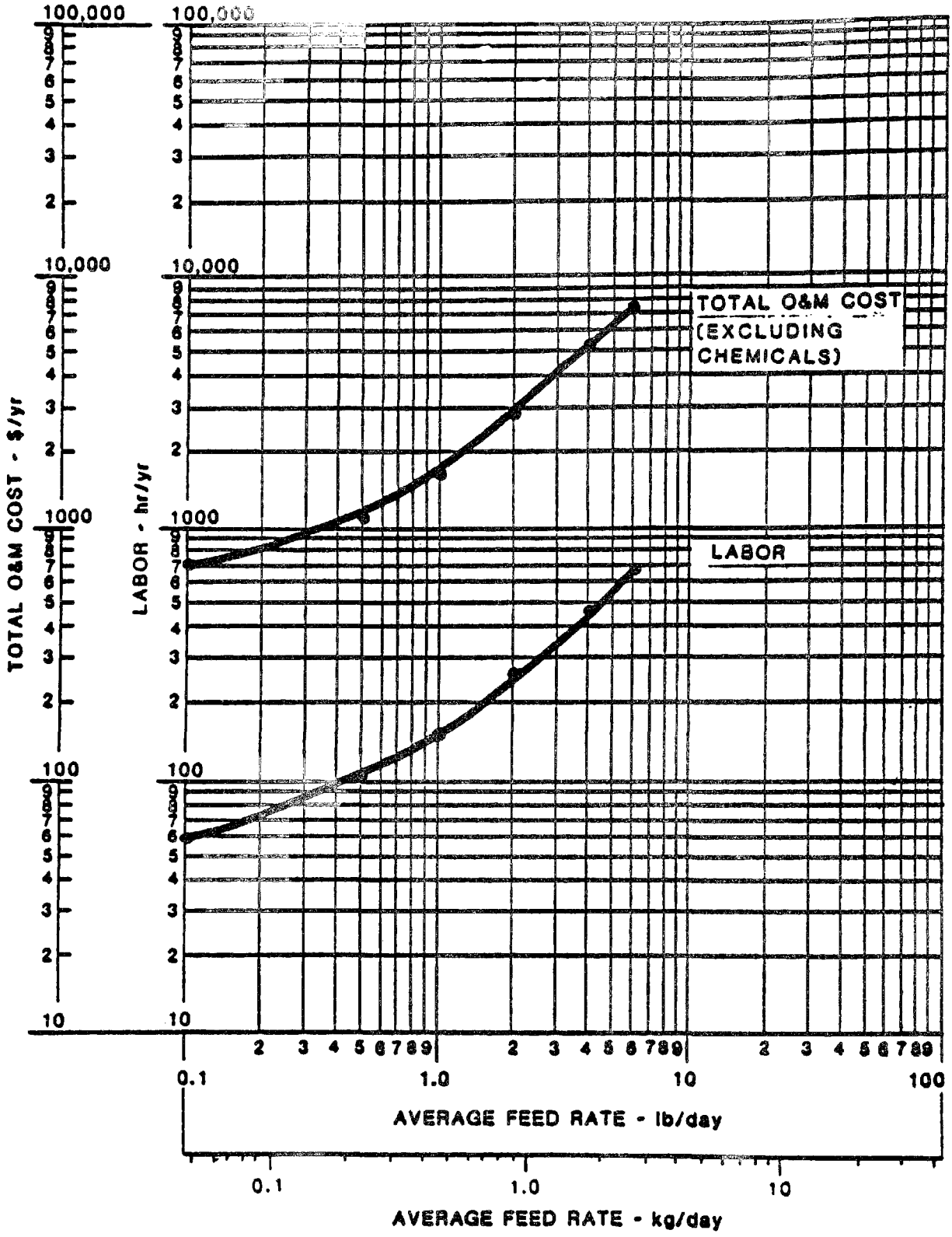

Figure 15. Operation and maintenance requirements for erosion feed chlorinators -- labor and total O&M cost (Gumerman et al., 1986).

On-Site Electrolytic Hypochlorite Ion Generation

Figure 16 shows construction costs for on-site hydrochlorite generation systems producing up to 100 lbs/day of chlorine. Figure 17 shows operation and maintenance requirements for on-site hypochlorite generation systems--building energy, process energy, and maintenance material; Figure 18 shows operation and maintenance requirements for labor and O&M cost. These curves are taken from Gumerman et al. (1986).

b. Ozone

i. Characteristics and Properties of Ozone

Ozone (O_3) is a very powerful oxidizing agent, second only to elemental fluorine among readily available chemicals. Because of its strong oxidizing ability, ozone also is a powerful disinfectant. It is an unstable gas at ambient temperatures and pressures, and decomposes rapidly to oxygen (from which it is made) at temperatures above 35°C. For this reason, it cannot be manufactured and packaged at a central manufacturing plant, as can chlorine. Therefore, ozone must be generated on-site and used at once.

Ozone has a characteristic odor which can be detected by most humans at low concentrations (0.01 to 0.05 ppm by volume), far below the levels of acute toxicity. However, olfactory fatigue has been noted in some instances. This means that as the length of exposure to an ozone-containing atmosphere increases, the odor of ozone may become less noticeable to the individual being exposed.

When added to water, ozone dissolves only partially. That is to say that ozone is only slightly soluble in water, about 2-10 times the solubility of oxygen, depending on the water temperature. The solubility of ozone in water is governed by Henry's Law, which states that the mass of ozone that will dissolve in a given volume of water, at constant temperature, is directly proportional to the partial pressure of the ozone gas above the water. Consequently, proper design of the ozone contacting system is very important to the proper application of ozone to water (see later discussion-iii).

The stability of ozone is greater in air than in water, but is not excessively long in either case. The half-life of ozone in water has been reported to range from 8 minutes to 14 hours, depending on the phosphate and carbonate concentrations of the water (Grunwell et al., 1983). With no phosphates or carbonates present and the water adjusted to pH 7.0 with sodium hydroxide, the half-life was 8 minutes.

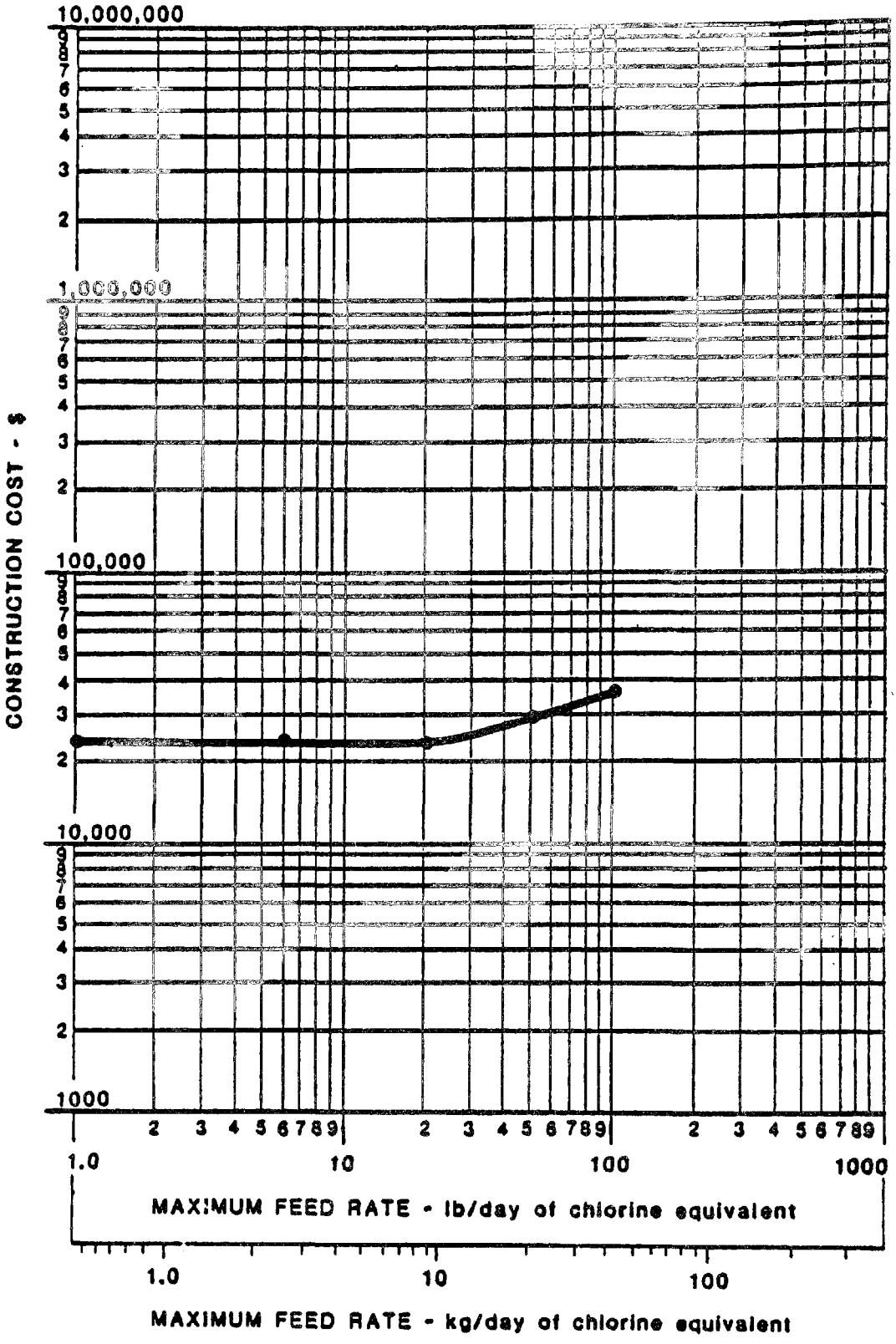

Figure 16. Construction cost for on-site hypochlorite generation systems (Gumerman et al., 1986).

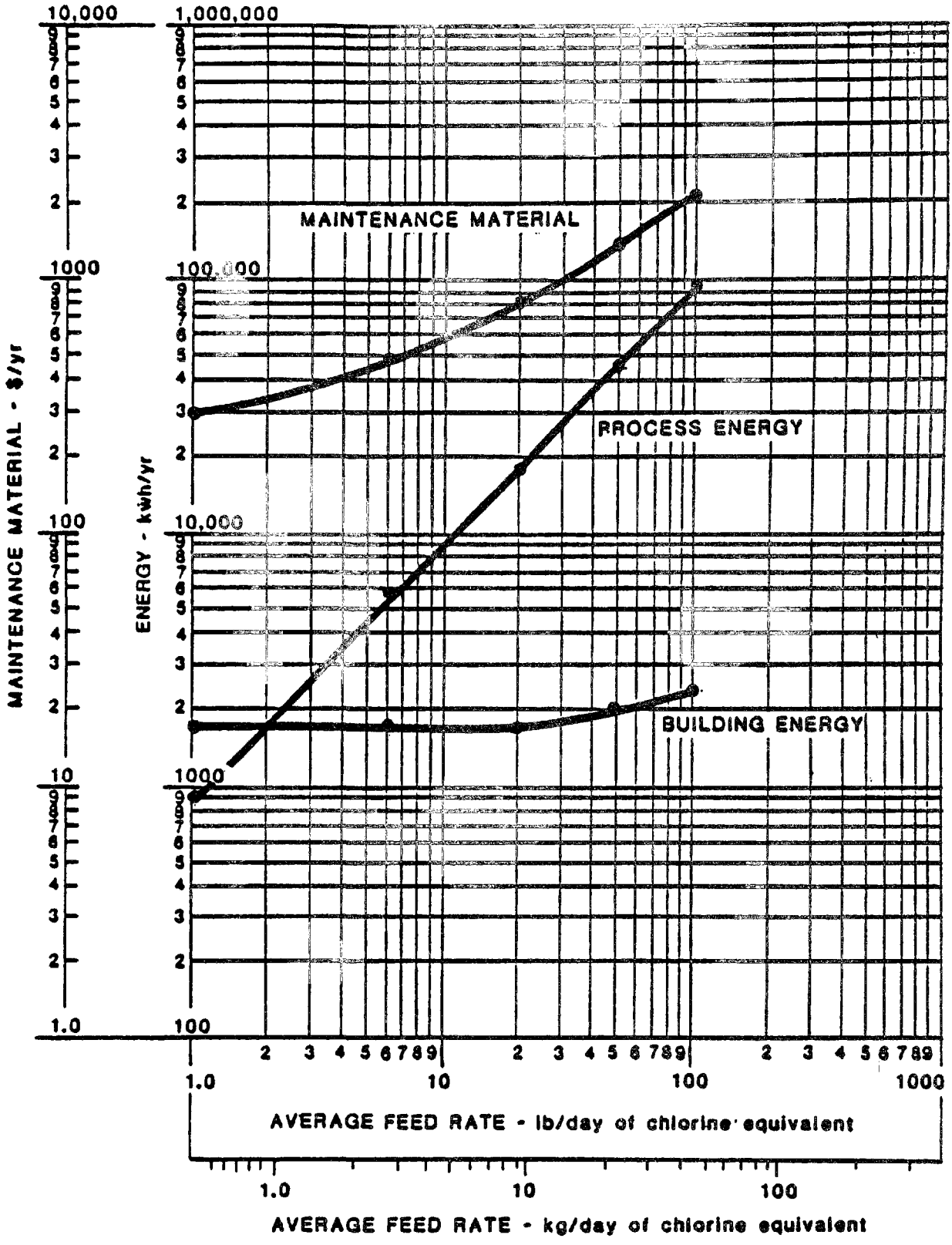

Figure 17. Operation and maintenance requirements for on-site hypochlorite generation systems -- building energy, process energy, and maintenance material (Gumerman et al., 1986).

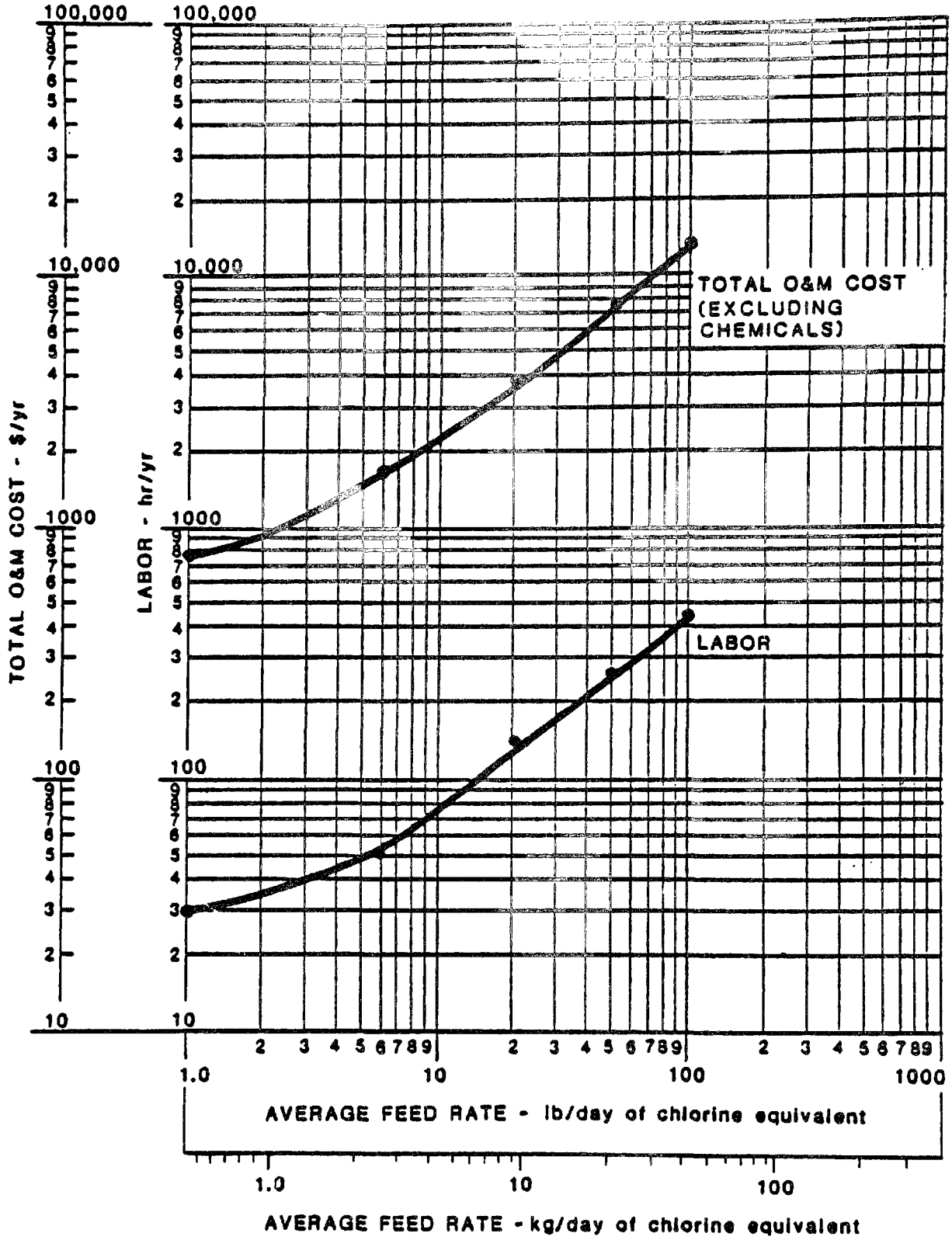

Figure 18. Operation and maintenance requirements for on-site hypochlorite generation systems -- labor and O&M cost (Gumerman et al., 1986).

ii. Generation of Ozone

For the on-site generation of ozone by means of corona discharge (the procedure used most for water treatment), an oxygen-containing gas (air, oxygen-enriched air, or pure oxygen) is dried and cooled, then passed between two electrodes separated by a discharge gap and a dielectric material across which high voltage potentials are passed. In recent years, the more modern ozone generating equipment has been designed to operate at high frequencies rather than high voltages.

Figure 19 is a schematic diagram of the essential components of a corona discharge ozone generator. For small water plants, ambient air dried to a dew point of minus 65°C (-65°C) will be the source gas fed to the ozone generator. It is imperative that the ambient air be dried rigorously in order to maximize the yield of ozone produced, as well as to minimize the formation of corrosive nitrogen oxides.

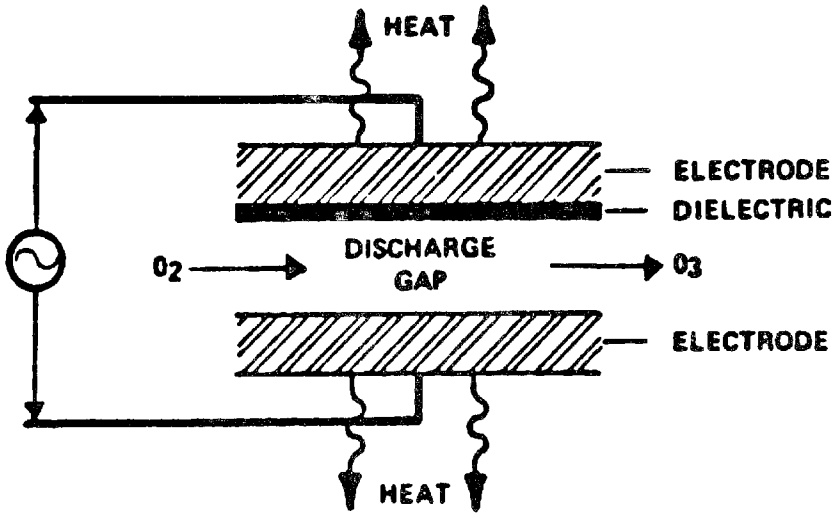

Figure 19. Typical corona discharge cell ozone generating configuration.

With properly dried air, the output from a corona discharge ozone generator will be dried, cooled air, containing 1% to 3.5% of ozone, which is partially soluble in water (about 2-10 times the solubility of oxygen). This produced mixture of ozone in air then must be mixed with the water to be treated, by a process known as contacting (see later discussion - iii).

Ozone also can be generated by passing UV radiation through ambient air. However, in this procedure, only small quantities of ozone can be generated, and at much lower concentrations (0.1 to 0.001%) than can be generated by corona discharge. This concentration is considered insufficient to provide enough ozone in water to cause a significant amount of oxidative or disinfective treatment.

When oxygen is used as the feed gas to the ozone generator, the concentration of ozone produced is effectively doubled over that produced when properly dried air is employed. This means that oxygen containing 2% to 7% (by weight) of ozone is generated in the same size corona discharge ozone generator and for the same expenditure of electrical energy as when dried air is used.

In the United States today, there are at least 35 operational water treatment plants using ozone. Only the new 540 mgd plant in Los Angeles is using oxygen as the feed gas. In the rest of the world, where ozone is used more extensively than currently in the U.S., fewer than a dozen water treatment plants are known to be using oxygen as the feed gas, although more interest is being shown in its use.

When the properly dried air or oxygen passes through the ozone generator, part of the oxygen dissociates as a result of being exposed to the high energy electrical field of the corona discharge:

$$O_2 + e^- \text{ ------> } 2[O] \quad \text{"fragments"}$$

oxygen

These oxygen "fragments" are highly reactive, and they combine rapidly with molecular oxygen, forming the triatomic molecule, ozone:

$$2[O] + 2\,O_2 \text{ ------> } 2\,O_3$$

oxygen fragments — oxygen — ozone

The overall reaction to produce ozone is the sum of the above reactions:

$$3\,O_2 + e^- \text{ <-----> } 2\,O_3$$

oxygen — energy — ozone

The reaction to produce ozone is reversible, meaning that once formed, ozone decomposes back to oxygen. This reverse reaction occurs quite rapidly above 35°C. Therefore, because reactions involving high energy electrical discharges also are accompanied by generation of considerable heat, ozone generators are designed to include a high degree of cooling, in order to minimize ozone losses by decomposition.

iii. **Contacting of Ozone With Water**

Because ozone is only partially soluble in water (2-10 times that of oxygen), the manner with which it is contacted with the water to be treated is of primary importance. In turn, the manner of contacting ozone with water depends upon the particular ozonation job or jobs to be accomplished.

For purposes of illustration, there are basically two types of reactions involving ozone: fast and slow. Fast ozonation reactions include the destruction or inactivation of microorganisms (disinfection), oxidations of iron, manganese, sulfide ions, nitrite ions, some organics, and lowering turbidity levels. On the other hand, other ozone oxidations, such as oxidation of many organic materials (specifically many pesticides and VOCs), are kinetically rather slow.

As a result, for the fast ozone reactions, the contacting objective is to add the requisite amount of ozone to the water as rapidly as possible, so that the solute being oxidized or inactivated will react as rapidly as possible. The rate of this type of ozonation reaction is dependent on the rate of transfer of ozone into solution. This type of reaction is termed "mass transfer controlled", and contact times, therefore, are relatively short.

For example, during disinfection with ozone, ozone is added first to satisfy the ozone demand of the water and to create a residual dissolved ozone level, then to maintain the requisite residual of ozone for a given period of time.

Slower ozone oxidations are dependent upon maintaining a low residual concentration of ozone in the water, but over a much longer length of time, because the chemical reaction rates are slow. These types of reactions are termed "reaction rate controlled".

Ozone can be generated under positive or negative air pressure. If generated under positive pressure, the ozone-containing air normally exits the ozone generator at approximately 15 psig. This is sufficient pressure for the gas to pass through porous diffusers installed at the base of a 16 foot column or tank of water. Fine bubbles containing ozone and air (or oxygen) rise slowly through this water column. During the time of bubble rise, the ozone contained in the bubbles diffuses from the gas phase into the water phase, where oxidation and/or disinfection takes place. The 16 ft height of water column maximizes the amount of ozone transferred from the tiny bubbles as they rise.

Other types of positive pressure ozone contactors include packed columns, static mixers, and high speed agitators. The water to be treated also can be sprayed through small orifices into an ozone-containing atmosphere (the atomizer, or spray-drying principle).

When ozone is generated under negative pressure, the air or oxygen is drawn through the feed gas preparation system, then through the ozone generator and into the contactor. The sub-atmospheric pressure can be created by employing a submerged turbine as the contactor. Thus, when the turbine is turned on, its whirling action creates a slight vacuum, drawing air through the entire ozonation system.

Other methods of creating sub-atmospheric pressure which are in common practice are by use of injectors or Venturi-type nozzles. Water to be treated is pumped past a small orifice (injector) or through a Venturi nozzle. In either case, a slight vacuum is created, which can be used to draw the

air/oxygen/ozone output of the ozone generating system. Contacting takes place during the mixing of gas with flowing water.

It can be appreciated that the diffuser and packed tower contactors require no energy to operate, whereas high speed agitators, static mixers, and all of the negative pressure contactors require energy for their operation.

As excellent discussion of the various types of ozone contactors has been assembled by Masschelein (1982).

iv. Destruction of Contactor Exhaust Gas

No matter how well designed the ozone contactor, it is rare, if ever, that 100% transfer of ozone to the water occurs, unless insufficient ozone is provided. Therefore, there will always be some excess ozone in the gases which exit the ozone contacting system. Particularly for disinfection with ozone, during which a dissolved residual of ozone is present for a predetermined length of time, there will always be ozone present in the contactor exhaust gases (off-gases). This excess ozone either must be reused or destroyed before discharge of the gases to the plant atmosphere.

Reuse of ozone can be effected if two stages of ozonation (one for oxidation, one for disinfection) are designed into the water treatment process. In this event, contactor exhaust gases from the later ozonation step are drawn into the earlier ozonation stage, for example, by means of a submerged turbine. However, even well-designed reuse of ozone in a second stage still will leave some excess ozone in the final exhaust gases, and this must be destroyed before discharge. Destruction of ozone (to produce oxygen from which it is generated) is accomplished by several methods:

- thermal destruction -- at 300-350°C, ozone decomposition requires only a few seconds,
- catalytic destruction -- at ambient temperatures with the appropriate catalyst (metal or metal oxide),
- adsorption and decomposition on moist granular activated carbon,
- exposure to UV radiation (254 nm wavelength).

This latter method is in use only in very large treatment plants, because even at 254 nm wavelength, there is a small amount of ozone generated.

v. Chemistry of Ozone in Water

Unlike chlorine, ozone does not react with water to produce disinfecting species. However, above pH about 6, ozone does decompose in water to produce the more reactive hydroxyl free radical:

$$O_3 + H_2O \text{ -----> } O_2 + 2(OH)\cdot$$

This reaction is accelerated at the higher pH values (above 8). In addition, hydroxyl free radicals are produced whenever ozone is exposed to UV radiation, or when ozone is applied in the presence of hydrogen peroxide. Ozone oxidation rates of some refractory organic materials are greatly accelerated by the simultaneous addition of UV radiation or H_2O_2 because of the formation of hydroxyl free radicals.

Thus, when ozone is added to water it can react as the O_3 molecule, as the hydroxyl free radical, or as a mixture of both.

Bicarbonate and carbonate ions are excellent scavengers of free radicals; therefore waters containing high alkalinity levels will quickly destroy the hydroxyl free radicals produced by the decomposition of ozone, and eliminate the benefits of the free radical oxidative mechanisms.

vi. **Establishing An Ozone Residual**

In order to attain the appropriate CT value to achieve 99.9% inactivation of Giardia lamblia cysts (Table IIA) a measurable residual level of ozone must be developed in water and maintained for the appropriate period of time. In operating drinking water treatment plants using ozone for disinfection (primarily in France, but also in many other countries of the world), it is customary to attain a dissolved ozone residual concentration of approximately 0.4 mg/L, then to maintain this concentration for a period of time of at least four minutes (laboratory) and 6-8 minutes in operating water treatment plants.

It can be appreciated that the water entering the ozone-for-disinfection contacting chamber has the highest ozone demand, whereas water exiting the contacting chamber has the lowest ozone demand. Therefore, part of the function of the ozone contacting system is to satisfy the short term, or immediate, ozone demand of the water. Since disinfection is a mass transfer controlled reaction (fast), a certain percentage of ozone is utilized initially to satisfy the short term ozone demand. After this ozone demand is satisfied, the contacting task becomes one of maintaining a specific ozone concentration for a specific time period.

These two tasks normally are conducted in two different contacting chambers, with the larger amount of ozone being applied to the first chamber. This procedure, which is employed to minimize the amount of ozone added, is shown in Figure 20. Approximately two-thirds of the total ozone required is added to the first chamber, in which the ozone demand of the water is satisfied, and a residual ozone level of about 0.4 mg/L is attained. The balance of the ozone (one-third) is added to the second chamber, in which the 0.4 mg/L ozone residual is maintained.

To attain the necessary contact time for the ozone with a 0.4 mg/L ozone residual, it is simply a matter of dividing 0.4 into the CT value from Table IIA taken at the appropriate temperature. The product is the minimum contact time (in minutes) required. Table XXIII shows the CT values and

contact times required for an ozone residual of 0.4 mg/L at various temperatures.

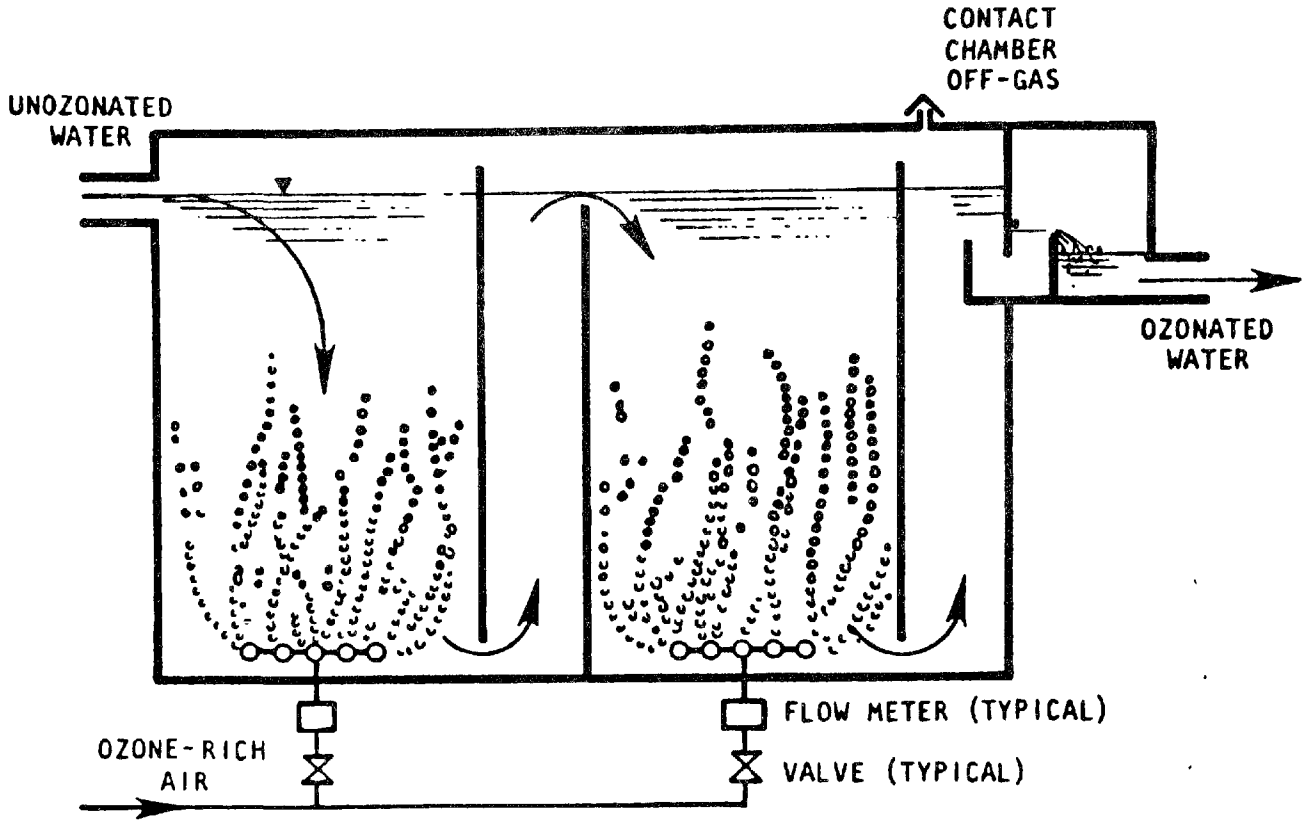

Figure 20. Two-compartment ozone contactor with porous diffusers.

TABLE XXIII. CT VALUES AND CONTACT TIMES FOR OZONE TO ACHIEVE 99.9% INACTIVATION OF Giardia lamblia AND > 99.99% INACTIVATION OF ENTERIC VIRUSES FOR 0.4 mg/L OZONE

		Temperature (°C)					
Disinfectant	pH	0.5	5	10	15	20	25
Ozone (0.4 mg/L)	6-9						
CT value		4.5	3	2.5	2.0	1.5	1.0
Contact Time (min)		11.25	7.5	6.25	5	3.75	2.5

If the dissolved ozone residual can be raised to 0.5 mg/L, the contact times will be somewhat lower. If the ozone residual is lower (i.e., 0.3 mg/L), the contact time will be somewhat longer. If only a 1-log or 0.5-log inactivation of Giardia is required, as when preozonation disinfection is practiced prior to filtration), the CT value (and therefore, the ozone contact time) required will be even lower (see Table IIB and IIC, respectively).

Many current ozonation systems in the U.S. today are designed to optimize the oxidative capabilities of ozone, not necessarily to optimize ozone disinfection. In these instances it is customary to provide a single ozone contact chamber. If single contact chambers are used for ozone disinfection, and the residual ozone concentration is measured at the outlet of the contact chamber, how should the ozone concentration and contact time be determined?

The initial response is to assume that the ozone residual concentration at the outlet is present throughout the contact chamber. Were this to be true, one would simply multiply the detention time in the contactor by the concentration of ozone in the water exiting the contactor to determine the CT value.

However, this assumption is incorrect. Considering only the first compartment of the 2-compartment ozone contactor in Figure 20, it must be realized that the water entering the upper part of the compartment contains no ozone and constantly exerts an ozone demand. Therefore it can be concluded that the upper portion of this compartment contains much less ozone than the lower portion. However, the ozonized water exits from the lower section with a measurable dissolved ozone residual.

It is clear from this reasoning that the true CT value of a single contact chamber is lower than that obtained by multiplying the detention time by the ozone concentration in the water exiting the chamber. As a first approximation only, one should assume that the average concentration of ozone throughout the contact chamber is, say, 50% of that measured at the outlet. But even this approximation may not be true.

If single ozone contact chambers are to be supplied, it is advisable to measure the dissolved ozone concentrations at various points in the chamber at the various water flow rates and ozone dosages with the actual water to be treated. In this manner, an ozone concentration profile can be developed for the particular contactor, and CT values can be calculated which are closer to the true value.

It must be recognized that if ozone is employed early in the water treatment process to oxidize iron and manganese, and if the levels of iron and manganese are sufficiently high, copious amounts of brown/black precipitate will be produced. These insoluble materials will interfere with the measurement of a dissolved ozone residual, even though a significant residual may be present.

vii. Factors Affecting the Disinfecting Efficiency of Ozone

It should be appreciated that because ozone is such a powerful oxidizing agent, it is not particularly selective. In other words, if ozone is used early in the water treatment process, for example, to oxidize iron and manganese, or color, or tastes and odors, a high degree of disinfection also will be obtained. Conversely, if ozone is used after filtration for disinfection, it will also oxidize any easily oxidizable materials still present.

Ozone's ability to disinfect is affected little by changes in water temperatures or pH, and it does not react with water, except as noted earlier. Also, ozone does not react with ammonia at any significant rate, except above pH 9. However, ozone does have a short half-life in water, decomposing to oxygen at a rate dependent upon the water temperature. This means that ozone will not have a lasting residual in the distribution, and therefore normally cannot be employed as the secondary disinfectant. Although there are a number of European, Canadian, and even two U.S. water treatment plants which do use ozone as the secondary disinfectant, these are the exception rather than the rule. In those cases in which ozone is the last treatment step, a combination of five factors must occur simultaneously (Miller et al., 1978):

- o cool water temperatures,
- o clean and short distribution system,
- o short residence time (< 12 hours)
- o low levels of organics,
- o no ammonia present.

In all other cases, a secondary disinfectant which provides a stable residual is added after ozone has been utilized as the primary disinfectant. One advantage of employing ozone as the primary disinfectant is that the oxidant demand of the water is satisfied simultaneously, which allows much lower dosages of chlorine, chlorine dioxide, or monochloramine to be utilized, normally less than 0.5 mg/L, to provide a stable, detectable, residual for the distribution system.

viii. Ozonation System Design

Figure 21 illustrates the five basic components of an ozonation system which employs ambient air as the generator feed gas. The essential components include air preparation, electrical power supply, ozone generation, ozone contacting, and ozone contactor exhaust gas destruction. The amount of ozone produced by an ozone generator is affected by the physical characteristics of the equipment, the power supply to the ozone generator, the moisture content and dust content of the feed-gas, the temperature of the ozonized gas, and the oxygen content of the feed gas. Each of these basic system components will be discussed below.

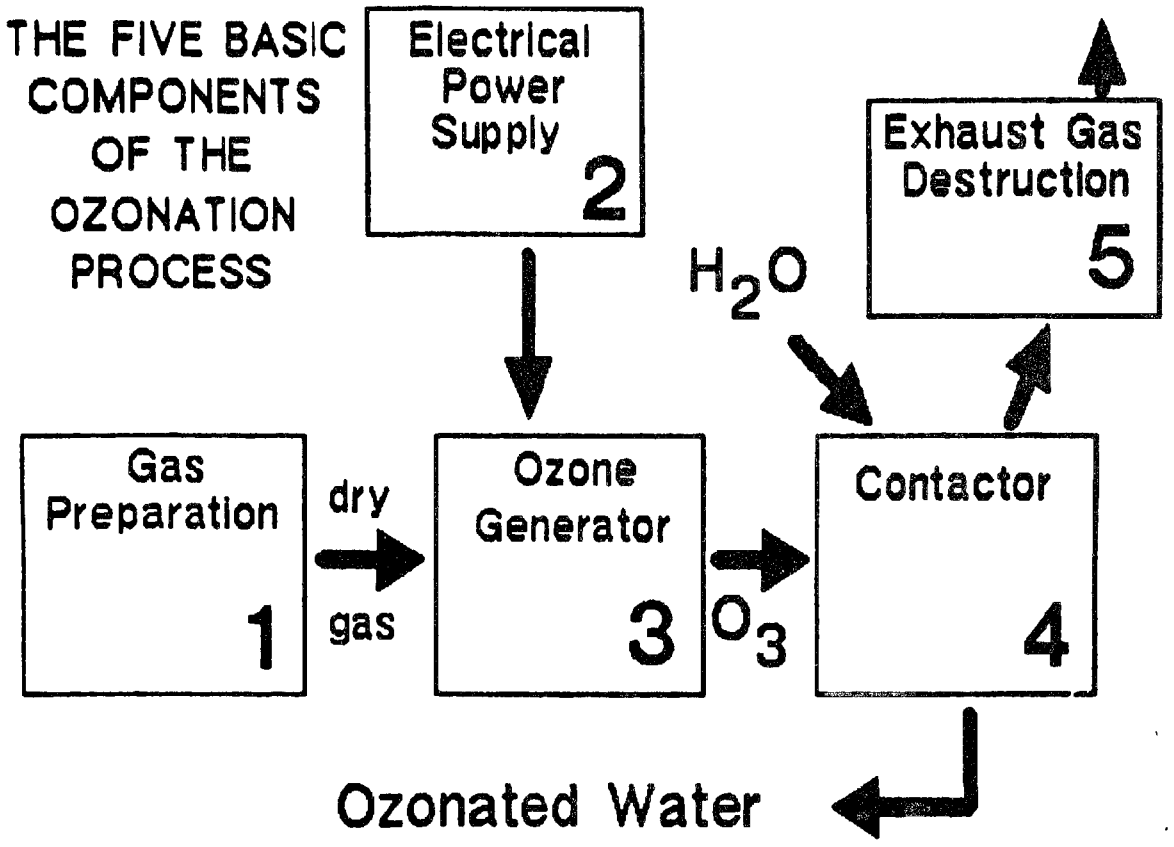

Figure 21. The five basic components of an air-fed ozonation system.

Air Preparation

Ambient air must be dried to a maximum dew point (a unit of moisture content of air) of minus 60°C. Even drier gas is preferable (lower than-60°C). This unit process must be designed conservatively, especially for warm, humid climates. Use of air having a dew point higher than -60°C will result in lower ozone production, slowly foul the ozone production (dielectric) tubes or plates, and increase corrosion problems in the ozone generator unit and downstream equipment as well.

Air feed systems typically are classified by their operating pressure. The most common is a low pressure system, which operates at pressures ranging from 69 to 103 kilopascals (kPa = 10 to 15 psig), although pressures up to 275 kPa (40 psig) have been reported when the gas pressure is reduced prior to the ozone generator. High pressure systems operate at pressures ranging from 480 to 690 kPa (70 to 100 psig), reduce the pressure prior to the ozone generator, and typically are used in small to medium sized applications. Either system may be used in conjunction with most ozone generators and with all of the contacting systems described.

The decision to use a high or low pressure air preparation system often is based on a qualitative evaluation of potential maintenance requirements, in addition to the quantitative capital cost evaluation. Some of the issues to consider are listed below:

1. High pressure air pretreatment equipment generally has higher maintenance requirements for the air compressors;

2. High pressure air pretreatment equipment generally has lower maintenance requirements for the desiccant dryers.

3. High pressure air pretreatment equipment generally has a lower capital cost. At small to medium sized installations this lower capital cost may offset the additional maintenance required for the air compressors and associated equipment, such as filters for the oil-type compressors. The design engineer should investigate the potential maintenance associated with the high and low pressure systems rather than evaluating the design on the basis of capital cost alone.

Another type of air feed-gas treatment system is the "nominal pressure" system, which typically operates at a negative or in some cases a slightly positive pressure. This type of air pretreatment system is designed to operate in conjunction with aspirating turbine, injector, and/or Venturi type contactors, all of which create the partial vacuum necessary to draw ambient air through the air pretreatment and ozonation systems. Since ozone disinfection of drinking water involves maintenance of a specific ozone contacting time to attain the required CT value, this type of contacting will require higher energy expenditures than the positive pressure contactors (and positive pressure air pretreatment systems). Therefore, nominal pressure air pretreatment systems are not considered appropriate for drinking water disinfection.

Figures 22 and 23 are schematic diagrams showing low pressure and high pressure air feed gas pretreatment systems, respectively. Figure 22 illustrates a dual component process, showing desired flexibility for the equipment provided. The precompressor filters are provided to protect the air compressors from damage due to large particles. The air compressors typically are positive displacement, oil-less units. Positive displacement compressors are used in order to obtain constant air flow at variable operating pressures. Variable pressures often are encountered due to variable pressure losses in downstream equipment and processes such as filters and ozone contact basins. Oil-less compressors are used to eliminate oil contamination of the downstream desiccant dryer medium and ozone generator dielectrics. Liquid-seal and rotary lobe compressors have been used most frequently.

The compressors may be followed by an after-cooler or a refrigerant dryer. These components are depicted by dotted lines in Figure 22, which indicate that they are optional. Typically, either one or the other option is provided. These cooling mechanisms are used to remove moisture in the air at minimal operating expense.

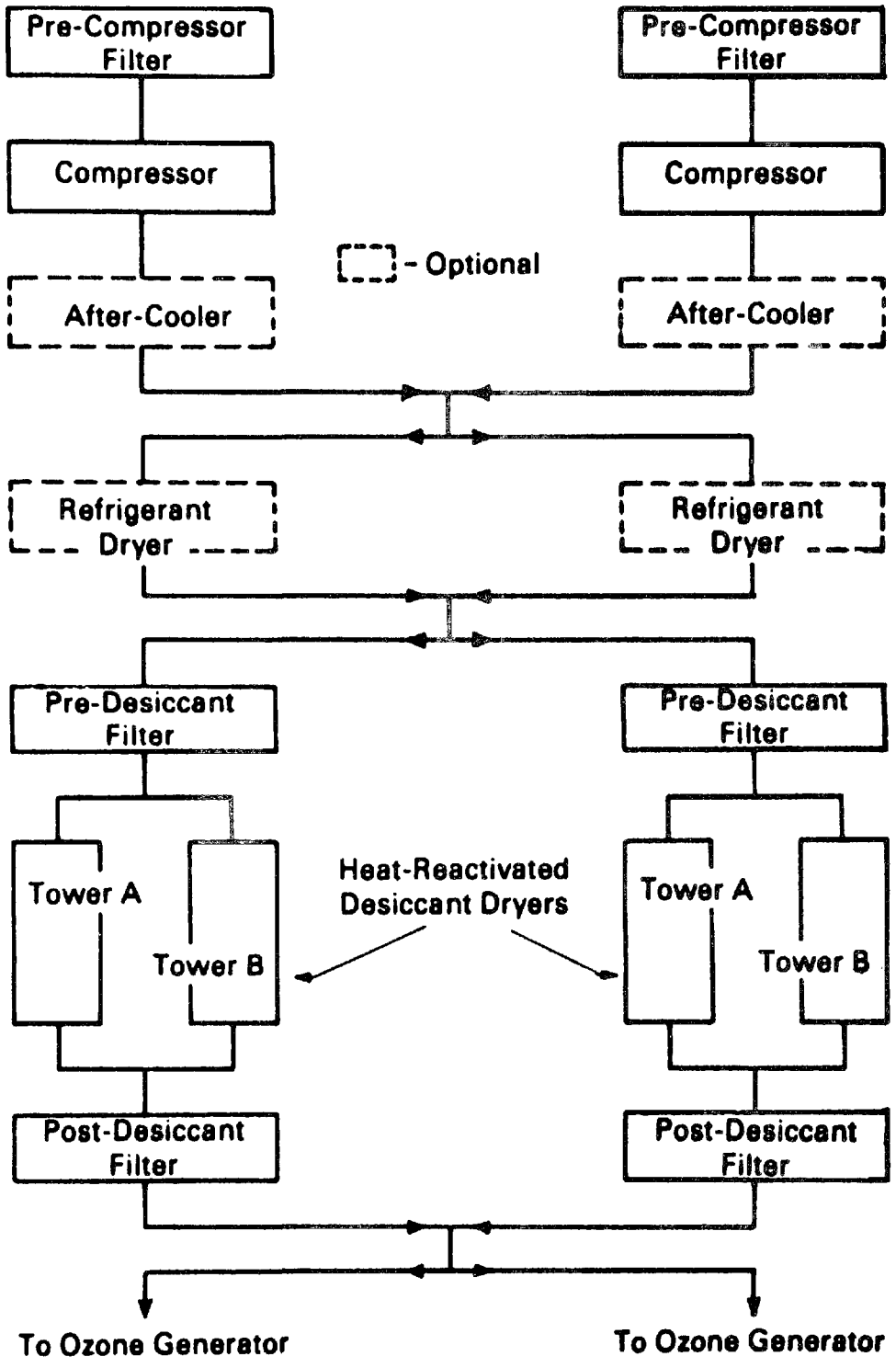

Figure 22. Example low pressure air feed-gas treatment schematic for ozone generation (U.S. EPA, 1986, p. 125).

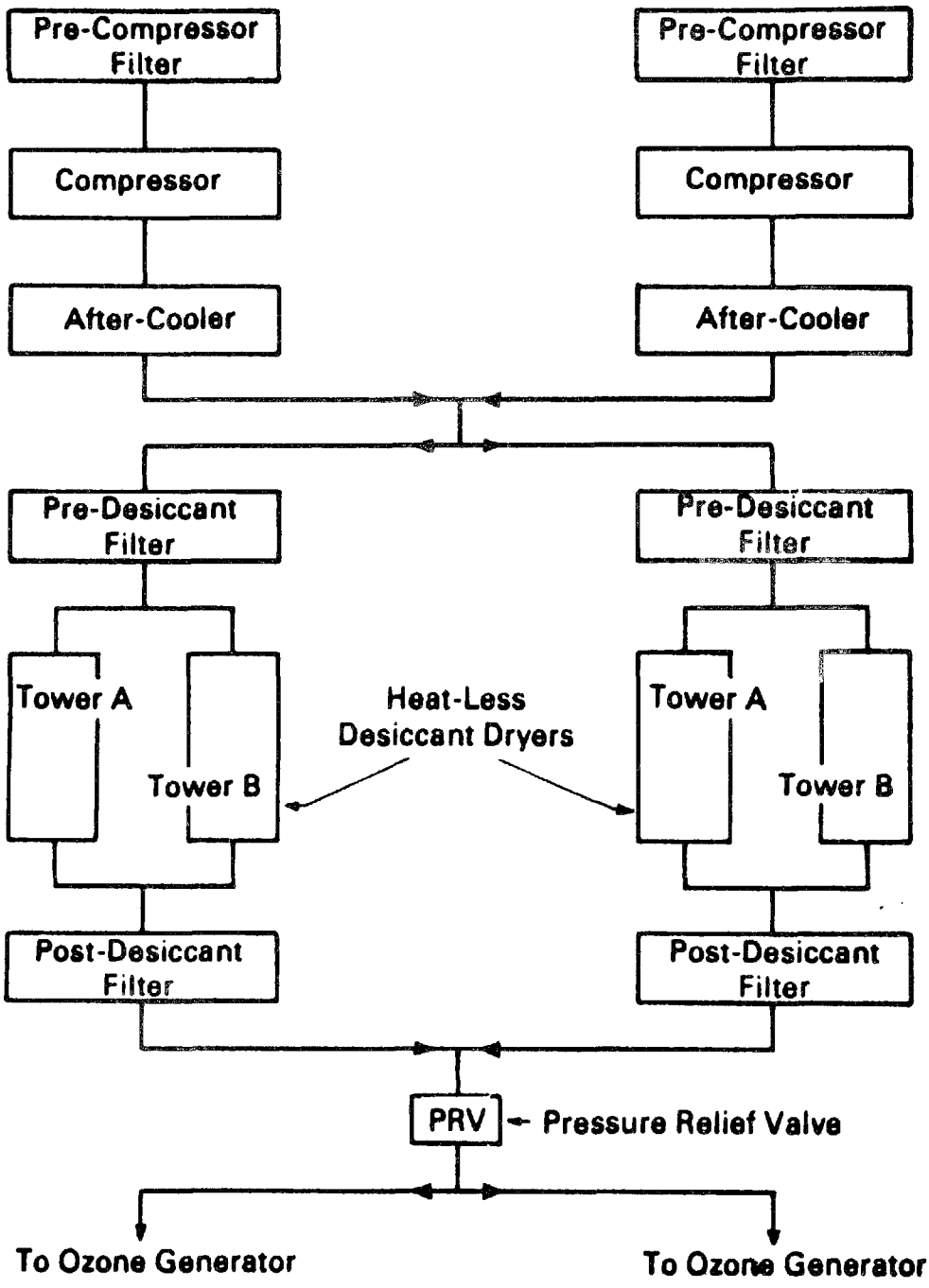

Figure 23. Example high pressure air feed-gas treatment schematic for ozone generation (U.S. EPA, 1986, p. 126).

The compressed, cooled air is directed to a predesiccant filter, which is used to remove dust and dirt particles greater than 3 to 5 microns in diameter. Particulate removal prior to the desiccant dryers reduces plugging in the desiccant medium.

Probably the most important component of the air treatment process is the desiccant dryer, which consists of two towers containing moisture-adsorbing media. One tower operates in the adsorption mode while the other tower is being regenerated. The low pressure system desiccant dryer uses heat for reactivation of the desiccant.

Post-desiccant filters are installed to remove particulates smaller than 0.3 to 0.5 micron in diameter. Two-stage filtration is preferred. The first stage filter removes particulates greater than 1 micron and the second stage removes particulates less than 0.3 to 0.4 micron in diameter.

In the high pressure air pretreatment system (Figure 8), the precompressor filters are used to remove larger particulates and protect the air compressors. These compressors typically are oil-less units; however, oil-seal compressors can be used if followed by extensive oil removal equipment.

Following the high pressure compressors, it is essential to provide after-coolers, to remove the heat of compression. The filter(s) before the desiccant dryer are used to remove particulates less than 3 to 5 microns in diameter when oil-less compressors are used. When oil-seal compressors are used, filtration to remove oil droplets less than 0.03 micron is provided.

The high pressure system desiccant dryer consists of two towers with moisture adsorbing media. One tower operates in the adsorption mode while the other is regenerating. Regeneration is accomplished without additional heat. Thus, the high pressure desiccant dryers are called heat-less units. The post-desiccant filters remove particulate matter less than 0.3 to 0.4 micron in diameter. The high pressure system also has a pressure reducing valve to regulate operating pressures in the ozone generator.

Air compressor, refrigerant dryer, and desiccant dryer design considerations are discussed in detail in U.S. EPA, 1986.

Electrical Power Supply

Supply line voltage (220/440 V), or frequency in some cases, is varied to control the amount of ozone being generated and its rate of generation. Because these two parameters are varied in many ozone generation systems, the electrical power subunit can represent a proprietary product of the ozonation system supplier. As a result, the electrical power system must be specified as an integral power supply system specifically designed for the ozone generator to be supplied. In other words, the power system should be designed for and purchased from the ozone generating system supplier.

Because the ozone generator uses high voltage (> 10,000 V) and in some cases also high frequency electrical current (up to a maximum of 2,000 Hz),

special electrical design considerations must be implemented. For example, special insulation must be provided for the electrical wire. A cool environment for the high voltage transformers should be provided, and the electrical transformers should be protected from ozone contamination due to minute ozone leaks which might occur on a periodic basis.

The electrical considerations for an ozone system should receive special attention. For example, a number of problems have been reported with dry-type potential transformers. Oil-cooled transformers apparently have performed more reliably. In view of the dependence of ozone generation on high frequency or high voltage electrical energy, the ozone generator supplier should be responsible for designing and supplying the electrical subsystems. However, the specifications should require that the frequency and voltage transformers be high quality units designed for ozone service. The ozone generator supplier should be requested to provide a record of successful electrical equipment performance.

Another item to consider in the design of an ozone generating system is the power factor. This is the ratio between the apparent power (kW) measured by a watt-hour meter and actual power (kVA) measured in terms of voltage and amperage. The relationship is shown by the equation:

$$\text{Power Factor} = \text{Apparent Power/Actual Power}$$

$$pf = kW/kVA$$

The power factor is UNITY when the voltage and current of an alternating current power supply are "in-phase" with each other, for example in a purely resistive circuit like a heating element. In a purely capacitive circuit, such as an ozone generator which has not reached the ionization potential of the dielectric, the voltage and current are 90 degrees out of phase. In this case, the power factor is ZERO. For a generator producing ozone, the voltage and amperage will be somewhere between 0 and 90 degrees out of phase; thus, the power factor will be less than 1.0. The actual power factor will vary depending upon the power supply to the ozone generator and the amount of electrical resistance developed within the electrical circuit.

The power factor may be corrected by installing inductors in the electrical circuit or by using the inductance created by the operation of motors in other areas of the treatment plant. However, caution must be exercised when using other plant equipment for power factor correction, because of the variable operating conditions of the equipment from hour to hour and from day to day. The inductance of other equipment should be used only to control the low power factor of the ozone generator when consistent equipment operation can be assured.

An operating ozone generator can decrease the power factor to 0.3 to 0.5, depending on the generator setting. Corrections normally will be cost-effective, since utilities that supply electrical power typically impose penalties for a low power factor.

Ozone Generators

The most common commercially available ozone generators can be classified as follows:

- o horizontal tube; one electrode water-cooled,
- o vertical tube; one electrode water-cooled,
- o vertical tube; both electrodes cooled,
- o plate; water- or air-cooled.

The operating conditions of these ozone generators can be subdivided as follows:

- o low frequency (50/60 Hz), high voltage (> 20,000 V),
- o medium frequency (600 Hz), medium voltage (< 20,000V),
- o high frequency (> 1,000 Hz), low voltage (< 10,000 V).

Currently, low frequency - high voltage units are most common, but recent developments in electronic circuitry are resulting in higher frequency units (and lower voltages) being used.

To determine the amount of ozone required to provide disinfection, the following steps are recommended:

1. Estimate the initial ozone demand of the water at the point of entry into the first chamber of the ozone contactor. The initial ozone demand is that quantity of ozone necessary to develop a stable residual ozone concentration at the outlet of the first contact chamber. In most ozone disinfection processes, the ozone residual attained is 0.4 to 0.5 mg/L, and the initial ozone demand is between 1 and 6 mg/L, depending upon the water quality at this point.

2. If the initial ozone demand is estimated, assume a 90% ozone transfer efficiency for the 2-chamber bubble diffuser contactor.

3. An additional amount of ozone will be required in the second chamber of the ozone contactor to maintain the residual of ozone for the appropriate period of time to attain the necessary CT value. Assume this amount of additional ozone will be 50% of that applied in the first chamber.

4. Determine the peak water flow through the plant, and from this, calculate the peak ozone requirement.

In operating ozone treatment systems, a single generator designed for peak use is never installed, in order to minimize energy costs during operation, provide backup capability, and to facilitate maintenance operations. The minimum production rate from an ozone generator is 10 to 25 percent of its

maximum production capability. On the other hand, the most cost-effective production rate of an ozone generator occurs at 60-70% of its maximum production rate.

Therefore, if the treatment plant requires, say, 100 lbs/day of ozone during normal production, and 150 lbs/day for peak operation, it is cost-wise to purchase three 60 lbs/day generators, and operate all three at about 65% of their capacity for normal production. This approach allows satisfying the occasional peak ozone demands, provides one standby generator during normal flows, and allows the down generator to be maintained on a periodic schedule.

Ozone Contactors

The different types of contactors have been discussed earlier. Selection of the specific type of contactor should be based upon the specific type of ozonation task contemplated. For disinfection, the most commonly used contactor is the two-chamber, porous plate or porous tube diffuser contactor shown in Figure 5. Housings for such contactor systems normally are constructed of concrete.

Destruction of Excess Ozone

Ozone destruction removes excess ozone in a contact basin off-gas prior to venting or prior to recycle or reuse of the exhaust gas. Safety is the major consideration. The maximum ambient air ozone concentration currently allowed by the OSHA for exposure of human beings over an 8-h working day is 0.0002 g/m^3 (0.1 ppm by volume). This concentration is significantly less that the ozone concentrations in contactor exhaust gases, normally greater than 1 g/m^3 (500 ppm by volume).

The primary methods for treating excess ozone in the exhaust gases are: thermal destruction (300-350°C for 3 sec), thermal/catalyst destruction, and catalyst destruction (metal catalysts or metal oxides). Moist granular activated carbon is used quite extensively in small scale European ozonation systems generating g/h quantities of ozone (< 2 mgd water supplies; large public swimming pools, etc.), but is not recommended (U.S. EPA, 1986, p. 137) for this purpose.

The most favored procedure currently involves passing the contactor exhaust gases through a catalytic ozone destruction unit, which contains a proprietary catalyst system based on manganese dioxide. Excess ozone is converted to oxygen, which may be discharged safely to the ambient atmosphere.

Ozone contactor exhaust gases are treated in this manner, rather than drying or recirculating through the ozone generator for economic reasons. It is more cost-effective to dry ambient air than to clean and redry the wet air exiting the ozone contactor.

Materials of Construction

Care must be taken in selecting materials of construction for those portions of the ozonation system in direct contact with either "dry" (before the contactor) or "wet" (after the contactor) ozone-containing gas. While reinforced concrete is an appropriate material for ozone contactors, the ozone-containing gas piping system should be 304-L or 316-L stainless steel for dry and wet services, respectively.

Monitoring the Ozonation System Operation

Equipment should be provided to monitor the operation of the components of the system. The minimum degree of instrumentation, all of which can be provided by the ozone equipment supplier as part of the package units, is as follows:

- Gas pressure and temperature devices at key points in the air preparation system. Simple pressure gauges and mercury thermometers will suffice.

- Continuous monitoring of the dew point measuring device to determine the moisture content of the dried air feed gas to the ozone generator. High dew point indications should be designed to sound an alarm and shut down the generator. Equipment for calibration of the dew point monitor should be provided as well.

- Means of measuring inlet/discharge temperatures of the ozone generator coolant medium (water and/or oil, or air) is required, as is a means of determining whether coolant is actually flowing through the generator. An automatic system shutdown should be provided if coolant flow is interrupted or if its discharge pressure exceeds specified limits.

- A means of measuring flow rate, temperature, pressure, and ozone concentration of the ozone-containing gas discharged from the ozone generator is required to determine the ozone production rate.

- A means of measuring the power input to the ozone generator is required.

Ozone Equipment Suppliers

Table XXIV is a listing of the major suppliers of corona discharge ozone generation equipment in the United States (Source: International Ozone Association, Pan American Committee, Norwalk, CT). Each of these suppliers provides the total ozonation system, including electrical power supply, air preparation equipment, contacting apparatus, and contactor off-gas destruction devices, as well as the appropriate monitoring and automation equipment.

TABLE XXIV. MAJOR U.S. OZONATION SYSTEMS SUPPLIERS

Name	Address
BBC Brown Boveri Inc.	1460 Livingston Ave., North Brunswick, NJ 08902
Capital Controls Co., Inc.	Box 211, 3000 Advance Lane, Colmar, PA 18915
Emery Chemicals Inc.	4900 Este Avenue, Cincinnati, OH 45232
Gould & Eberhardt Industries	P.O. Box 190, Sutton Road, Webster, MA 01570
Griffin Technics Corp.	178 Route 46, P.O. Box 330, Lodi, NJ 07644
Hankin Environmental Systems	71 Route 206 South, Somerville, NJ 08876
Infilco Degremont Inc.	P.O. Box 29599, 2828 Emerywood Parkway, Richmond, VA 23229
Mitsubishi, Electric Sales, MEDAMA, Inc.	5757 Plaza Drive, Cypress, CA 90630-0007
Ozone Research and Development Corporation	3840 North 40th Avenue, Phoenix, AZ 85019
PCI Ozone Corporation	One Fairfield Crescent, West Caldwell, NJ 07006
Trailigaz Ozone of America	1 Jenkintown Plaza, 211 West Avenue, Suite 210, Jenkintown, PA 19046
Welsbach Ozone Systems Inc., Division of Polymetrics, Inc.	101 Nicholson Lane, San Jose, CA 95134

ix. **Costs of Ozonation Systems**

Equipment Costs

These will include estimates for ozone generation equipment and ozone contacting systems, both of which are supplied by the ozone systems manufacturers. Water supply systems treating 0.5 mgd and less will require a

daily ozone generation capacity from three to 21 pounds, and will be able to dose ozone at average levels of up to 3-5 mg/L. At these production levels, ozone normally will be generated from dried air, not oxygen, in order to avoid the costs of oxygen generation, recovery and recycle equipment.

As mentioned earlier, the new 540-mgd Los Angeles drinking water plant uses oxygen as the feed gas to the ozone generators. A new German ozone generator, currently marketed in the U.S. by Capital Controls Co. (the CAPOZON system) is designed to generate ozone from pure oxygen, in small diameter dielectric tubes. Because of this new design, this system is claimed to be capable of generating unusually high concentrations of ozone (14%) in oxygen. This system may find application for drinking water treatment plants in the future.

Ozonation equipment to be purchased includes the following:

- o air preparation equipment (drying and chilling)
- o ozone generator
- o ozone contactor
- o ozone destruction unit
- o instrumentation and controls

For generation of large quantities of ozone (100 lbs/day and higher), approximately $1,200 per pound of ozone generation capacity per day will be required to procure the air preparation, ozone generation, and contacting equipment. Ozone destruction and instrumentations and controls will be in addition to this figure.

For smaller quantities of ozone, costs will be higher, but will vary significantly from site to site.
For the small production quantities of ozone required by small water treatment plants serving less than 10,000 persons per day (three to 21 pounds per day), all items except the contactor can be assembled into a single skid-mounted unit. If the contactor selected is the turbine type, it also can be included in the skid-mounted assembly unit.

Diffuser contactors for small ozonation systems generally are constructed of polyvinyl chloride (PVC) pipe standing on end, or of fiberglass reinforced plastic (FRP) tanks. A contact chamber containing diffusers should be approximately 18-ft high, providing a water depth of 16-ft and a detention time of 10-20 minutes, to attain the appropriate CT value required for 99.9% inactivation of Giardia lamblia cysts and/or 99.99% inactivation of enteric viruses. These conditions will maximize the transfer of ozone from gas phase to aqueous solution when employing diffuser contacting systems.

Tables XXV and XXVI list equipment cost estimates obtained from two ozonation systems suppliers in 1982, for various daily ozone generation rates. Ozone supplier A (Table XXV) provided estimates for ozone dosages provided estimates for ozone dosages of 3 and 5 mg/L at water flow rates of 500,000 gal/day, 350,000 gal/day, and 180,000 gal/day. This breakdown shows that equip-ment costs for air pretreatment and ozone generation capacity available from this supplier depend upon the dosage required at a particular

TABLE XXV. COSTS OF OZONATION EQUIPMENT FOR SMALL WATER SUPPLY SYSTEMS (Company A - May 1982)

Size of water supply	500,000 gpd		350,000 gpd		180,000 gpd	
Maximum dosage of ozone (mg/L) at peak flow	5	3	5	3	5	3
Daily ozone requirement (lbs)	21	14	14	7	7	5
Contact chamber diameter (14 ft high, 4 compartments, 4 diffusers, Derakane fiberglass reinforced plastic)	6 ft	6 ft	5 ft	5 ft	4 ft	4 ft
EQUIPMENT COSTS						
Air preparation + ozone generation unit	$31,500	$25,000	$25,000	$22,000	$22,000	$19,500
Contact chamber with diffusers	$11,500	11,500	10,200	10,200	9,900	9,900
Monitoring Instrumentation						
1) Ozone in generator product 2) Ozone in ambient plant air 3) Ozone dissolved in water 4) Dew point monitor in air preparation unit	$15,000	15,000	15,000	15,000	15,000	15,000
Ozone Destruction Unit	$6,700 (10 cfm)	5,000 (7 cfm)	5,000 (7 cfm)	4,200 (3 cfm)	4,200 (3 cfm)	4,200 (3 cfm)
TOTAL EQUIPMENT COSTS	$64,700	$56,500	$55,200	$51,400	$51,100	$48,600
Power requirement kWh	13.3	10.1	10.1	5.0	5.0	3.65

TABLE XXVI. COSTS OF OZONATION EQUIPMENT FOR SMALL WATER SUPPLY SYSTEMS (Company B - May 1982)

Flow Rate	0.1 mgd		0.2 mgd		0.3 mgd		0.4 mgd		0.5 mgd	
Maximum ozone dosage, (mg/L), at peak flow	3		3		3		3		3	
Daily ozone requirement (lbs/day)	3		6		7		12		14	
Equipment Costs	**LP****	**HP*****	**LP**	**HP**	**LP**	**HP**	**LP**	**HP**	**LP**	**HP**
Air preparation + ozone generator*	-	$17,500	$33,200	$30,200	$38,500	$35,500	$43,000	$40,000	$49,800	$46,800
Power requirements (kWh/lb of O_3 generated)	10.5	20	10.5	13.5	10.5	13.5	10.5	13.5	10.5	13.5
Ozone contactor with diffusers	$8,500		$12,000		$16,000		$21,000		$29,000	
Ozone Monitors										
- O_3 generation****	or 2,000		or 2,000		or 2,000		or 2,000		or 2,000	
- O_3 room or contact chamber exhaust	2,200		2,200		2,200		2,200		2,200	
- dew point	3,500		3,500		3,500		3,500		3,500	
TOTAL EQUIPMENT COSTS -	$33,700-35,700	$54,900-52,900	$51,900-49,900	$64,200-62,200	$61,200-59,200	$73,700-71,700	$70,700-68,700	$88,500-86,500	$85,500-83,500	

* includes air preparation, ozone generation, ozone destruction and system controls.

** air preparation unit includes air filters or separators, compressor delivering air at 8-12 psig to a refrigerative cooler and a dual tower desiccant dryer.

*** same as LP air preparation system, except compressor delivers air at 80-120 psig. HP system takes less space requires less maintenance, but requires more energy.

**** $4,000 instrument is an automatic, continuous reading in-line monitor.
$2,000 instrument is not automatic and utilizes wet chemistry.

water flow rate. In addition, the size (and cost) of the ozone destruction units required also varies, as does the power requirement to operate the total ozonation system.

Ozone Supplier A can provide four monitors with his system. All are optional, but all are recommended for optimal performance and minimal labor and downtime. These will monitor:

- o the dew point in the air preparation unit,
- o ozone output of the generator,
- o ozone in the plant ambient air (in case of leaks),
- o dissolved ozone residual in the water.

The cost of these four monitors is constant at $15,000, regardless of system size in the range shown in Table XXVI (5 to 21 pounds per day).

Table XXVI shows similar data for Ozone Supplier B. In this case, equipment costs are presented for water flows of 100,000, 200,000, 300,000, 400,000, and 500,000 gal/day. Average ozone dosages are taken as 3 mg/L, and the daily ozone output required varies from 3 lbs/day for treating 100,000 gal/day to 15 lbs/day for treating 500,000 gal/day.

Ozone Supplier B offers two types of air preparation equipment, however, and estimates are presented for each. One type operates at high pressures (80-120 psig), and the other at low pressures (8-12 psig). The high pressure air treatment units are lower in capital cost, but require more energy for their operation.

Ozone Supplier B does not normally provide a residual dissolved ozone monitor, but offers two types of monitor for ozone output from the generator. The automatic, in-line continuous reading monitor costs $4,000; the non-automatic monitor requires wet chemistry determinations to develop data at some period of time after the sample has been taken, and costs $2,000.

Therefore, cost data presented in Table XXVI vary by the differences between costs for high and low pressure air preparation equipment, and by the costs of the two ozone generator monitors.
In 1987, Ozone Supplier A estimated that the cost for a 5-lb/day ozone generator, sufficient to treat 180,000 gal/day at an applied ozone dosage of 3 mg/L, to be $20,500. This confirms that costs for ozone generation equipment in 1983 are still current, for the smaller water treatment plants.

Installation Costs

Costs for installation of the ozonation equipment include labor and material costs for piping water to and from the ozone generators (if they are water cooled), for piping ozone-containing air to the contactor chamber, for piping water to and from the contactor, and for piping contactor off-gases to and from the ozone destruction unit. Electrical wiring costs also must be considered in these costs. Ozonation equipment suppliers contacted advise

that for production of up to about 30 lbs/day of ozone, installation costs will be roughly the same, and will average 15% to 25% of the equipment costs of the largest units estimated in Tables XXV and XXVI. The actual figures for the two equipment suppliers then become:

Supplier	Cost of Equipment (500,000 gpd plant)	Installation Cost (15% to 25%)
A	$64,700	$ 9,705 - $16,175
B	$85,000	$12,750 - $21,250

Housing Costs

The power supply, air preparation equipment, ozone generation equipment, and turbine contacting units can be installed rela-tively easily, in areas on the order of 10 x 17 feet. However, diffuser contacting units are tall (18 feet) and bulky, and normally are installed outside existing buildings (above ground) or underground inside buildings being constructed. Alternatively, a 170 ft^2 Butler building can house the ozonation system, except for above-ground diffuser unit. Such a building costs about $6,000.

Construction Costs for Ozone Contactors

Construction costs for ozone contactors are based upon concrete contactors which use serpentine flow in an upflow/downflow configuration. Ozone dissolution equipment is located at the bottom of the downflow pass, thus providing countercurrent flow. The conctruction costs include the ozone dissolution equipment and manways which can be used for access to the interior of the contactor. Figure 24 shows the construction costs for ozone contactors having volumes between 2,000 and 18,000 gal (Gumerman et al., 1986).

Construction Costs for Ozone Generation and Feed Systems

Construction costs for ozone generation and feed systems using air as the feed gas include air preparation equipment, the ozone generator, ozone destruction equipment for contactor off-gases, and a building to house the equipment. For oxygen feed installations, the construction costs include the ozone generator, ozone off-gas destruction equipment, and the building. Ozone generators and the contactors are housed in a sealed room, which contains an ozone leak detector. In the event of an ozone leak, this detector will activate an alarm and the building ventilation system, and shut down the ozone generator.

Piping is included for the ozone generator cooling water, ozone, and water to and from the ozone contactor. Off-gases from the ozone contactor are destroyed using a combination thermal/catalytic destruct device.

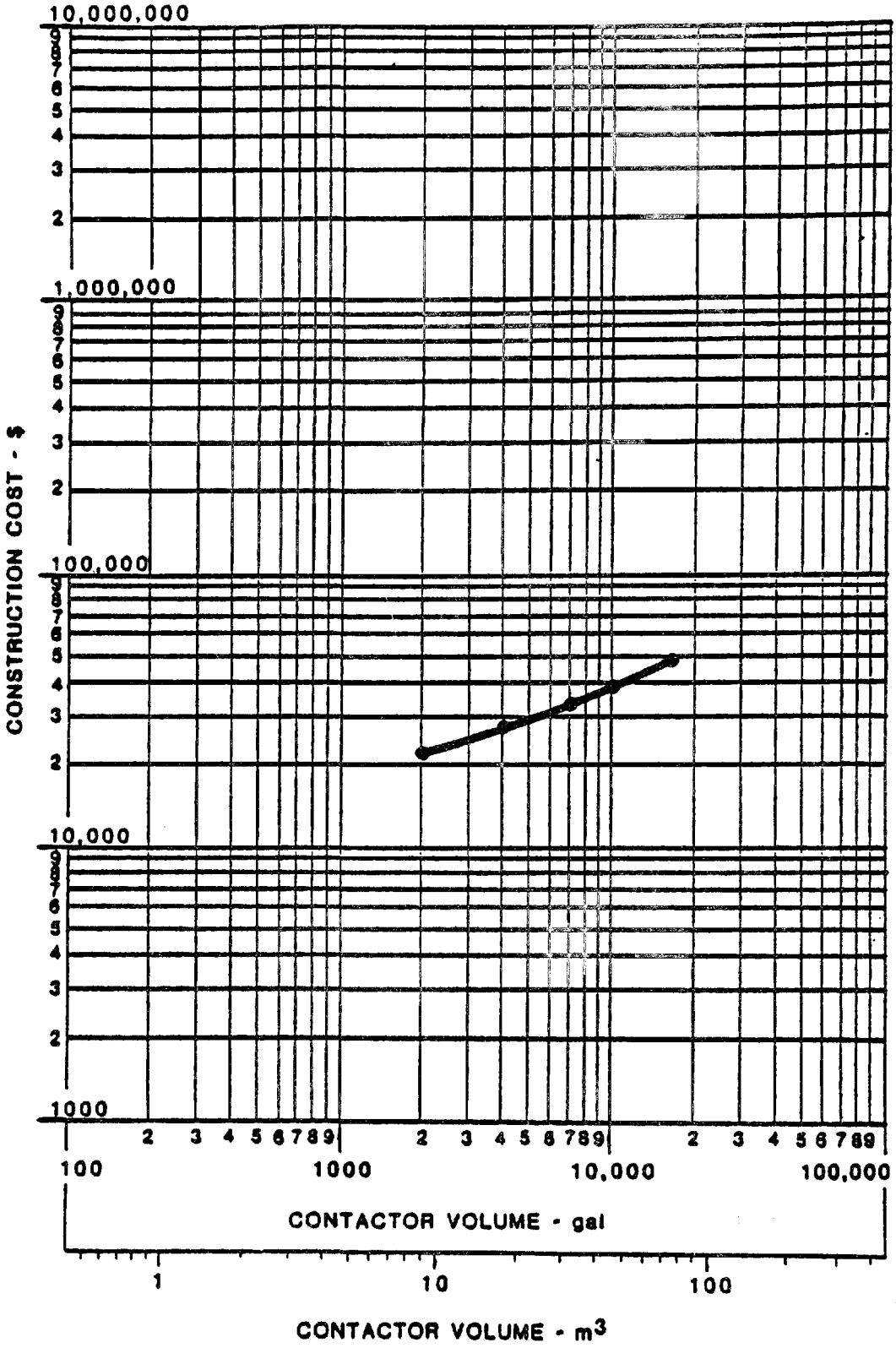

Figure 24. Construction cost for ozone contactors (Gumerman et al., 1986).

The building ventilation system consists of an intake louver and motorized damper on one side of the building, and a fan, ductwork, and motorized damper on the opposite side of the room. This system is designed to change the room air once every two minutes, when activated. The ventilation system can be activated by the ozone detector, a switch activated by opening the building door, or a switch located on the building exterior. A shutdown switch for the ozone generator is also located on the building exterior.

Construction costs are presented in Figure 25 for ozone generation and feed systems (Gumerman et al., 1986).

Operation and Maintenance Costs

Operating costs for ozonation systems vary, and depend upon a number of factors:

- o method of air preparation,
- o method of cooling the generator (water or air),
- o if water-cooled, the amount of refrigeration required for cooling water,
- o method of contacting,
- o dosage of ozone required,
- o pumping of generator coolant,
- o method of contactor off-gas destruction.

Air Preparation: High pressure versus low pressure, versus sub-atmospheric pressure desiccant system with or without addition of air chiller.

Ozone Generator Cooling: Air versus water. If water, the amount of cooling required. In northern climates, water produced at the plant generally is cold enough to serve as the generator coolant the year round. In southern climates, generator cooling water must be refrigerated most, if not all, of the year.

Method of Contacting: Diffuser contactors require no added energy. Ozone/air mixtures normally are generated under a sufficient pressure to overcome the head of 16 feet of water. On the other hand, turbine diffusers require energy for their operation, but take up much less space than diffuser contactors. For disinfection with ozone, however, the appropriate reaction time must be provided after initial contacting has been achieved to attain the appropriate CT value to assure inactivation of Giardia lamblia cysts and/or enteric viruses.

Contactor Off-Gas Destruction: Thermal versus catalytic destruction. Operating costs of these techniques vary.

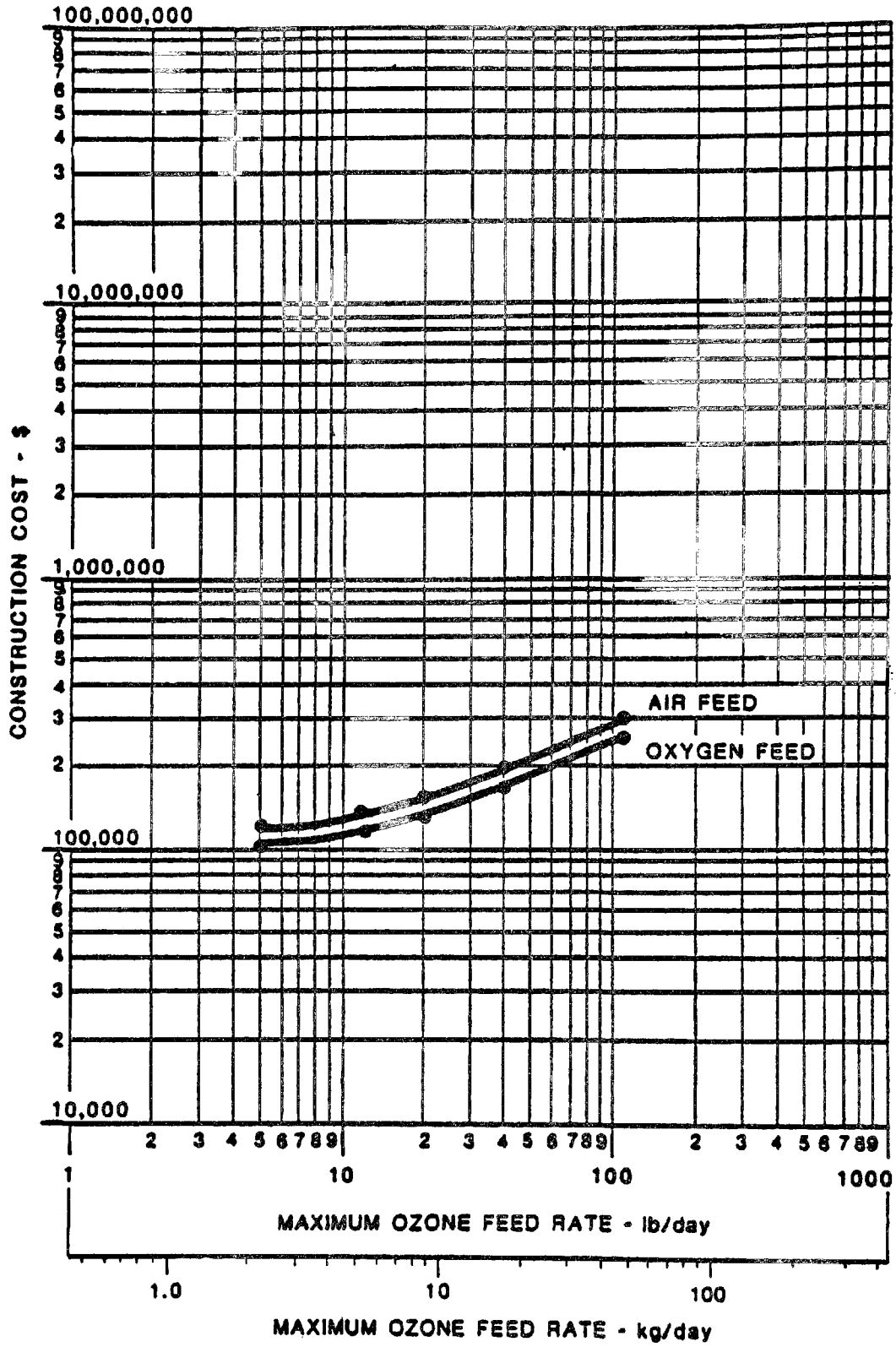

Figure 25. Construction cost for ozone generation and feed systems (Gumerman et al., 1986).

Maintenance material requirements are for periodic equipment repair and replacement of parts. Air preparation systems contain air prefilters which must be replaced frequently. Tube-type ozone generators normally are shut down once per year for cleaning of the tubes and other general maintenance. This can require several man-days of time, depending upon the number of ozone generators in the system. Spare parts normally consist of replacement tubes, which can be broken during cleaning, or which can deteriorate after years of operation at high voltages, or more rapidly if the air is improperly treated.

Labor requirements are for periodic cleaning of the ozone generation apparatus, annual maintenance of the contacting basins, and day-to-day operation of the generating equipment (average 0.5 h/day).

Operating and maintenance costs for equipment of Ozone Suppliers A and B are summarized in Table XXVII. Also included are building heating costs (which are taken to be the same up to 0.5 mgd) and costs for maintenance materials and O&M labor. There are no chemicals costs related to ozone generation, except for periodic changing of desiccant in air preparation systems (normally after 10 years of use).

Electrical energy is a major component of operating costs, representing 26% to 43% of total O&M costs at small plants (0.1 mgd) increasing to 59% to 65% at the larger plants (0.5 mgd).

Building energy costs (which are approximately the same for all small size plants up to 0.5 mgd) include energy costs for heating, lighting, and ventilation. Labor costs (which are independent of the plant sizes listed--0.1 to 0.5 mgd) account for 54% to 70% of total O&M costs at the small plants, but only 30% to 36% at the 0.5 mgd plant.

Figure 26 shows operation and maintenance requirements for ozone generation, feed, and contacting systems -- building energy, process energy, and maintenance material for systems feeding 5 to 250 lbs/day of ozone. Figure 27 shows O&M requirements for labor and total O&M cost. Both figures are taken from Gumerman et al. (1986).

Summary Statement Regarding Costs for Ozonation Systems

Because of the many differences in methods of air pretreatment, ozone contacting, contactor off-gas destruction, monitoring, and other operational parameters, equipment costs given above should not be considered as more than general guidelines. Vendor quotes should be obtained at the time ozone is being considered by the small water supply system.

It should be noted that vendor quotes obtained for estimating purposes are likely to be somewhat higher than firm bids made to specifications. This is because the market for ozonation systems currently is quite competitive, and suppliers usually bid their best prices when responding to clear specifications.

TABLE XXVII. OPERATING AND MAINTENANCE COSTS FOR SMALL OZONE SYSTEMS APPLYING 3 mg/L DOSAGE

Water Flow Rate (mgd)	Electrical Energy (kWh/yr) Building*	Process	Total	x $0.07/kWh =	Maintenance Material	Labor (hrs/yr)	x $10/hr =	Total Cost ($/yr)
Supplier A								
0.18	6,570	6,661	13,231	$ 926	$120	250	$2,500	$ 3,546
0.35	6,570	12,775	19,345	$1,354	200	250	2,500	4,054
0.50	6,570	51,611	58,181	$4,073	300	250	2,500	6,873
Supplier B (High Pressure Air Preparation)								
0.10	6,570	21,900	28,470	$1,993	$120	250	2,500	$ 4,613
0.20	6,570	29,565	36,135	$2,529	120	250	2,500	5,149
0.30	6,570	34,493	41,063	$2,874	200	250	2,500	5,574
0.40	6,570	59,130	65,700	$4,599	250	250	2,500	7,349
0.50	6,570	68,985	75,555	$5,289	300	250	2,500	8,089

* Estimated from data of Hansen et al. (1979)

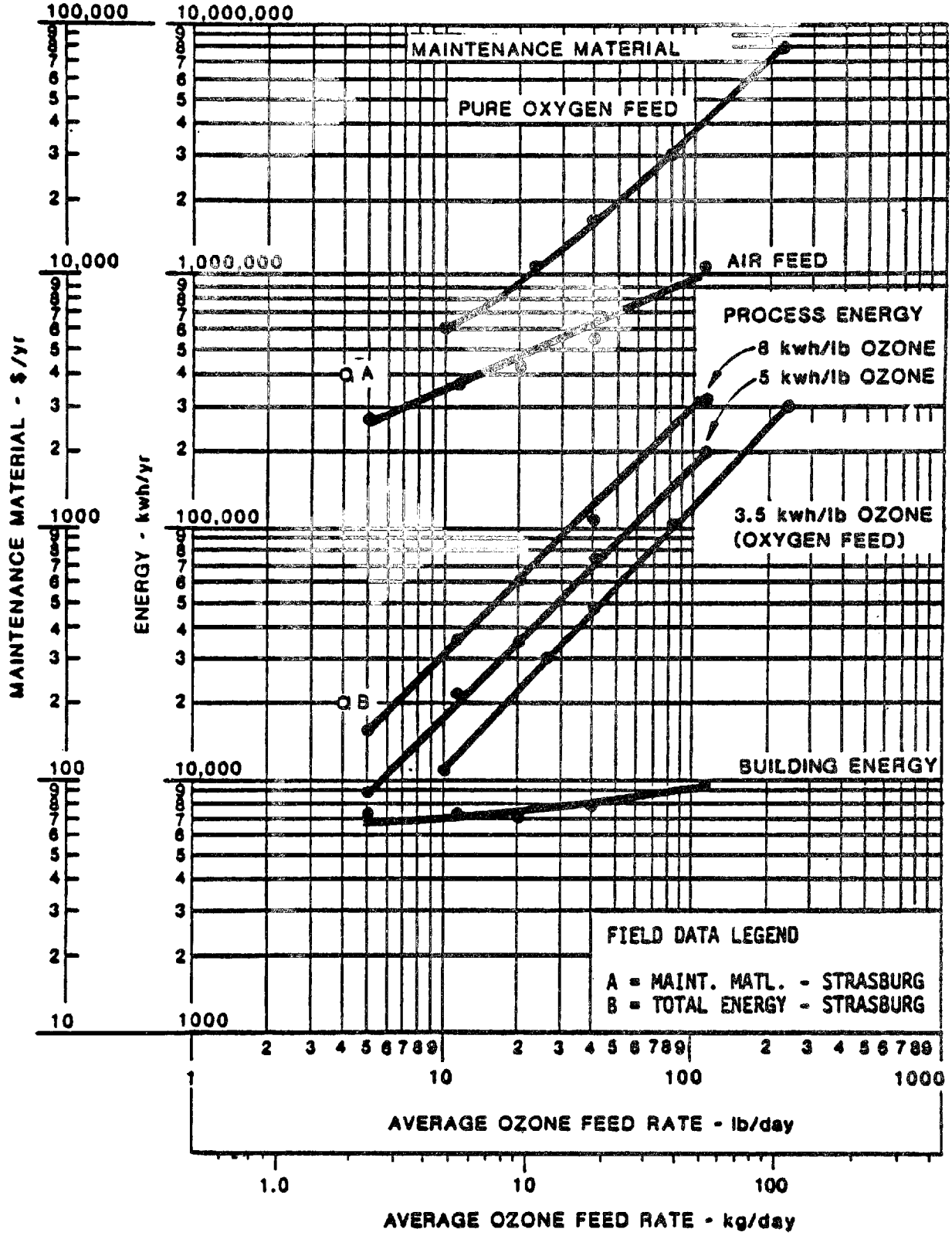

Figure 26. Operation and maintenance requirements for ozone generation, feed, and contacting systems -- building energy, process energy, and maintenance material (Gumerman et al., 1986).

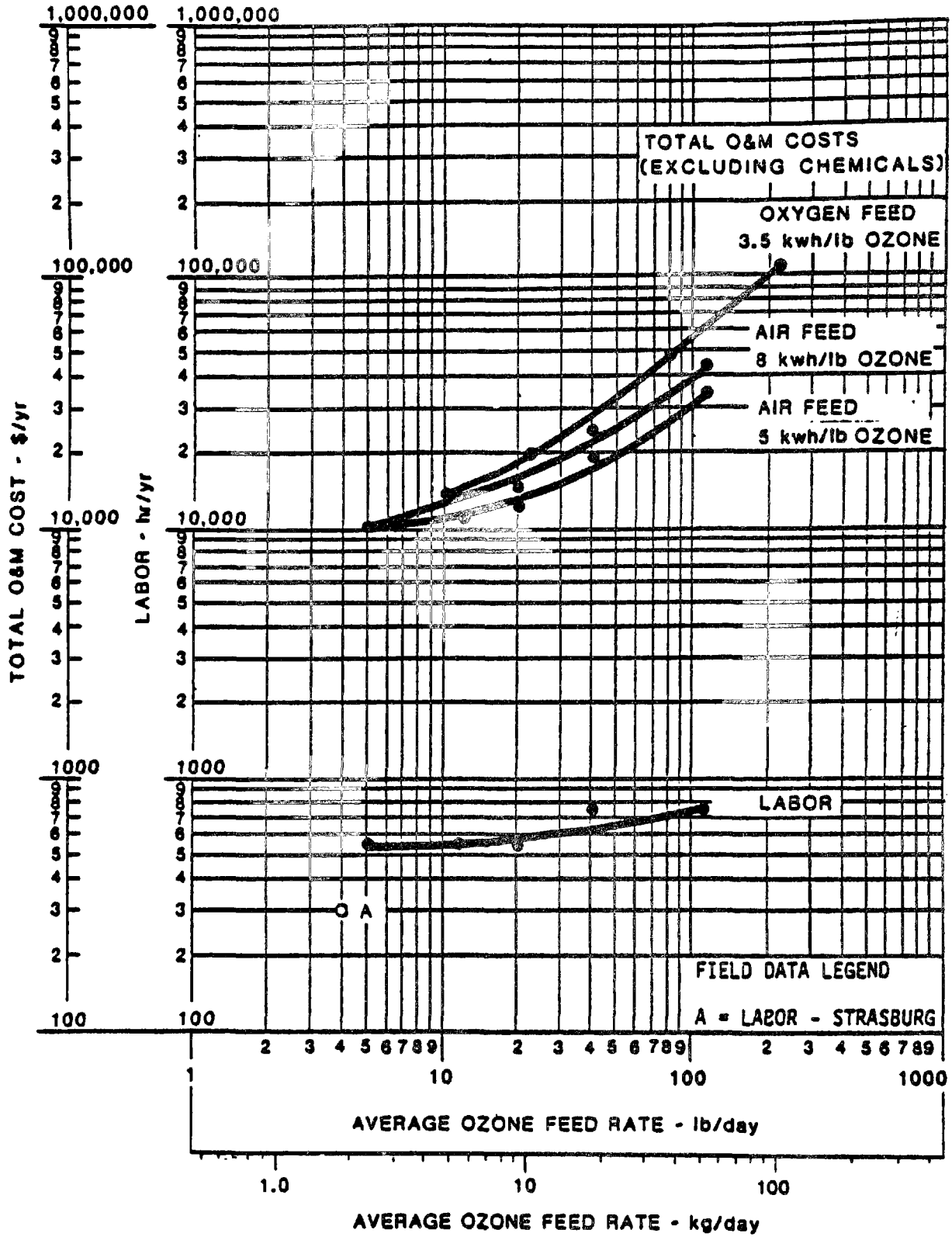

Figure 27. Operation and maintenance requirements for ozone generation, feed, and contacting system -- labor and total O&M cost (Gumerman et al., 1986).

c. Ultraviolet Radiation

Much of this discussion is taken from U.S. EPA, 1983, and 1986.

The effectiveness of UV radiation as a bactericide and virucide has been well established. It is a physical disinfecting agent compared to the chemical disinfectants, chlorine, chlorine dioxide, ozone, and monochloramine. Radiation at a wavelength of 254 nm penetrates the cell wall and is absorbed by the cellular nucleic acids. This can prevent replication and cause death of the cell. Since UV radiation is not a chemical agent, no toxic residual can be produced. Although certain chemical compounds can be altered by the radiation, the energy levels used for disinfection are far too low for this to be a significant cause for concern.

Major advantages of UV radiation are its simplicity, lack of impact on the environment and aquatic life, and minimal space requirements. Required contact times are very short, on the order of seconds rather than minutes. The equipment is simple to operate and maintain, but fouling of the quartz sleeves or Teflon tubes must be dealt with on a regular basis. Fouling normally is handled by mechanical, sonic, or chemical cleaning. High concentrations of suspended solids, color, turbidity, and soluble organic matter in the water can react with or absorb the UV radiation, reducing the disinfection performance.

i. General Description of the UV Process

Disinfection by UV radiation relies on the transference of electromagnetic energy from a source (lamp) to organism cellular material (specifically the cell's genetic material). The lethal effects of this energy result primarily from the cell's inability to replicate. The effectiveness of this radiation is a direct function of the quantity of energy, or dose, absorbed by the organism. This dose is described by the product of the rate at which energy is delivered, or intensity, and the time to which the organism is exposed to this intensity.

The primary artificial source of UV energy, at present, is the low pressure mercury arc lamp. It is almost universally accepted as the most efficient and effective source for disinfection systems application. The primary reason for its acceptance is that approximately 85% of its energy output is nearly monochromatic at the wavelength of 253.7 nm, which is within the optimum wavelength range of 250 to 270 nm for germicidal effects. The lamps are long [standard lengths are typically 0.75 and 1.5 m (2.5 and 4.9 ft) arc lengths] thin tubes [typically 1.5 to 2 cm (0.6 to 0.8 in) in diameter]. The radiation is generated by striking an electric arc through mercury vapor; discharge of the energy generated by excitation of the mercury results in the emission of the UV radiation.

The UV demand of a water is quantified by a spectrophotometric measurement at the key wavelength of 253.7 nm; this expresses the absorption (or transmittance) of energy per unit depth. The output is

absorbance units/cm, or a.u./cm. The percent transmittance can be determined from this unit by the expression:

$$\% \text{ Transmittance} = 100 \times 10^{-(\text{a.u./cm})}$$

The term most often used for design purposes is the UV absorbance coefficient, α, expressed in base e:

$$\text{UV absorbance coefficient, } \alpha = 2.3 \text{ (a.u./cm)}$$

The unit for α is cm^{-1}.

A second major concern is the provision of adequate exposure time to the microorganisms in order to meet the dose requirement at a given intensity. The key is to have plug flow through the system, such that each flow element resides in the reactor for the same amount of time. Perfect plug flow is not possible to achieve, of course. Some dispersion will exist, such that there will be a distribution of exposure times about the ideal, theoretical exposure time. A design objective is to minimize this distribution.

The basic premise to understand is that the UV radiation must be absorbed before it can have a disinfecting effect. Photochemical damage occurs to the deoxyribonucleic acid (DNA) macromolecules which interferes with the ability of the cells to replicate. Cell death following UV radiation is almost entirely attributable to the photochemical damage of these compounds.

On the other hand, if the amount of radiation received by the organism is not a lethal dose, but only damaging, photoenzymatic repair can occur, and the effects of the UV radiation can be reversed. The phenomenon has been termed "photoreactivation". This repair mechanism is unique to UV radiation, but is not universal, and there is no clearly defined delineation of characteristics which suggest which species would have the ability to repair and which would not.

The enzymatic mechanism generally involved in photoreactivation requires subsequent (or concurrent) exposure to light at wavelengths between 300 and 500 nm. Such light is available in sunlight and in most incandescent and fluorescent light sources.

Therefore, to assure that disinfection occurs with no chance for photoreactivation, attention must be paid to designing the UV disinfecting system to provide sufficient UV dose for an appropriate period of time. As a general rule of thumb (U.S. EPA, 1986, p. 215), if a 3-log reduction of microorganisms is required to meet the disinfection criteria, the system should be designed to provide a 4-log reduction, to account for the effect of photoreactivation.

Table XXVII lists some of the major suppliers of UV disinfection equipment for water treatment systems.

TABLE XXVII. MAJOR SUPPLIERS OF UV DISINFECTION EQUIPMENT

Name	Address
Aquafine Corp.	25230 W. Ave Stanford, Valencia, CA 91355
Aquionics Inc.	21 Kenton Lands Road, Box 18395, Erlanger, KY 41018
Atlantic Ultraviolet	250 Fehr Way, Bay Shore, NY 11706
Ultra Dynamics Corp.	1631 Tenth St., Santa Monica, CA 90404
Ultraviolet Purifications	299 Adams St., Bedford Hills, NY 10507
Ultraviolet Technology Inc.	8930 Osage Ave., Sacramento, CA 95828

ii. UV Disinfection System Design

In all, the design of a UV system must accommodate a few simple considerations:

- o satisfy the UV demand of the water,
- o maximize the use of the UV energy being delivered by the lamps, and
- o provide the conditions which encourage plug flow.

UV lamps can be suspended outside the liquid to be treated or submerged in the liquid. In either design, the intent is to get the energy into the liquid as efficiently as possible. Typically, if the lamp is to be submerged in the liquid, it is inserted into a quartz sleeve to minimize the cooling effects of the water. Lamps can be placed in the liquid with the lamp perpendicular to the direction of water flow. Other configurations may have the lamp parallel to the flow, or the lamp may be suspended above the flowing liquid. As the lamp emits radiation, the intensity will attenuate as the distance from the lamp increases; this is simply due to the dissipation or dilution of the energy as the volume that it occupies increases. A second attenuation mechanism involves the actual absorption of the energy by chemical constituents contained in the water. This, analogous to the chlorine or ozone demands, is the "UV demand" of the water.

The key points to be addressed when evaluating or specifying the design of a UV reactor are as follows:

1. Residence Time Distribution (RTD). This should be constructed at a number of flow conditions for an existing system. It should also be required when specifying commercial systems. The RTD provides key information on the actual or anticipated hydraulic behavior of a reactor.

2. Plug Flow. As a guideline, an aspect ratio greater than 15 should be incorporated into the reactor design. Maintenance of plug flow within a reactor will be influenced by the approach and exit conditions. The design should have minimal disturbances at the inlet and exit planes of the lamp battery. Directional changes in the flowpath would best be made outside of the lamp battery.

3. Dispersion Number: A key goal is to minimize the dispersion number, **d**. A design goal should be to have **d** between 0.02 and 0.05. This would be representative of a plug flow reactor with low to moderate dispersion. This can be accomplished by increasing the product of ux (u = velocity of water as it travels through the reactor, in cm/sec; x = the average distance traveled by an element of water while under direct exposure to UV radiation, in cm), even in a system with a relatively high dispersion coefficient.

The designer should be aware, however, that extended lengths and higher velocities will cause higher head losses. In certain situations, some adjustment of the dispersion number may be necessary in order to meet specific head loss requirements.

4. Turbulence: Radial turbulence is necessary due to the non-uniform intensity field. The reactor design should induce an estimated Reynold's Number greater than 6,000 at minimum flow. If possible, it would be beneficial to confirm the laminar/turbulent flow transition velocity by direct head loss measurements on the lamp battery.

5. Head Loss: Direct measurements should be required for full-scale modules or scaleable pilot units as part of commercial equipment specifications. These should be determined over a wide velocity range and should exclude entrance and exit losses.

6. Effective Volume: Maximal use of the reactor lamp battery is essential to keep the process cost-effective. This will be related directly to the reactor's inlet and outlet design. The goal must be to have equivalent velocities at all points upon entering and upon exiting the lamp batteries. Stilling walls (perforated baffles), and weirs should be incorporated into reactor designs to assure this. Guidelines for specifying commercial

equipment should require the ratio θ/T to be greater than 0.9 and/or the ratio of t_p/T to be greater than 0.9.

iii. Estimating the Average Intensity in a UV Reactor

The second element of UV dose, after time, is the intensity of energy during the exposure time. Intensity is the rate (or flux) of delivery of photons to the target. In UV process design models, the rate of bacterial inactivation is described as a function of the intensity. By this fact, it becomes important to be able to quantify the intensity in a given system. The intensity in a reactor is a function of the UV source (output), the physical arrangement of the source relative to the water (the arrangement of the lamps and their placement in or out of the liquid), and the energy sinks present which will attenuate the source output before it can be utilized for disinfection processes.

Lamps used in UV disinfection systems generally have lengths of approximately 0.9 and 1.6 m. The arc length defines the active, light-emitting portion of the lamp [0.75 m and 1.5 m (2.5 and 4.9 ft., resp.), respectively]. The diameter of the lamp is small, typically 1.5 and 1.9 cm. The lamp envelope is made of fused quartz or other highly transparent (to the 253.7 nm wavelength) glass material, such as Vycor.

In the quartz systems, the individual lamps are sheathed in quartz sleeves only slightly larger in diameter (2.3 cm) than the lamp, and the entire lamp/quartz bundle is submerged in the flowing liquid. In systems where the water does not contact the quartz or lamp surface, separate conduits carry the waters. The conduits are translucent to the UV light, with the lamps placed near the outside conduit wall.

iv. Water Quality Considerations in the Design of a UV Disinfection System

Without question, a major element in the effective design of a UV disinfection system is a clear and concise understanding of the characteristics of the water to be treated. These are directly related to the degree of pretreatment the material will receive before the disinfection step and will affect the sizing and performance of the disinfection system. Necessary pretreatment ranges from very minimal, as in the case of a groundwater which requires no treatment other than disinfection, to full conventional treatment of a polluted surface water.

The four water quality parameters which most affect the design or performance of a UV disinfection system are the flow rate, initial microorganism density, suspended solids (or turbidity), and the UV absorbance of the water at the point of application of UV radiation.

1. Flow Rate: The flow rate is set by design of the main plant and projections of the hydraulic load to the plant. In evaluating the design

requirements for the disinfection process, some consideration should be given to the equalization effects of the treatment processes before disinfection. This can have an effect on the sizing of the UV system.

Flow estimates should be for the design year of the plant. There should be some knowledge of the progressive increase in the flows through the design life of the plant in order to determine if the system can be phased in by the addition of modules as the demand increases. Some consideration also should be given to the hydraulic load to the unit.

For disinfection, average flows are not critical to the design sizing; rather they are important to estimating average utilization of the system for operation and maintenance needs. Peak flows should be used for sizing, particularly reflecting diurnal variations.

2. Initial Microorganism Density: The performance of a UV disinfection unit is related directly to the initial density of the indicator organisms. This is not a parameter which is generally monitored at a treatment plant, particularly one already employing chlorine for disinfection. In the case of disinfection by UV, however, it is critical. Performance is given by the log of the survival ratio, N/N_0, or by the number of "logs" the density is reduced.

3. Suspended Solids (Turbidity): From the development of the UV disinfection model, it is clear that the occlusion of bacteria in the particulates will have a significant effect on the design of a UV system. It is recommended (U.S. EPA, 1986) that the turbidity measurement be used as the primary indicator to quantify these particulates.

4. UV Absorbance: The one parameter which is solely in the venue of UV disinfection is the "UV demand" of the water. Some organic and inorganic compounds in the water may absorb energy at the 253.7 nm wavelength. This absorbance will affect the intensity of the radiation within the reactor; in specific design situations, the level of absorbance will affect the sizing of the system and possibly the configuration (spacing) of the lamps. The final product of these calculations is the average nominal intensity as a function of the UV absorbance coefficient.

v. System Design and O&M Considerations for the UV Process

The design basis and the process elements which are key to the design of a UV system are:

- the hydraulic behavior of the unit,
- calculation of the intensity in the reactor, and

o generation of the appropriate water characterization data.

In this section are presented other peripheral topics which the designer (and operator) must consider. These factors will affect the operation and maintenance of the system, and the overall economics. Specifically, these factors include the elements which affect the reactor intensity (lamp output, lamp aging, and attenuation of intensity due to fouling of reactor surfaces), and methods for monitoring for lamp aging and unit fouling.

Factors Affecting UV Intensity in a Reactor

UV Lamp Output: Output at any given time will be influenced by lamp temperature and by the voltage potential applied across the lamp. Additionally, output at the resonant frequency will always degrade with time of operation due to any number of "aging" factors. In the submerged systems, it is not practical under most design conditions to control the lamp temperature. In the non-contact systems, such as the tubular arrays, it is possible to maintain the lamps at their optimum wall temperature by controlling the temperature of the ambient air surrounding the lamps. This is being practiced currently in commercial applications. Heat given off by the lamp ballasts is circulated into the lamp reactor in cases where heat is required; otherwise fans vent the reactor with cooler outside air. These operations are controlled thermostatically.

Voltage: Radiance is a function of the arc current. This can be exploited by adjusting the voltage, in order to vary the output of the lamp. Decreasing the voltage will result in a decrease in the current. Such a control mechanism has been installed at full-scale facilities as an energy conservation measure. During periods of low UV demand, the lamps are "dimmed" by slowly turning the lamp supply voltage down. This results in a reduction in the power draw of the lamp. Generally, the lamp intensity can be reduced to levels no less than 50% before the lamp current becomes too low and the lamp will begin to flicker and eventually turn off.

Lamp Aging: A number of factors combine to effectively age a lamp and limit its useful life. These include failure of the electrodes, plating of the mercury to the interior lamp wall (blackening), and solarization of the lamp enclosure material (reducing its transmissibility). These all cause a steady deterioration in the lamp's output at the 253.7 nm wavelength, such that its output at the end of the lamp's life can be 40 to 60 percent of its nominal output.

The output of the lamp throughout its life is affected primarily by the extent of blackening and solarization of the glass tube; the actual life of the lamp is governed by the condition of the electrodes. Germicidal lamps are typically of the hot cathode type; these will deteriorate progressively with increasing number of starts. Thus, the lamp life expectancy generally is rated according to the number of times the lamp is started, or the burning cycle. The lamp life normally cited by most manufacturers is 7,500 hours,

based on a burning cycle of eight hours. The average UV output at this point is estimated to be 70% of the lamp output at 100 hours (note that the nominal output of the low pressure mercury arc lamps represents its output after a 100 hour "burn-in" period).

Monitoring the Lamp Intensity

The procedure for monitoring the lamp intensity is by comparison with that of a new lamp, but after the 100 hour burn-in time. The first step is to measure the intensity, at a fixed distance, of three to five new lamps which have been burned for about 100 hours. The average of the five then becomes the benchmark to determine the relative output of the lamps in use (percent of new lamp average). Each lamp should be tagged and given an I.D. number; this allows direct monitoring of individual lamps and allows the operator to keep an appropriate mix of lamps in a system and to know when to discard a lamp.

The same procedure is used to monitor the transmittance of a quartz sleeve. In this case, a single lamp is used. First the intensity is measured with and without a new, clean quartz sleeve in place over the lamp. Similar measurements then are taken with the unit's quartz sleeves and compared to the transmittance of the new quartz. This can be done before and after the quartz is cleaned.

vi. System Design Considerations for Effective Maintenance

An overriding concern in the proper maintenance of the UV reactor for effective performance is to keep all surfaces through which the radiation must pass as clean as possible. The effects of surface fouling on energy utilization efficiency are critical, and very often can be pointed to as the reason for non-performance of a particular system. Other concerns relate primarily to the accessibility to UV reactors and to keeping adequate records to control replacement cycles and maintenance schedules.

Reactor Maintenance

The most reliable method to determine if a reactor is becoming dirty and requires cleaning is by visual inspection. The unit should be drained and the surfaces observed for fouling. In open systems, this can be done rather conveniently and quickly. Reactors which are sealed vessels can be difficult. These designs should accommodate such visual inspections by incorporating large portholes or manways in the reactor shell.

Generally the surfaces of submerged quartz systems contacted by the water will become coated by inorganic scale, very much like boiler scale. This will be especially the case in areas where there is hard water. Additionally, the inside surface of the quartz and the outer surfaces of the Teflon tubes

eventually will develop a grimy dust layer, primarily from airborne dirt and water vapor.

Fouling of the reactor's internal surfaces will be signaled by reduced performance efficiency, or by reductions in the intensity measured by in-line probes. While these may provide some signal of fouling, it is still necessary to be able to inspect the surfaces physically.

It is appropriate to completely overhaul the reactor, cleaning all interior surfaces, and determining the lamp outputs and quartz (or Teflon) transmittances. Each lamp is removed from the reactor and washed with a mild soap solution, rinsed, and swabbed with an alcohol (isopropyl) soaked rag (cheesecloth). Then the interior surfaces of the quartz sleeves are cleaned by the same procedure by using a gun-barrel type cleaning rod to swab the interior surfaces. At the same time, each lamp, which is tagged with an I.D. number, is measured for relative output. Those which are below a specified level are discarded and replaced with new lamps. These new lamps also are tagged with a number. In this manner, each lamp can be traced on the basis of operating time and output. A reactor lamp inventory then can be mixed and controlled to maintain a minimum average output level.

In similar fashion, the quartz should be monitored for transmittance. It may be cumbersome, however, to remove all the quartz from a system. It is recommended instead (U.S. EPA, 1986, p. 233) that a representative fraction of the quartz sleeves be monitored; 10-15% of the quartz inventory would be sufficient. The same quartz should always be monitored; these would be considered as representative of all quartz in the system. If the tagged quartz begins to show marked deterioration due to aging and wear, it then may be appropriate to broaden the monitoring and to begin replacing the quartz sleeves. The replacement can be accomplished gradually. As with new lamps, eventually there will be a mix of old and new quartz in the system. There is little experience in determining the effective life of the quartz sleeves; certainly it will vary by site, but generally should be between four and seven years.

In Teflon systems, the lamps are removable on racks; they should be cleaned and monitored in the same manner as the quartz systems. The Teflon tubes should be cleaned on occasion; this can be done by swabbing the tubes with soapy water/alcohol. A non-abrasive material should be used. Each tube also should be monitored for transmittance, just as with the quartz sleeves. This may not be as straightforward, however, because of their limited accessibility and problems in getting direct measurements with a UV radiometer/detector.

vii. **Costs for Disinfection With UV Radiation**

Construction Costs

Table XXVIII summarizes costs developed in 1978 by Hansen et al. (1979). By 1982, these costs had increased about 15% (U.S. EPA, 1983) for the size

TABLE XXVIII. CONSTRUCTION COSTS FOR ULTRAVIOLET LIGHT DISINFECTION

Cost Category	Plant Capacity (gpd) 14,400	28,800	187,200	374,400	748,800	1,123,200
Excavation and Sitework*	$ 60	$ 60	$ 60	$ 60	z$ 80	$ 110
Manufactured Equipment	800	1,125	4,485	8,685	17,365	26,050
Concrete*	250	250	250	250	280	300
Labor*	110	170	250	300	400	500
Pipe and Valves*	60	150	350	450	750	1,000
Electrical and Instrumentation*	430	430	430	430	480	480
Housing*	1,500	1,500	1,500	1,500	1,800	2,000
SUBTOTAL	3,210	3,885	7,225	11,675	21,155	30,440
Miscellaneous and Contingency*	470	560	1,010	1,580	2,830	4,060
TOTAL	$3,680	$4,445	$8,335	$13,255	$24,085	$34,500

* Data from Hansen et al. (1979).

ranges listed. Data presented are for single and multiple UV lamp disinfecting units ranging in water throughput capacity from 14,400 gal/day to 1,123,200 gal/day.

All UV generating units are quite compact; for example, the 1,123,400 gal/day unit occupies an area of less than 24 ft^2. Costs listed in Table XXVIII include equipment costs of the UV units, and the related costs of piping, electrical equipment, equipment installation, and a building to house the equipment.

Figure 28 shows construction cost curves for UV disinfection systems (Gumerman et al., 1986).

Operating and Maintenance Costs

These are shown in Table XXIX (for 1979) for the same size plants as in Table XXVIII. Process energy is required for the mercury lamps operating inside of the UV generating units. Continuous 24-hr/day operation is assumed, with only occasional shutdown to clean cells and replace UV lamps which have become weakened by lengthy use. Building energy requirements are for heating, lighting, and ventilation.

Maintenance materials are related to the replacement cost of the UV lamps, which usually are replaced after operating continuously for about 2,000 hours (about eight months). Labor requirements are related to occasional cleaning of the quartz sleeves which surround the mercury vapor lamps, and periodic replacement of the weak UV bulbs.

It is noteworthy that replacement bulb costs at the smallest plant (14,400 gal/day) are only about 9% of the total O&M costs, whereas at the largest plant size (1,123,200 gal/day), replacement bulb costs are about 48% of the total O&M costs. This reflects the fact that the larger UV generating units contain a greater number of UV bulbs per unit volume of water treated.

Figure 29 plots estimated labor requirements for the operation and maintenance of UV systems (Scheible et al., 1985). Figure 30 shows operating and maintenance requirements for UV disinfection systems--building energy, process energy, and maintenance materials -- treating 5,500 gal/day to 1 million gpd. Figure 31 shows O&M requirements for labor and total O&M cost. Figures 30 and 31 are taken from Gumerman et al. (1986).

2. Secondary Disinfectants

There are disinfectants which are added in small dosages to waters which have been treated with primary disinfectants. The purpose of secondary disinfectants is to maintain a small residual disinfectant in the distribution system.

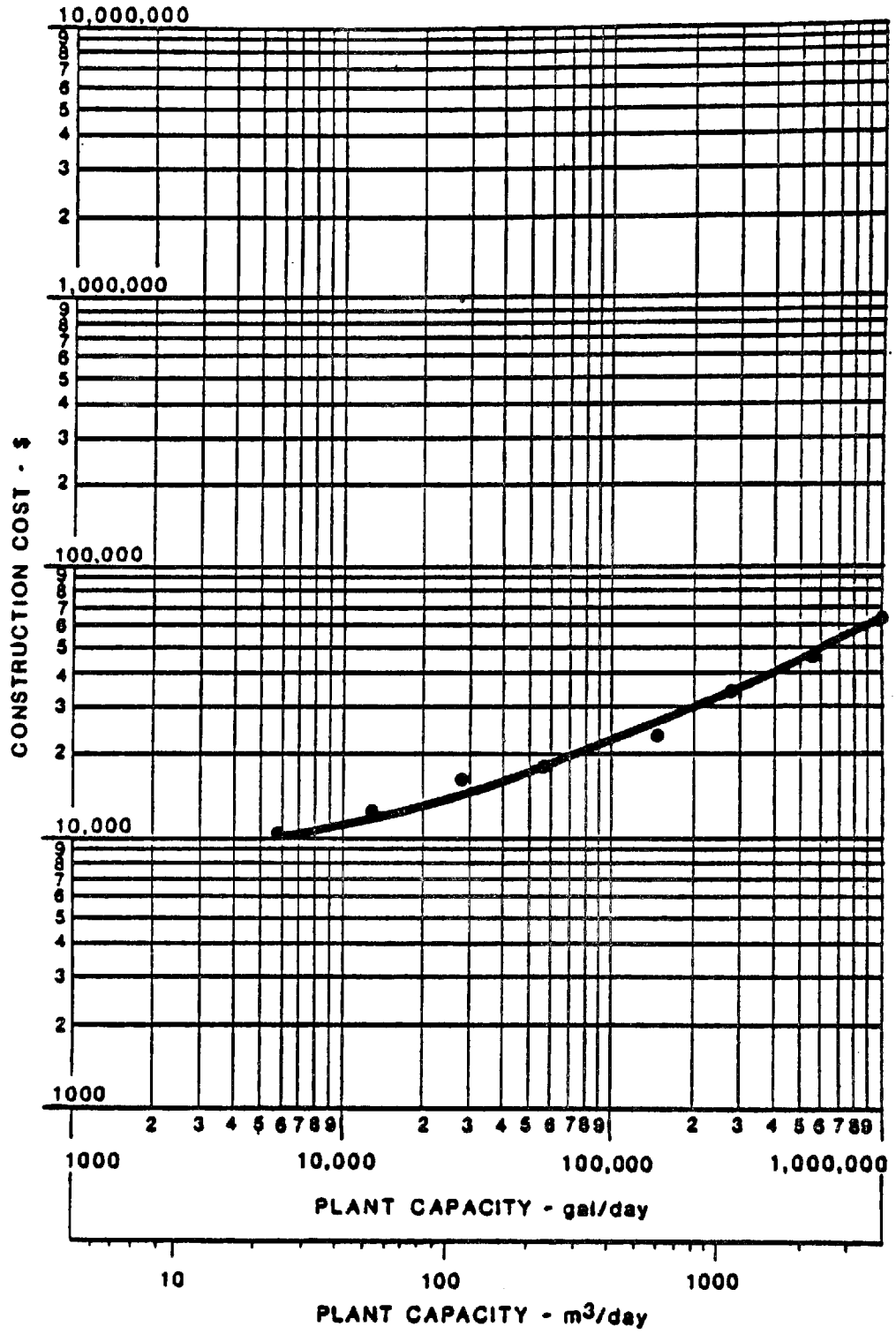

Figure 28. Construction cost for ultraviolet light disinfection (Gumerman et al., 1986).

TABLE XXIX. OPERATION AND MAINTENANCE SUMMARY FOR ULTRAVIOLET LIGHT DISINFECTION

Plant Flow Rate (gpm)	Energy (kWh/yr* Building	Process	Total	x $0.07/kWh =	Maintenance Matl.*($/yr)	Labor (hr/yr)	x $10/hr =	Total Cost ($/yr)
14,400	10,260	440	10,700	$ 749	$ 100	24	$240	$ 1,089
28,800	10,260	800	11,140	780	140	24	240	1,160
187,200	10,260	5,260	15,520	1,086	600	24	240	1,926
374,400	10,260	10,510	20,770	1,454	1,120	30	300	2,874
748,800	12,310	21,020	33,330	2,333	2,250	36	360	4,943
1,123,200	13,340	31,540	44,880	3,142	3,300	42	420	6,862

* Data from Hansen et al. (1979).

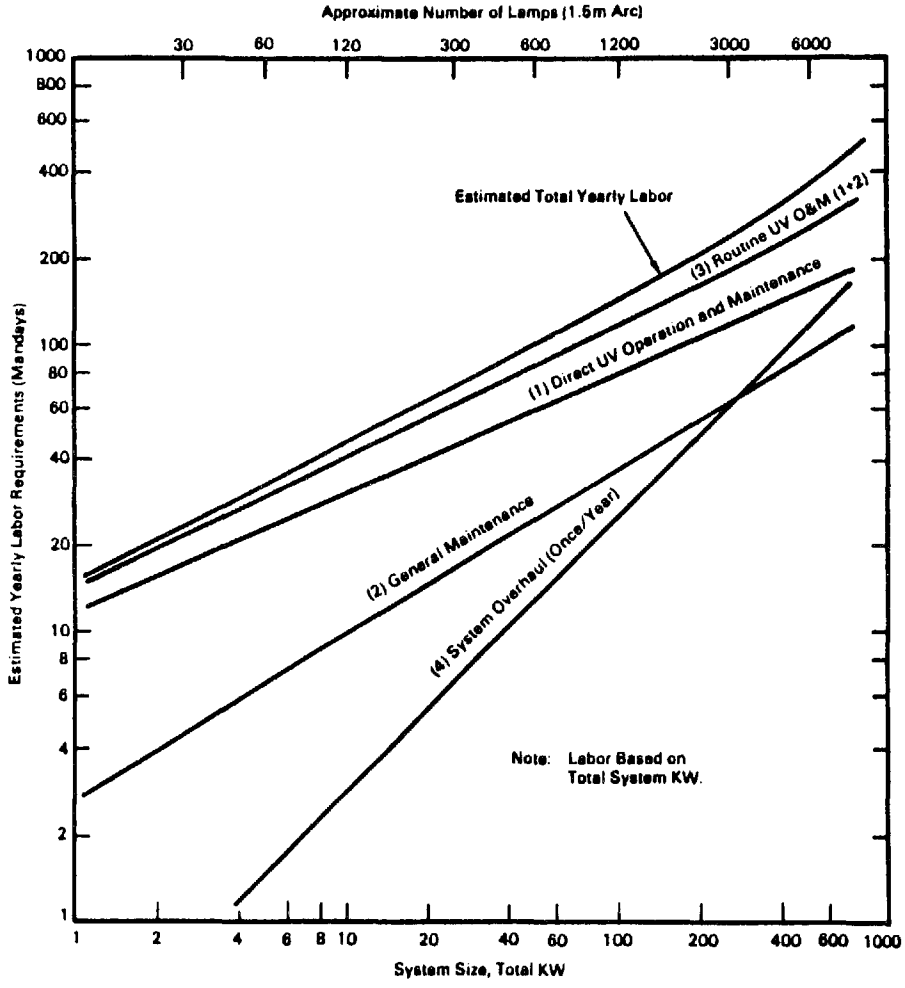

Figure 29. Estimate of labor requirements for the O&M of UV systems (Scheible et al., 1985).

In point of fact, there are three secondary disinfectants in prevalent use: chlorine, chlorine dioxide, and monochloramine. Considerations pertaining to chlorine as a secondary disinfectant are essentially the same as were discussed earlier for chlorine as a primary disinfectant.

a. Chlorine Dioxide

Chlorine dioxide (ClO_2) is an unstable, greenish-yellow gas, explosive in air in concentrations above 4%. Because of this instability, it is always generated in solution, on-site, and is used immediately without storage. As long as care is taken to keep chlorine dioxide in solution and storage of solutions is avoided, there will be no explosion hazards. Chlorine dioxide is readily soluble in water and is decomposed by sunlight.

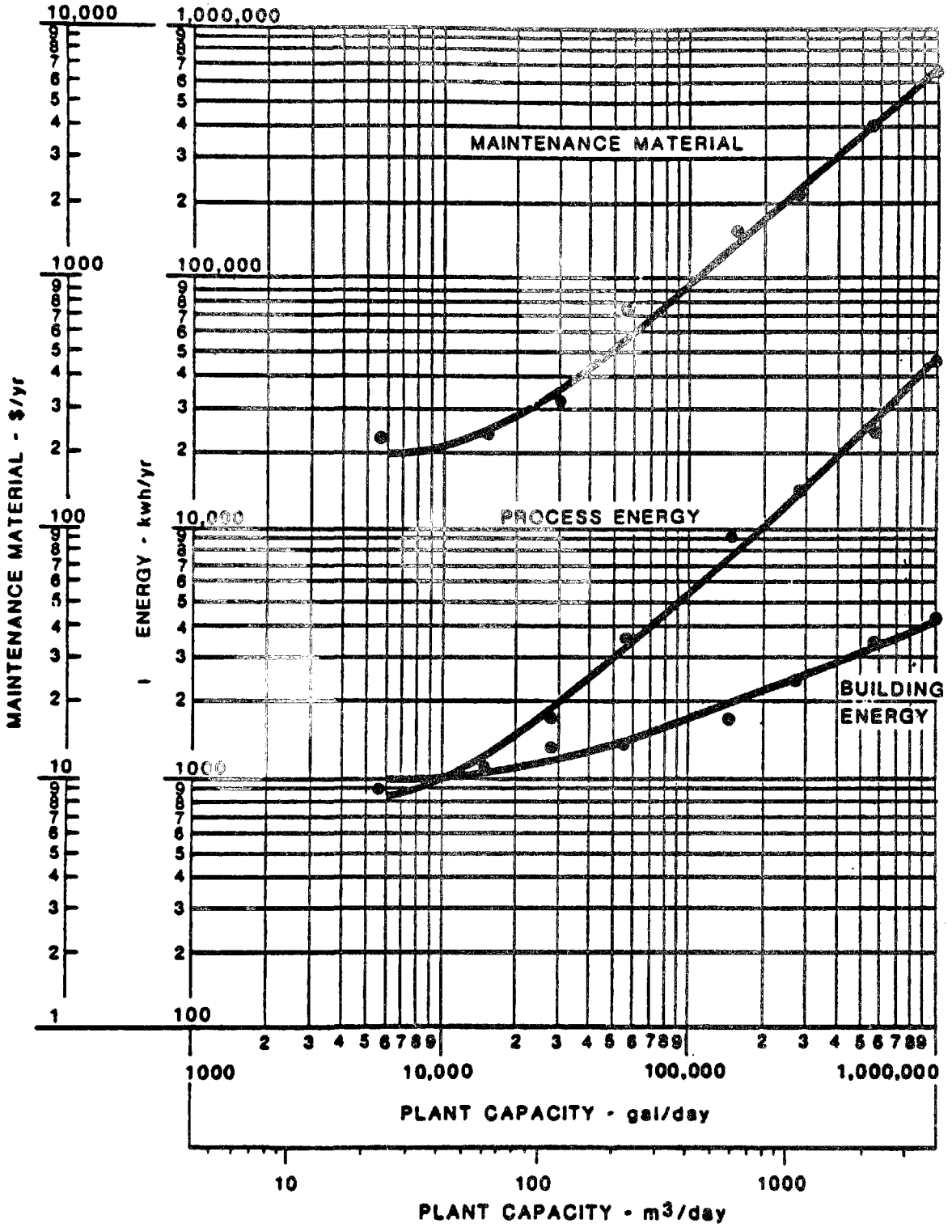

Figure 30. Operation and maintenance requirements for ultraviolet light disinfection -- building energy, process energy, and maintenance material (Gumerman et al., 1986).

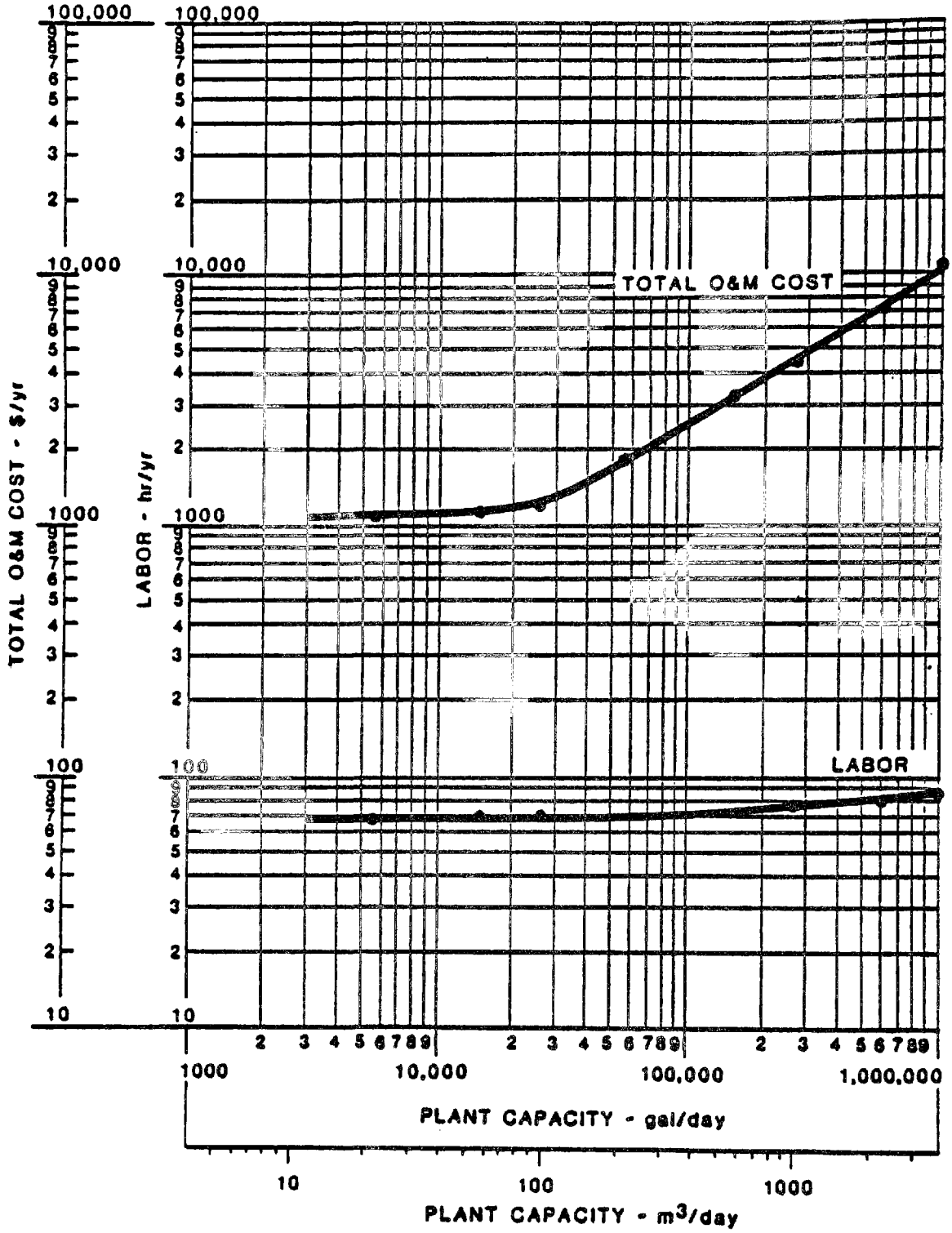

Figure 31. Operation and maintenance requirements for ultraviolet light disinfection -- labor and total O&M cost (Gumerman et al., 1986).

The material is a more powerful oxidizing agent and a better biocide than is chlorine. In addition, when chlorine dioxide is prepared in the absence of excess free chlorine, its use will not produce trihalomethanes, or other chlorinated organic by-products of current public health concern. Additionally, chlorine dioxide has been used in pretreatment to oxidize phenolic compounds and to separate iron and manganese from organic complexes which are stable to chlorination. No oxidation of bromide ion to produce hypobromous acid has been observed using chlorine dioxide free of excess free chlorine.

Distribution system residuals of dissolved chlorine dioxide are longer-lasting than those of chlorine, because there is no reaction with ammonia or formation of chlorinated organic materials. Additionally, chlorine dioxide is not known to impart tastes and odors to water, as does chlorine.

Recent health effects studies have shown (NAS, 1987) that chlorine dioxide produces hematological effects in both humans and laboratory animals. For these reasons, the U.S. EPA (1981) currently advises that the total concentration of chlorine dioxide and its decomposition products (chlorite and chlorate ions) be maintained below 1 mg/L. This allows a maximum applied dosage of 1.2-1.4 mg/L (Werdehoff & Singer, 1986).

Gaseous chlorine dioxide has a strong, disagreeable odor, similar to that of chlorine gas, and is toxic to humans when inhaled. It is detected by the human nose at concentrations between 1.4 and 1.7%. When present at 4.5% concentrations, it irritates the respiratory mucous membranes and may cause severe headaches. At concentrations below 6% in air, it may be compared with chlorine with respect to its toxicity (Masschelein, 1979). Eventual intoxications appear by local irritations of the nervous system, ocular and respiratory mucous membranes, without substantial resorption or systemic poisoning (Ehrlicher, 1964). There are no cumulative effects in cases of repeated exposure (Haller & Northgraves, 1955).

i. Generation of Chlorine Dioxide

For drinking water treatment, chlorine dioxide is generated from solutions of sodium chlorite, $NaClO_2$. This material, purchased as a solid (80% $NaClO_2$) or most normally, as a 25% aqueous solution, is treated with aqueous solutions of chlorine or hypochlorous acid), and sometimes with a strong mineral acid such as sulfuric or hydrochloric acids.

Three processes used in water treatment plants for the generation of ClO_2 employ (a) gaseous chlorine, (b) sodium hypochlorite solution and mineral acid, and (c) mineral acid. Each process is summarized below.

1. Gaseous Chlorine

This is a two-step procedure, beginning with the formation of hypochlorous acid upon dissolution of gaseous chlorine into water:

$$Cl_2 + H_2O \text{ ------> } HOCl + HCl$$

chlorine — water — hypochlorous acid — hydrochloric acid

These intermediate products then react with sodium chlorite to produce chlorine dioxide:

$$HOCl + HCl + 2NaClO_2 \text{ ----> } 2ClO_2 + 2NaCl + H_2O$$

hypochlorous acid — hydrochloric acid — sodium chlorite — chlorine dioxide — sodium chloride — water

The overall result of these reactions is summarized by the equation:

$$Cl_2 + 2NaClO_2 \text{ ----> } 2ClO_2 + 2NaCl$$

chlorine — sodium chlorite — chlorine dioxide — sodium chloride

According to the stoichiometry of this equation, one mole of chlorine reacts with two moles of sodium chlorite to produce two moles of chlorine dioxide. In water supply practice, some molar excess of chlorine actually is employed so as to insure conversion of the maximum amount of chlorite ion to chlorine dioxide. Therefore, the recommended ratio of reactants is two moles of chlorine per mole of sodium chlorite. On a weight basis, 1.57 parts of chlorine gas are added per part of $NaClO_2$ (calculated on a 100% solids basis when solutions of sodium chlorite or 80% solids materials are employed).

Under these conditions of excess chlorine gas being added, the product ClO_2 solution also will contain an amount of hypochlorous acid/hypochlorite ions. These can react with THM and TOX precursor materials to produce THMs and TOX materials.

2. Sodium Hypochlorite and Mineral Acid

This also is a two-step process, in which sodium hypochlorite solution reacts with hydrochloric acid to form hypochlorous acid, which then reacts with sodium chlorite to form chlorine dioxide:

$$NaOCl + HCl \text{ ----> } NaCl + HOCl$$

sodium hypochlorite — hydrochloric acid — sodium chloride — hypochlorous acid

$$HOCl + HCl + 2NaClO_2 \text{ ----> } 2ClO_2 + 2NaCl + H_2O$$

hypochlorous acid	hydrochloric acid	sodium chlorite	chlorine dioxide	sodium chloride	water

In this procedure, as in the gaseous chlorine and sodium chlorite procedure, excess chlorine is utilized to insure conversion of the maximum amount of chlorite ion to chlorine dioxide. The ClO_2 solution so produced also will be able to form some THMs and TOX because of the presence of excess hypochlorous acid.

3. **Mineral Acid**

This process involves mixing a solution of acid with a solution of sodium chlorite, and the reactions are as follows:

$$5NaClO_2 + 4HCl \text{ ----> } 4ClO_2 + 5NaCl + 2H_2O$$

sodium chlorite	hydrochloric acid	chlorine dioxide	sodium chloride	water

When sulfuric acid is the strong mineral acid, the reactions can be depicted as follows:

$$10NaClO_2 + H_2SO_4 \text{ ----> } 8ClO_2 + 5Na_2SO_4 + H_2O + HCl$$

sodium chlorite	sulfuric acid	chlorine dioxide	sodium sulfate	water	hydrochloric acid

The exact ratios of reactants will depend upon which mineral acid is employed for the production of chlorine dioxide.

When generated using mineral acid, excess chlorine is not required. Consequently, solutions of chlorine dioxide prepared in this manner do not contain free residual chlorine, thus no more than trace amounts of chlorinated organic by-products can be synthesized. In addition, pure chlorine dioxide does not oxidize bromide ion to produce hypobromous acid, which then can produce brominated organic derivatives. With excess free chlorine available, however, bromide ion can be oxidized in water to form hypobromous acid.

In all three cases, the appropriate aqueous solutions of reactants are metered into a chlorine dioxide reactor (a cylinder containing Raschig rings, glass beads, or hollow glass cylinders) where intimate mixing of the reacting solutions occurs (see Figures 32 and 33). The size of the reactor and the residence time of the reacting solutions are such that after a few seconds, the solution exiting the reactor displays a strongly yellow color of chlorine dioxide. This solution then is pumped directly into the water to be treated.

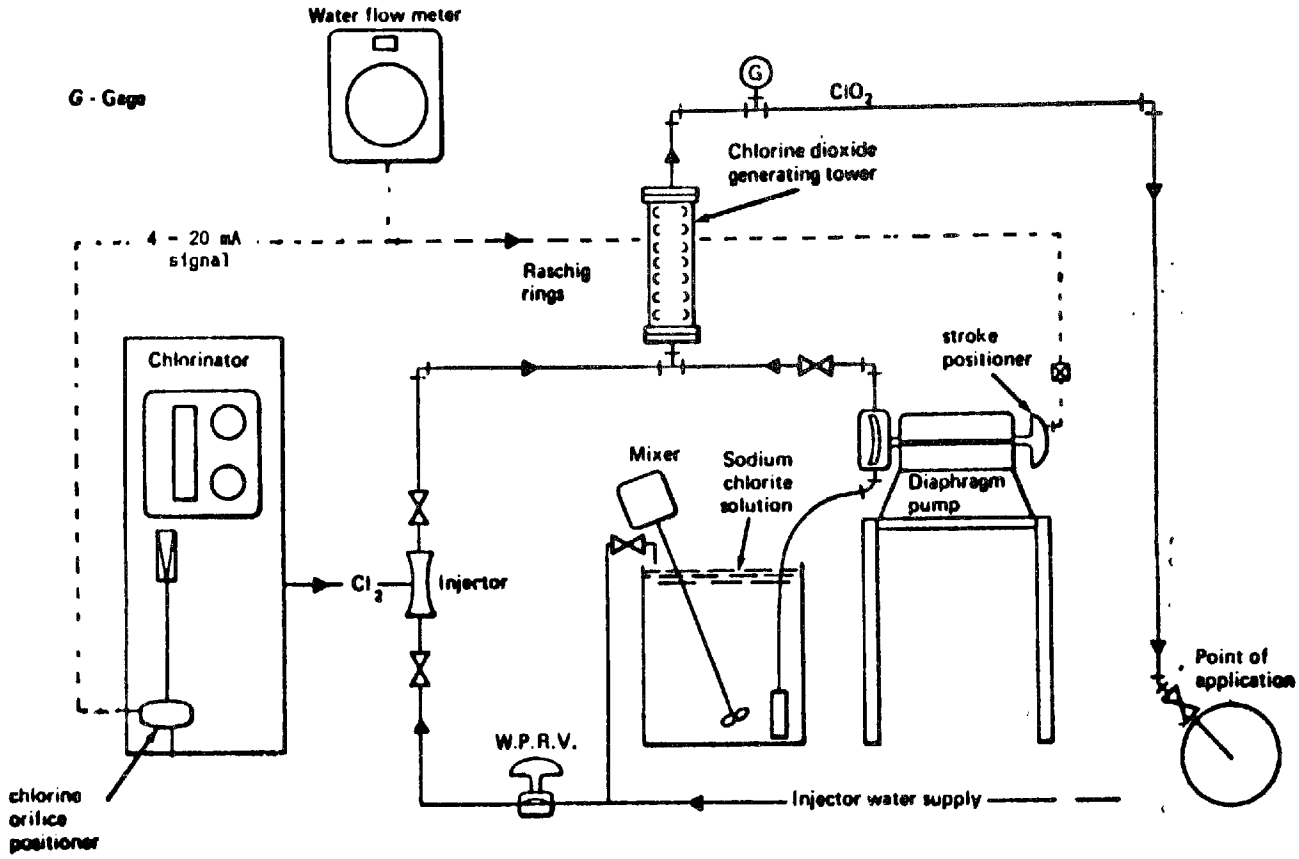

Figure 32. Schematic diagram of an automatic feed, automatic flow-proportional chlorine dioxide system: generation from chlorine and sodium chlorite (courtesy Capital Controls Co., Inc.).

In this manner, solutions of chlorine dioxide are generated as the material is required and used immediately, without storage. Appropriate metering and control instrumentation can be installed with the chlorine dioxide reactor so that the generation and addition of chlorine dioxide is paced by the flow rate of the water to be treated. As a result, the unit operates without the need for constant manual attention.

ii. Oxidation-Reduction Reactions of Chlorine Dioxide

At neutral pH (= 7) chlorine dioxide dissolves totally in water without hydrolysis reactions. On the other hand, when performing its function as a chemical oxidant or disinfectant in water, chlorine dioxide is chemically

reduced. One of the reaction products is the chlorite ion, from which ClO_2 was formed initially:

$$ClO_2 + e^- \text{ ----> } (ClO_2)^-$$

chlorine dioxide — reducing agent — chlorite ion

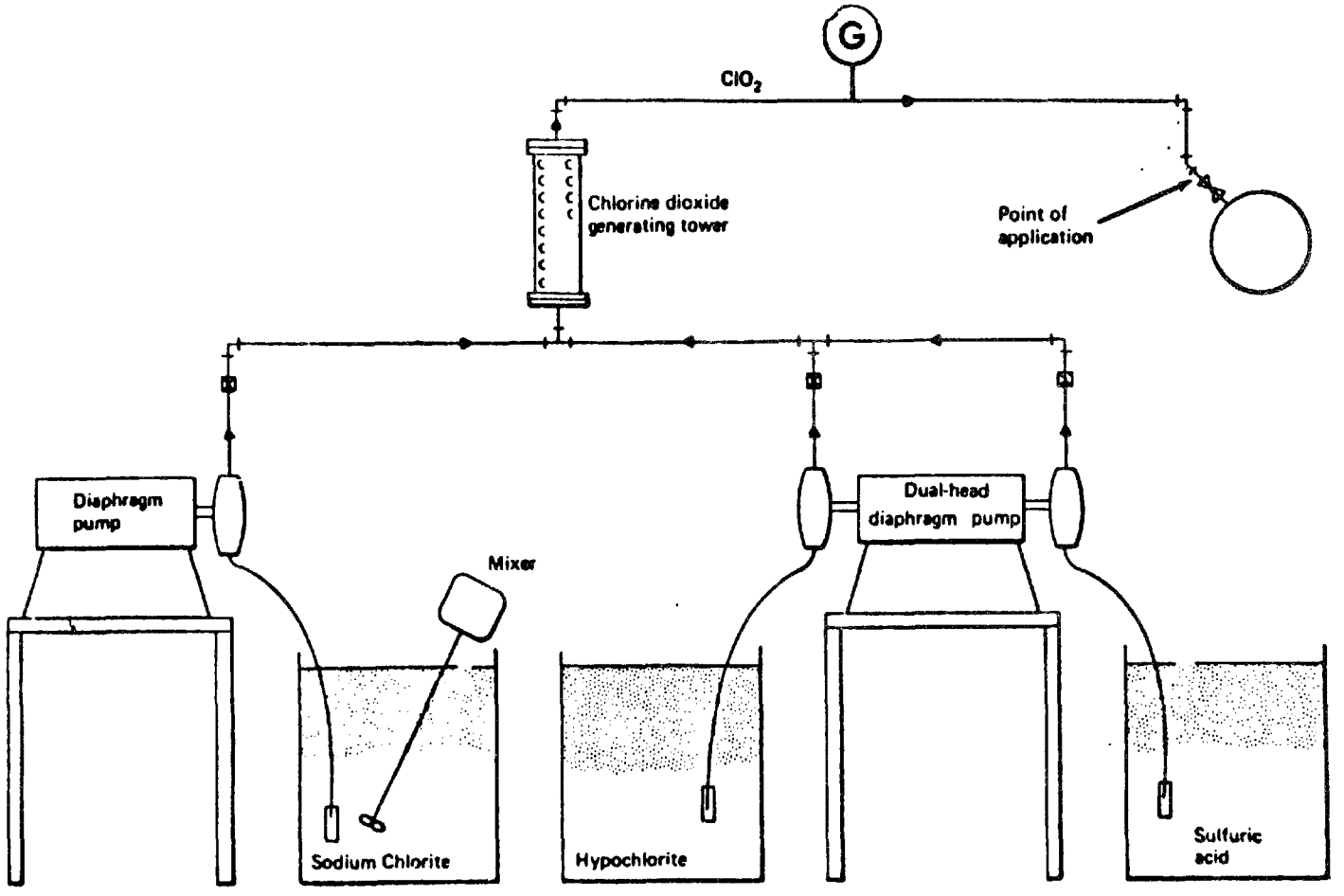

Figure 33. Manual feed equipment arrangement for generating chlorine dioxide from sodium hypochlorite solution and mineral acid (U.S. EPA, 1983).

In strongly acid (pH $\leq$ 2) or strongly alkaline (pH $\geq$ 11) solutions, chlorine dioxide undergoes disproportionation (self oxidation and reduction):

$$2ClO_2 + H_2O \text{ ----> } (ClO_2)^- + (ClO_3)^- + 2H^+$$

chlorine dioxide — water — chlorite ion — chlorate ion — hydrogen ion

These disproportionation reactions are accelerated by the presence of hypochlorous acid and hypochlorite ion. Therefore, when chlorine dioxide is generated in the presence of excess chlorine and at pH below 2 or above 11, chlorite and chlorate ions will be formed as well.

iii. Establishing a Chlorine Dioxide Residual

Because the cost of chlorine dioxide is higher than that of chlorine, and because of the hematological effects upon both humans and laboratory animals, only small dosages of chlorine dioxide (maximum residuals of 1 mg/L total of ClO_2, chlorite, and chlorate ions) currently are recommended by EPA for drinking water treatment (U.S. EPA, 1981; 1987a). However, a primary advantage of pure chlorine dioxide is that it does not react with ammonia or with THM precursors to produce THMs, or with TOX precursors to produce TOX, as does chlorine. This means that if the water has been pretreated to remove most of the oxidant-demanding constituents (or does not contain them initially), the total ClO_2 dosage can be used to provide primary or secondary disinfection at the recommended 1 mg/L maximum oxidant residual level.

In laboratory studies, Werdehoff & Singer (1986) have shown that about 70% of the ClO_2 added is converted to chlorite ion. Therefore a chlorine dioxide dosage of 1.2 to 1.4 mg/L is the maximum practical dosage in order not to exceed the recommended 1 mg/L residual of total oxidant. This value has been confirmed by Lykins & Griese (1986) in pilot plant and full-scale plant studies at Evansville, IN (see Case History -- Evansville, IN, Section VIII.C.1).

Another major advantage of pure chlorine dioxide is that it does not oxidize bromide ion to produce hypobromous acid. This means that bromine-containing THMs and TOX derivatives will not be formed when this material is used for oxidation/disinfection.

iv. Factors Affecting the Efficiency of Secondary Disinfection With Chlorine Dioxide

Chlorine dioxide is a more effective disinfectant than chlorine or hypochlorous acid. Because it does not react with water, ammonia, bromide ions, or most organic nitrogen compounds, it is not "wasted" in extraneous reactions of this type. It is less sensitive to changes in pH (except at very low and very high values), maintaining its disinfection capabilities over the pH range of 6 to 10.

On the other hand, because it is a powerful oxidizing agent, chlorine dioxide can and will react with oxidizable impurities contained in a raw or treated water. Thus, it is important to ensure that oxidant-demanding components of the water have been removed to as low a level as is feasible, consistent with the costs involved, before chlorine dioxide is added.

v. Chlorine Dioxide Systems Design

Table XXX is a partial listing of current suppliers of chlorine dioxide equipment. Several different types of generation equipment are available, which vary depending upon the supplier, but also upon the generation process chosen (gaseous chlorine versus sodium hypochlorite plus acid, versus acid plus sodium hypochlorite, for example). Pertinent aspects of each type of chlorine dioxide generation equipment will be discussed in this subsection.

TABLE XXX. PARTIAL LISTING OF CHLORINE DIOXIDE EQUIPMENT SUPPLIERS

Name	Address
Capital Controls Co., Inc.	P.O. Box 211, Colmar, PA 18915
CIFEC	10 Avenue de la Porte Molitor, F-7500, Paris, France
Clow Corporation	408 Auburn Ave., Pontiac, MI 48058
Fischer & Porter Co.	County Line Road, Warminster, PA 18974
Olin Water Services Co.	9393 W. 110th St., Overland Park, KS 66210
ProMinent Fluid Controls	1005 Parkway View Drive, Pittsburgh, PA 15205
Rio Linda Chemical Co., Inc.	410 North Tenth Street, Sacramento, CA 95813
Wallace & Tiernan Division Pennwalt Corp.	25 Main St., Belleville, NJ 07109

1. Gaseous Chlorine Plus Hypochlorite Solution

All three of the chlorine dioxide generation procedures described earlier are in general use in the United States at this time for application in small water treatment facilities. The most commonly used procedure involves addition of gaseous chlorine to sodium chlorite solutions. A schematic diagram of chlorine/sodium chlorite equipment is shown in Figure 32.

The gaseous chlorine procedure is particularly applicable when a gaseous chlorination system already exists at the treatment plant. The reaction by which chlorine dioxide is generated is as follows:

$$Cl_2 + 2NaClO_2 \text{ ----> } 2ClO_2 + 2NaCl$$

chlorine	sodium chlorite	chlorine dioxide	sodium chloride

This equation indicates that 71 lbs (26.48 kg) of chlorine mixed with a solution containing 181 lbs (67.5 kg) of 100% $NaClO_2$ will produce 135 lbs (50.36 kg) of chlorine dioxide. However, the ratio of reagents recommended by most suppliers of chlorine dioxide generating equipment is 1:1 by weight. This means that more than double the stoichiometric amount of chlorine required by the above equation is utilized. This excess of chlorine over that required results in a faster reaction rate and insures a more complete conversion of chlorite ion to ClO_2.

However, because a large excess of chlorine is employed, solutions of chlorine dioxide prepared by this technique also will contain some free available chlorine, mostly as hypochlorous acid. This amount of free chlorine will produce some quantity of trihalomethanes and other halogenated (TOX) materials.

2. Hypochlorite, Chlorite, and Mineral Acid

The production of chlorine dioxide using sodium hypochlorite solution with sodium chlorite and strong mineral acid is illustrated in Figure 33, and is well suited to most small water systems. Dosages of each chemical can be derived from the equations given earlier.

In this system, all three reactants are in solution. Utilization of strong acid increases the conversion of chlorite ion to chlorine dioxide. Solution feed pumps of equal capacities can be used by adjusting the solution strength of each of the reactants. Thus, the chlorine dioxide production and addition rates can be paced by the flow rate of the water being treated and/or by its secondary disinfectant demand.

Sodium chlorite is available in 55-gal (208.33 L) drums, either as a solid (80% active $NaClO_2$) or as a solution containing 30% $NaClO_2$ (33% solids). If not used directly from the drum, sodium chlorite solution is stored in poly(vinyl chloride) (PVC) or fiberglass tanks and transferred by means of PVC, rubber, or Tygon tubing systems. Diaphragm pumps incorporating PVC as the material in contact with the solutions are used for pumping sodium chlorite solutions. Provision must be made for immediate washdown of any spills of the chemical. This precaution is generic to **all** chlorine dioxide generating systems.

3. The CIFEC System for Generating Chlorine Dioxide

A schematic diagram of this system, developed in France, but in use at several U.S. water treatment plants, is illustrated schematically in Figure 34. The system produces ClO_2 from gaseous chlorine, in high yield, and containing little excess free chlorine.

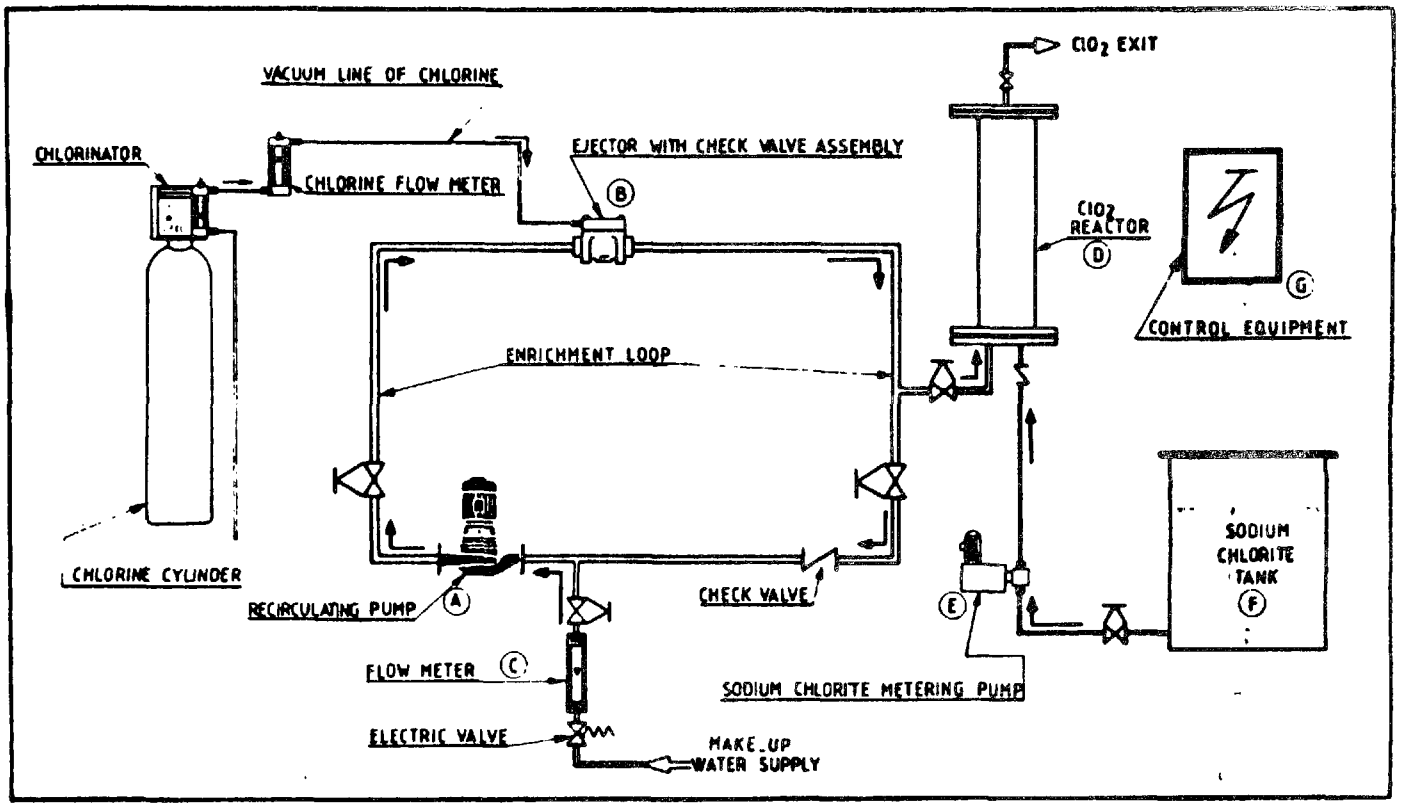

Figure 34. Schematic of the CIFEC chlorine dioxide generating system.

Gaseous chlorine is passed into water which is circulated continuously in what is referred to as an "enrichment loop". Under these conditions, dissolved chlorine (hypochlorous acid) concentrations become higher than can be achieved in a single pass. As a result, the pH of the hypochlorous acid solution is lowered to below 4. This solution then is pumped into the ClO_2 reactor along with a solution of sodium chlorite. As long as the pH of the hypochlorous acid solution is below 4.0, conversion of chlorite ion to chlorine dioxide is significantly higher than the single pass method employing elemental chlorine gas. Therefore, chlorine dioxide is produced which is free of significant quantities of free chlorine.

4. Rio Linda Chlorine Dioxide Generator

Figure 35 shows a schematic diagram of a newer acid/chlorite chlorine dioxide generator marketed by Rio Linda Chemical Co., Inc. Chlorine dioxide is generated by addition of dilute hydrochloric acid to sodium chlorite solution. The novel principle of this generator is the mixing of acid with concentrated sodium chlorite solution just before the two solutions reach the reactor. The two solutions are brought together in an eductor by means of a vacuum created by water flow through the eductor. Such a system eliminates a pump and allows the system to occupy a smaller space.

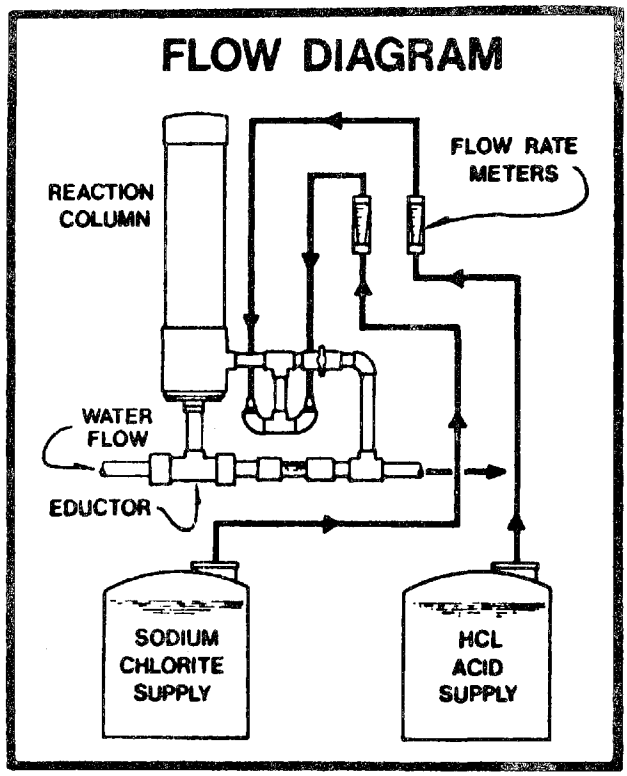

Figure 34. Schematic of the Rio Linda Chemical Co. acid/$NaClO_2$ chlorine dioxide generator.

vi. Miscellaneous Comments

Because several types of chlorine dioxide equipment are available, as well as three processes for its production, it is considered inappropriate to attempt to provide detailed instructions in this document for the preparation of chemical solutions and feed rates. However, the small water utility choosing to install chlorine dioxide generating equipment can have confidence that

each equipment vendor will provide detailed recipes for preparing and metering the appropriate solutions to his chlorine dioxide reactor so as to produce an aqueous solution of chlorine dioxide of known and constant concentration for addition to the plant process water.

A final point to be noted is that the currently recommended maximum concentration of total oxidants (chlorine dioxide, chlorite and chlorate ions) of 1 mg/L means that a water utility processing 0.5 mgd (1,893 m^3/day) and dosing a maximum of 1 mg/L of chlorine dioxide will require a maximum ClO_2 production rate of only 4 lbs (1.82 kg)/day. Smaller systems will require even less ClO_2. At such low dosage levels, two of the three vendors of chlorine dioxide contacted recommend that their units be operated intermittently, collecting ClO_2 solution in an enclosed holding tank for metering into the water being processed. This is because at the low flow rates of reactant solutions, mixing is less efficient in the chlorine dioxide reactor. Consequently, conversion of chlorite ion to chlorine dioxide is less efficient.

vii. Costs of Chlorine Dioxide Generating Systems

Hansen et al. (1979) summarized costs for the generation of chlorine dioxide from equal parts of 2.4% sodium chlorite solution, 25% sulfuric acid solution and 1% sodium hypochlorite solution. Suppliers contacted in 1982 had changed the design of their generation systems for small water supply systems to use 33% hydrochloric acid rather than 25% sulfuric acid.

Equipment costs estimated by Hansen et al. (1979) assumed the use of a dual head diaphragm pump for simultaneous addition of hypochlorite and acid solutions, and a single head pump for the addition of sodium chlorite solution. Detention time in the chlorine dioxide reactor is estimated at 12 seconds, and the generating equipment costs are assumed to be constant up to 50 lbs/day of chlorine dioxide.

At a maximum chlorine dioxide dosage rate of 1 mg/L, a 1 mgd water treatment plant would dose 8 lbs/day. At the same dosage level, a 2,500 gal/day water facility would require only 0.2 lb/day of chlorine dioxide.

Equipment Costs

Quotes were obtained (U.S. EPA, 1983) from three suppliers of chlorine dioxide generation equipment sized so as to prepare ClO_2 at the rate of 8 lbs/day (for a 1 mgd water treatment plant). These are shown in Table XXXI. Supplier A's recirculating loop system (CIFEC) is the highest in equipment price; their lowest cost unit was priced at $34,000 in 1982. This unit operates with a special recirculating pump designed to handle hypochlorous acid below pH 4, plus a sodium chlorite solution pump and all necessary instrumentation to allow automatic operation, with shutdown provisions in the event of cessation of water flow.

TABLE XXXI. 1982 VENDOR QUOTES -- CHLORINE DIOXIDE GENERATORS

Vendor	ClO_2 production capacity (lbs/day)	space required*	Reactants	Unit Cost
Recirculating loop Supplier A (French)	1-10	2x3x6 ft	Cl_2 gas + $NaClO_2$ solution	$34,000 (1 rate, adjust manually)
				$38,000 (2 rates (adjust automatically)
				$41,700 (3 rates (adjust automatically)
(prices delivered to New York)				
Supplier B	4	3.5x4x1.5 ft (wall-mounted	HCl, NaOCl $NaClO_2$ solutions	$25,000 (installed)
Supplier C	14-140	4x3x1.5 ft	Cl_2 gas + $NaClO_2$ soln.	$ 4,320** (floor mount)
		37.5x27x 6.5 in.	same	$ 3,600** (wall mount)
Supplier C	14-140	4x3x1.5 ft	HCl + $NaClO_2$ soln.	$ 4,320 (floor mount)
		37.5x27x 6.5 in.	same	$ 3,600 (wall mount)

* all units require additional space for solution tank(s).
** this unit requires a chlorinator for operation, which is not included in price estimates.

The next lowest in price is the system from Supplier B, which generates chlorine dioxide from 33% hydrochloric acid, 12% sodium hypochlorite, and 25% sodium chlorite solution. This unit cost $25,000 (installed) in 1982, and includes three solution pumps, water flow rate detector, and switches to shut down the unit if the water flow stops. This unit is wall mounted and requires 3.5 x 4 ft of wall space, plus floor space for drums of the three chemical solutions used to feed the generator. For volumes of ClO_2 sufficient to treat flows in communities of 5,000 and 2,500 population, this unit is said to be capable of continuous operation, with no loss in efficiency of conversion of chlorite ion to chlorine dioxide. However, to supply the needs of systems serving as few as 25 persons, the unit would have to be operated intermittently, with ClO_2 solution being stored in a holding tank for later metering into the water.

Supplier C provides two types of chlorine dioxide generators for small water supply systems. One uses acid/sodium chlorite, the other uses chlorine gas and sodium chlorite. These units cost $3,600 in 1982, if wall-mounted, and $4,320 for a floor-mounted cabinet. The single size unit offered by this supplier is designed to generate up to 140 lbs/day. In order to produce 8 lbs/day or less, a small water utility would have to install a holding tank and operate the generator intermittently.

The chlorine gas/sodium chlorite generator of Supplier C requires a gas chlorinator to feed chlorine gas. Therefore, in new plants considering use of this type of equipment, the cost of a chlorinator must be added to the cost of the chlorine dioxide generator. In existing plants currently using gas chlorination, the chlorinator already is in place and would not represent additional equipment cost.

Because equipment quotes for generating chlorine dioxide vary so widely, water treatment personnel are advised not to try applying past equipment cost estimates. Technology for generating and applying chlorine dioxide is changing rapidly (as opposed to technologies for addition of gaseous or aqueous chlorine), and new suppliers enter the market from time to time. It is more advantageous to seek quotations from the various suppliers as to the various methods for generating ClO_2. Select the methods most appropriate to the specific water treatment plant, then determine what piping and wiring will be needed to install the equipment selected.

Figure 36 (Gumerman et al., 1986) shows that the construction costs for chlorine dioxide generating and feed equipment are constant for feed rates of up to about 45 lbs/day.

Operation and Maintenance Costs

Hansen et al. (1979) concluded that, in general, O&M costs for generating ClO_2 are independent of the quantities generated. Process energy requirements, which are for metering pumps and mixer for preparing chlorite solution from solid sodium chlorite, are estimated at 1,240 kWh/yr. Energy requirements for 40 ft^2 of building space to house the equipment would be 4,100 kWh/yr, resulting in total energy requirements of 5,340 kWh/yr. Maintenance material requirements would be for minor equipment repair only, amounting to about $100/yr. Labor is required for preparation of solutions and periodic maintenance of the equipment. Annual labor requirements are estimated to be 1 h/day, or 365 h/yr.

Annual O&M costs of $4,124/yr (based on $0.07/kWh power cost and $10.00/h labor cost) are summarized in Table XXXII. Figures 37 and 38 (Gumerman et al., 1986) show the estimated O&M requirements for chlorine dioxide generation and feed equipment -- building energy, process energy, and maintenance material (Figure 37) and labor and total O&M cost (Figure 38).

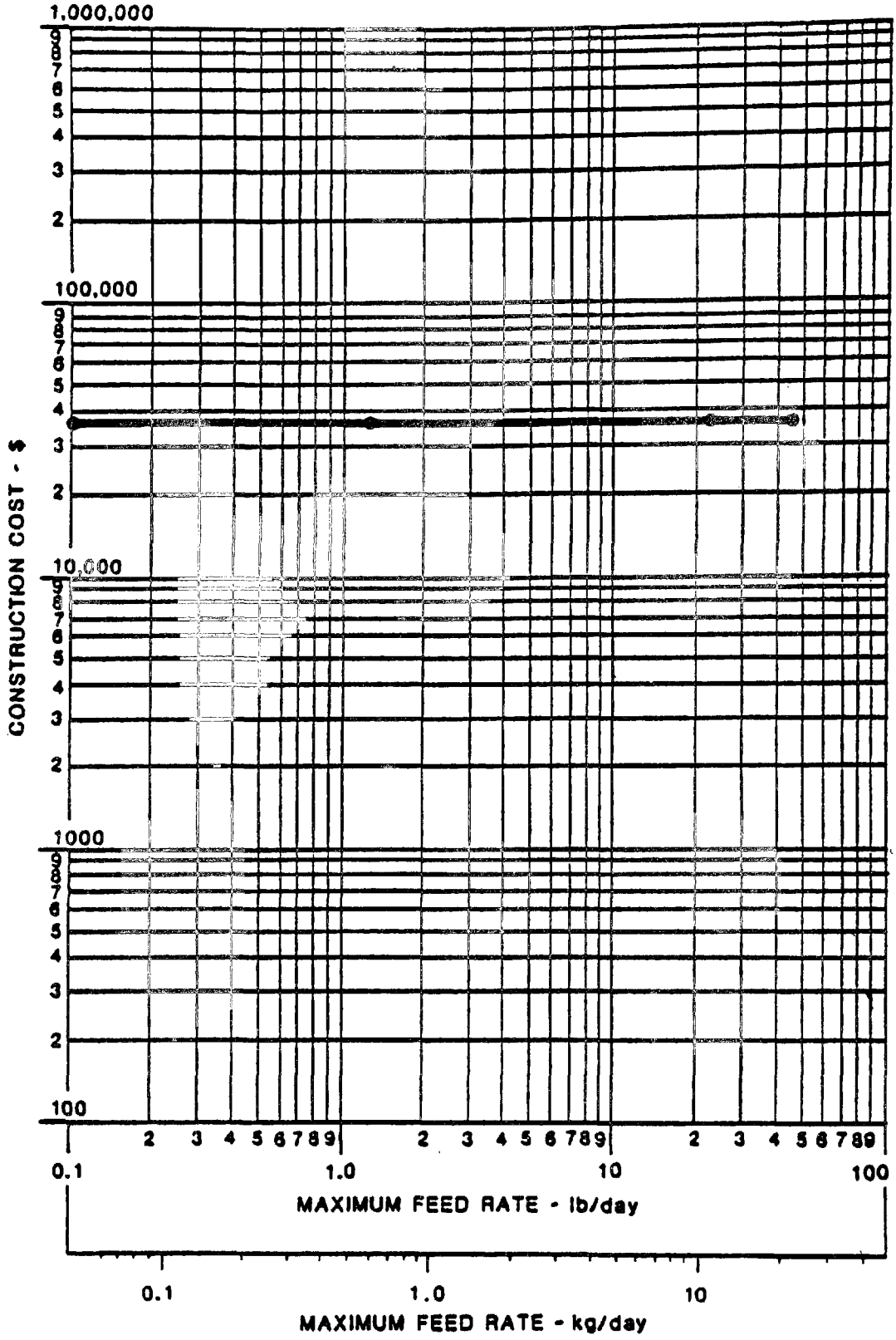

Figure 36. Construction cost for chlorine dioxide generation and feed equipment (Gumerman et al., 1986).

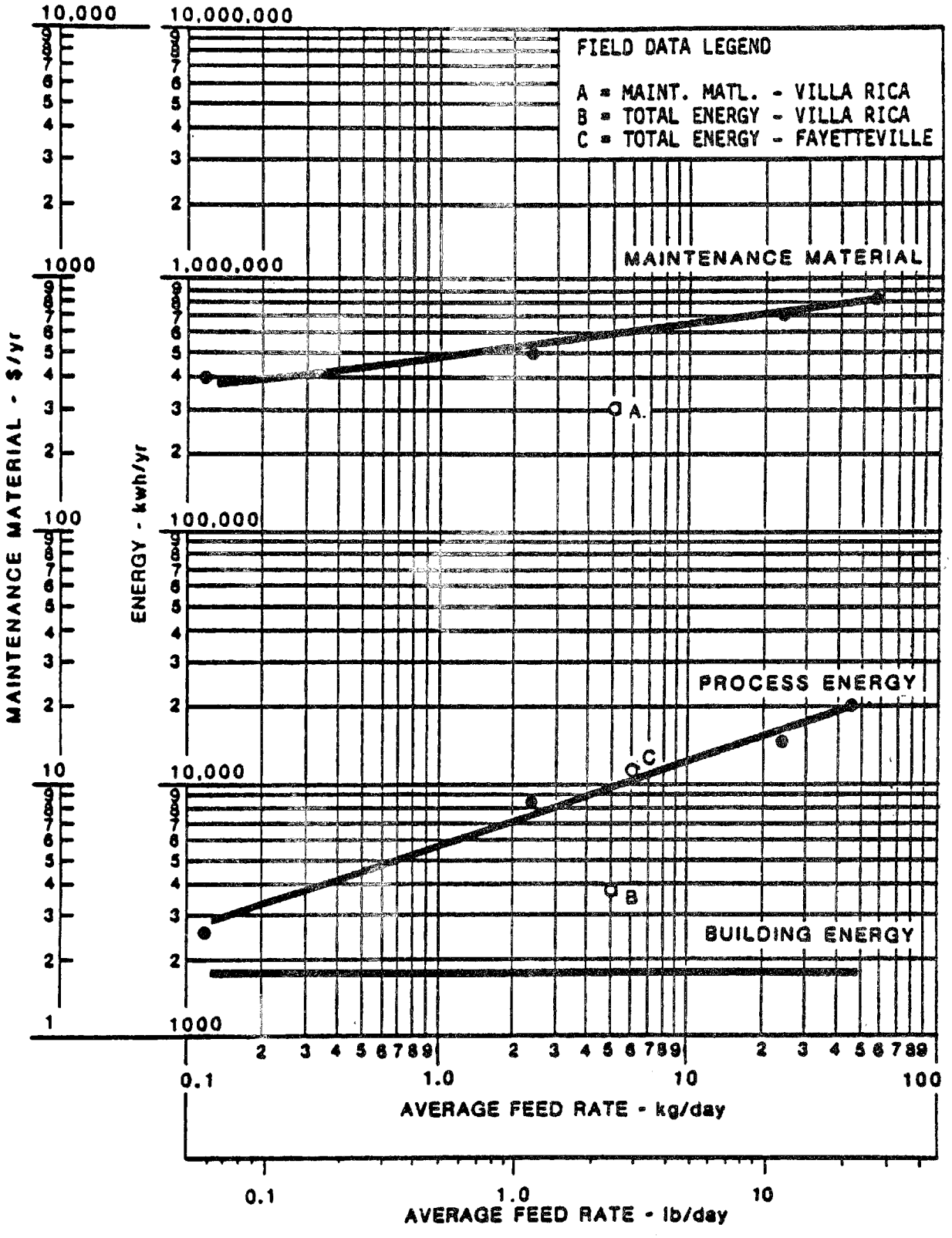

Figure 37. Operation and maintenance requirements for chlorine dioxide generation and feed equipment -- building energy, process energy, and maintenance material (Gumerman et al., 1986).

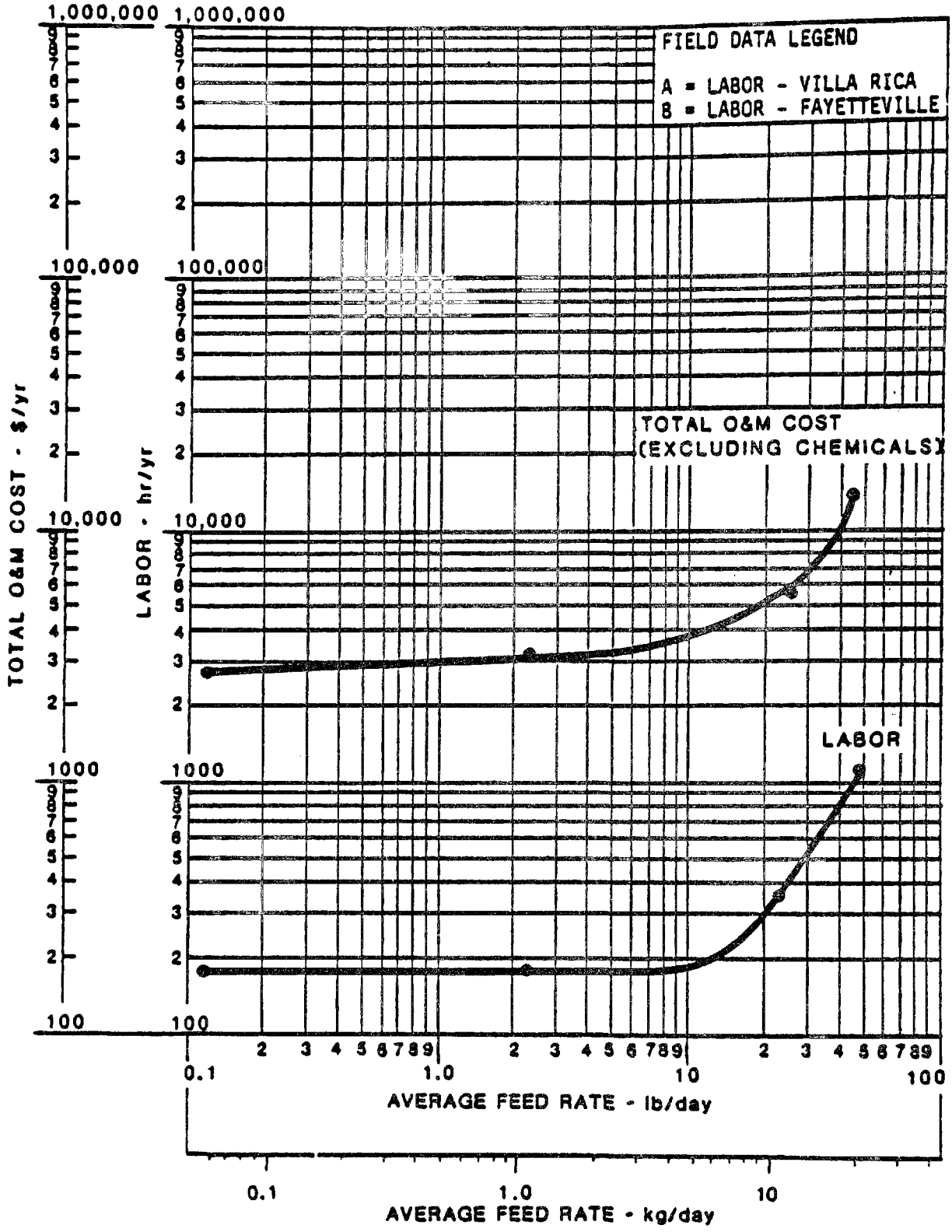

Figure 38. Operation and maintenance requirements for chlorine dioxide generation feed equipment -- labor and total O&M cost (Gumerman et al., 1986).

TABLE XXXII. OPERATION AND MAINTENANCE SUMMARY FOR ClO_2 GENERATING AND FEED SYSTEMS

Item	Requirements*	Cost
ELECTRICAL ENERGY		
Process	1,240 kWh/yr x $0.07 =	$ 86.8
Building	4,100 kWh/yr x $0.07 =	$ 287.0
TOTAL	5,340 kWh/yr x $0.07 =	$ 373.8
MAINTENANCE MATERIAL		$ 100/yr
LABOR	365 h/yr x $10.00 =	$3,650
Total Annual O&M Cost		$4,124

* based on estimates of Hansen et al., 1979

Chemical Costs

At a production rate of only 8 lbs/day (maximum for a 1 mgd water treatment plant at a 1 mg/L applied chlorine dioxide dose), chemical costs are not as significant as pumping costs. Nevertheless, 1982 chemical costs were as follows:

gaseous chlorine	$0.47/lb
sodium chlorite	1.55-1.65/lb
HCl	0.10/lb
NaOCl	0.93/gal (15% solution)

Prices for chlorine and sodium chlorite in 1987 were about 30% lower.

A chlorine dioxide production rate of 8 lbs/day equates to 2,920 lbs/yr. If the chemicals cost for ClO_2 is arbitrarily assumed to be $1/lb, a 1 mgd water treatment plant can expect to pay about $2,920 in addition to the annual O&M costs. On the same basis, chemical costs at a 2,500 gal/day plant would be $2,920/400 = $7.30/yr for producing chlorine dioxide at $1.00/lb.

b. **Chloramination**

Chloramines are formed when water containing ammonia is chlorinated, or when ammonia is added to water containing chlorine (hypochlorite or hypochlorous acid). This is accomplished currently by adding gaseous ammonia (purchased as the anhydrous liquid, NH_3, in 150 lb cylinders for small water treatment systems) directly to the water, or by adding a solution of ammonium sulfate, $(NH_4)_2SO_4$ (purchased in 100 lb bags, 98% pure; 25% available NH_3).

i. Chemistry of Chloramination

Three chloramine compounds can be produced, depending on the ratios of chlorine and ammonia which are utilized:

$$NH_3 + HOCl \text{ ----> } H_2O + NH_2Cl$$

ammonia — hypochlorous acid — water — monochloramine

$$NH_2Cl + HOCl \text{ ----> } H_2O + NHCl_2$$

dichloramine

$$NHCl_2 + HOCl \text{ ----> } H_2O + NCl_3$$

nitrogen trichloride

The distribution of the chemical species of chloramines is a function of pH and of the amount of chlorine added. For example, in the pH range of 7 to 8 and a chlorine to ammonia weight ratio of 3:1, monochloramine is the principal product. At higher chlorine to ammonia ratios or at lower pH values (5 to 7), some dichloramine will be formed. If the pH drops below 5, some nitrogen trichloride (often erroneously called "trichloramine") may be formed. Formation of this compound should be avoided because it imparts undesirable taste and odor to the water.

Figure 39 (National Academy of Sciences, 1980) shows the relative percentages of monochloramine and dichloramine produced as the pH changes, for different weight ratios of chlorine to ammonia. At a pH value of about 5.7, approximately equal amounts of mono- and dichloramines are present in solution.

Care also should be taken not to exceed chlorine to ammonia ratios of 5:1. This is the ratio existing at the peak of the breakpoint curve, above which all of the ammonia will have been removed, chloramines will be absent, and free residual chlorine will be present.

ii. Establishing a Chloramine Residual

Generation of chloramines is conducted on-site, in solution, as required, simply by adding the appropriate amount of chlorine to waters already containing ammonia, or by adding ammonia to waters already containing chlorine, then allowing a short holding time to be certain that the chemicals have had time to react with each other to form chloramines. Usually, chloramine-forming reactions are at least 99% complete within a few minutes.

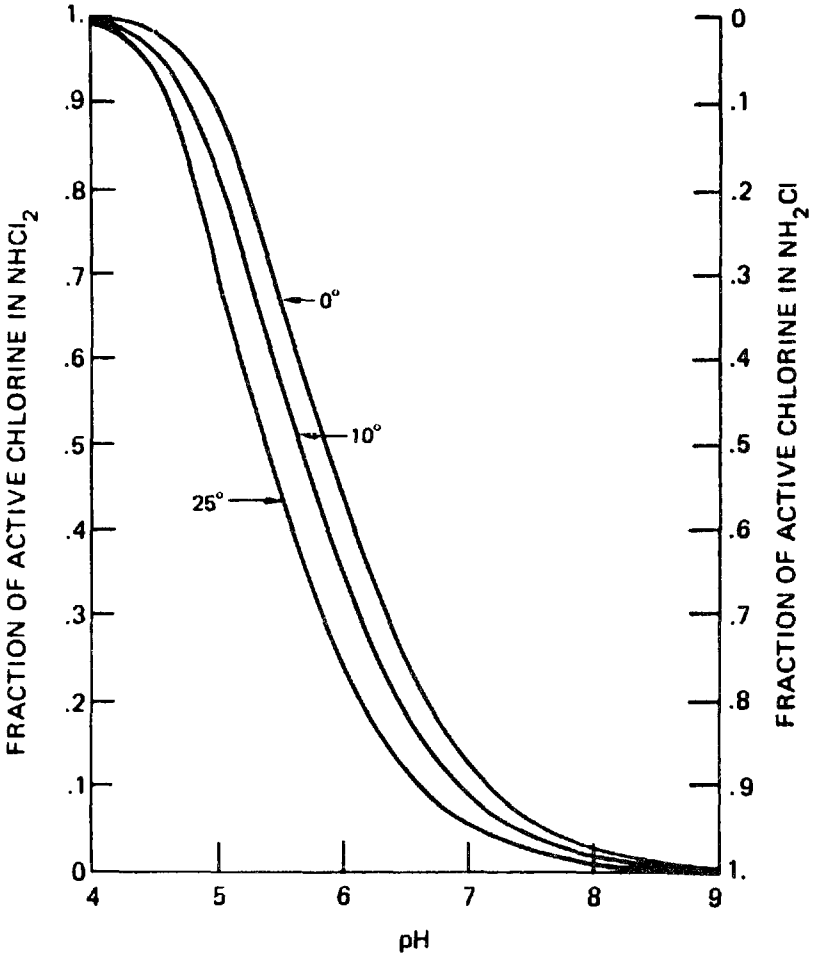

Figure 39. Proportions of mono- and dichloramines in water with equimolar concentrations of chlorine and ammonia (NAS, 1980).

However, the National Academy of Sciences (NAS, 1987) has recommended rejection of the first approach (adding chlorine to ammonia-containing water). Furthermore, when using the second approach, the NAS recommends addition of sufficient chlorine to produce a slight residual of free chlorine above that required to oxidize nitrogen (particularly the organic nitrogen compounds), followed by addition of ammonia to form monochloramine.

iii. Chloramination System Design

Ammonia is available as the anhydrous gas (NH_3), as a 29% water solution (aqua ammonia), or in powdered form as ammonium sulfate $(NH_4)_2SO_4$. Gaseous ammonia is supplied in 150-lb (68.1 kg) cylinders (for small water systems), similar to gaseous chlorine. Aqua ammonia is supplied in 55 gallon

(208.33 L) drums. Ammonium sulfate is available in 100-lb (45.4 kg) bags (98% pure, 25% available ammonia).

Gaseous ammonia normally is added to the treated water using systems and equipment similar to those used for gaseous chlorine. Aqua ammonia and ammonium sulfate solutions are handled using systems and equipment similar to those for sodium hypochlorite and calcium hypochlorite solutions, respectively. Aqua ammonia is basic and odorous, but is non-corrosive.

Sizing of the treatment facility must take into consideration the intended 3:1 chlorine/ammonia ratio.

A 25% to 30% solution of ammonium sulfate in water is prepared in a plastic or fiberglass container and added to the water by means of a chemical metering pump. Solutions of ammonium sulfate are stable, but are acidic, and therefore can be corrosive to some metals. Materials which will withstand dilute sulfuric acid also will easily resist any possible corrosion effects of dilute ammonium sulfate solutions.

iv. Costs for Chloramination

Generation of chloramines requires the same equipment for chlorination (gaseous or aqueous hypochlorination) plus equipment for the addition of ammonia (gaseous or aqueous). Costs for chlorination equipment and for its operation and maintenance have been presented earlier. In this section, costs for addition of ammonia are presented.

During January 1983, costs for liquid ammonia were $0.40/lb (in 150-lb cylinders), $0.70/lb of contained ammonia in 28% solution (purchased in 55 gal drums), and $0.51/lb for solid ammonium sulfate (purchased in 100 lb bags), in the Washington, DC - Baltimore area.

Cost calculations given below are based on the following reaction of chlorine gas and ammonia to produce monochloramine:

$$NH_3 + Cl_2 \text{ ----> } ClNH_2 + HCl$$

In addition, the calculations assume a dosage of 2.5 mg/L of chloramine as the secondary disinfectant. This is the maximum level currently recommended by the EPA to be dosed into water supplies (U.S. EPA, 1987a). It is further assumed that the chloramines will be produced by adding ammonia to water already containing free available chlorine. Finally, cost calculations are based upon chlorine added as the gas. By using previously described calculations involving solutions of sodium hypochlorite or of calcium hypochlorite, the amounts of these chlorinating agents required to produce monochloramine can be calculated readily.

1. **Costs for Monochloramine From Anhydrous Ammonia + Chlorine Gas**

A 2,500 gal/day water treatment plant will require 0.05 lb/day (23.66 g) of monochloramine at a dosage of 2.5 mg/L. According to the stoichiometry of the above equation for the generation of monochloramine from ammonia and chlorine, each gram-molecular weight (weight of one mole of compound expressed in grams) of monochloramine will require 1 gram-molecular weight each of ammonia and chlorine. Thus:

$$17\ g\ NH_3 + 71\ g\ Cl_2 \text{ ----> } 51.5\ g\ ClNH_2 + 36.5\ g\ HCl$$

Since 23.66 g of monochloramine are required each day, the corresponding amounts of ammonia and chlorine required are:

Ammonia: (23.66/51.5) x 17 = 7.81 g/day

Chlorine: (23.66/51.5) x 71 = 32.61 g/day

Dividing the grams of each reactant by 454 (the number of grams per pound), gives a daily requirement of 0.017 lb of ammonia and 0.0715 lb of chlorine. Multiplying each of these figures by 365 days yields the annual number of pounds of ammonia and chlorine required. Finally, annual costs for each are calculated by multiplying the annual requirements by the current costs:

Ammonia: 0.017 lb/day x 365 = 6.205 lb/yr x \$0.40/lb = \$2.48/yr

Chlorine: 0.0715 lb/day x 365 = 26.10 lb/yr x \$0.47/lb = \$12.27/yr

The sum of these two numbers (\$2.48 + \$12.27) = \$14.75, total annual costs for the 2,500 gal/day facility.

A 1 mgd facility will require 400 times the amounts of chemicals at the same 2.5 mg/L dosage, therefore:

\$14.75 x 400 = \$5,898, annual chemical costs.

2. **Costs for Monochloramine From Aqua Ammonia + Chlorine Gas**

From the preceding calculations, the 2,500 gal/day facility will require 6.205 lbs/yr of anhydrous (gaseous) ammonia. If the source of ammonia is 28% aqueous ammonia, the calculation of costs is as follows:

1 gal of 28% ammonia weighs 8.34 lbs and contains 8.34 x 0.28 = 2.34 lbs of ammonia.

6.205 lbs/yr ammonia requires 6.205/2.34 = 2.55 gal/yr of aqua ammonia.

At $0.70/lb of ammonia contained in aqua ammonia, the annual cost of aqua ammonia is:

6.205 lbs x $0.70/lb = $4.35/yr.

The annual cost of gaseous chlorine is $12.27/yr, therefore the total annual chemical costs are:

$4.35 + $12.27 = $16.62/yr.

The 1 mgd water treatment plant will require 400 times the amounts of chemicals:

$16.62/yr at the 2,500 gal/day plant x 400 = $6,648/yr at the 1 mgd plant.

3. **Costs for Monochloramine From Ammonium Sulfate + Chlorine Gas**

One pound of ammonium sulfate contains 0.2576 lb (28.76%) of available ammonia. The 2,500 gal/day plant using solid ammonium sulfate will require 6.205 lbs of anhydrous ammonia annually. To obtain this amount of available ammonia requires 6.205/0.2576 = 24.09 lbs/yr of ammonium sulfate. At $0.51/lb, the 2,500 gal/day plant will require:

24.09 lbs/yr x $0.51/lb = $12.29/yr + $12.27 for chlorine = $24.55/yr.

The 1 mgd facility will require 400 times as much chemicals, or:
$24.55 x 400 = $9,820/yr.

3. Oxidants

a. Potassium Permanganate

Although potassium permanganate is not recommended as a primary disinfectant for coping with Giardia cysts or enteric viruses, it can be quite effective as a non-halogenated, preoxidizing agent for removal of many tastes and odors, colors, iron, manganese, sulfide, nitrite, and many dissolved organic materials. As such, the use of potassium permanganate in place of prechlorination can be viewed as a procedure to control disinfection by-products. The major supplier in the United States is Carus Chemical Company, P.O. Box 1500, LaSalle, IL 61301 (815-223-1500). Literature describing this versatile is readily available from this supplier.

This chemical is shipped as a solid, dark purple in color. It is readily soluble in water, and solutions of 1-4% in water are recommended for the treatment of potable water supplies. For example, to make a 4% solution, 0.33 pound of solid potassium permangante are added per gallon of water, and the mixture agitated 15-30 minutes using a 750-1000 rpm mixer.

Addition of permanganate solutions to the raw water or in the rapid mix is recommended for water treatment applications. This is because as the permanganate ion performs its oxidative work, it is converted into lower valent manganese compounds, which are insolble. Thus potassium permanganate is always added ahead of filtration.

To feed 1 mg/L of permanganate to the raw water using a 4% solution, the metering pump should be set to dispense 9.5 mL/min for every 100 gal/min of flow.

Figure 40 shows construction costs for potassium permanganate systems feeding 1 to 250 lbs/day. Figure 41 shows operation and maintenance requirements for potassium permanganate feed systems -- process energy and maintenance material. Figure 42 shows O&M requirements for labor and total O&M costs. These three figures are taken from Gumerman et al. (1986).

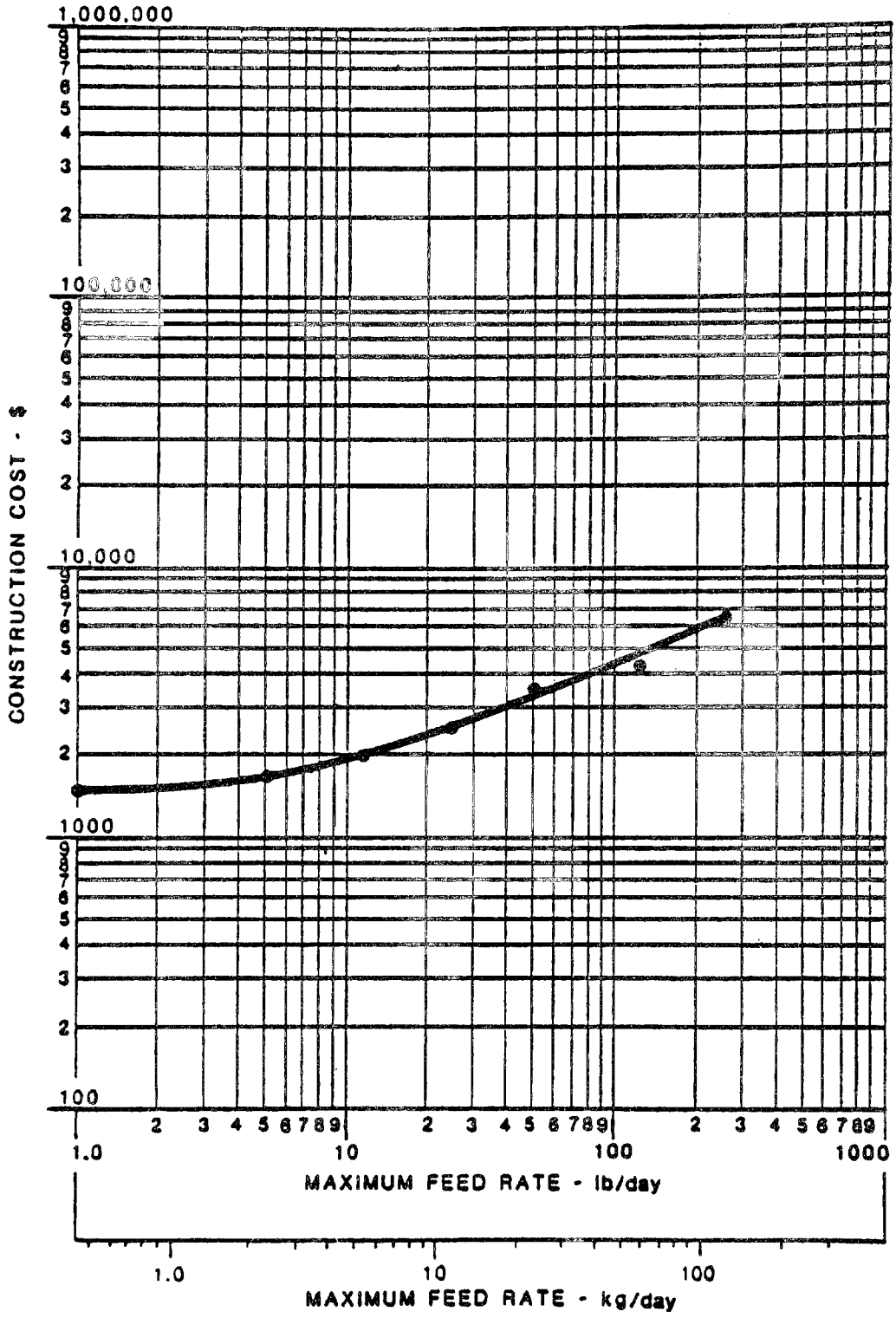

Figure 40. Construction cost for potassium permanganate feed systems (Gumerman et al., 1986).

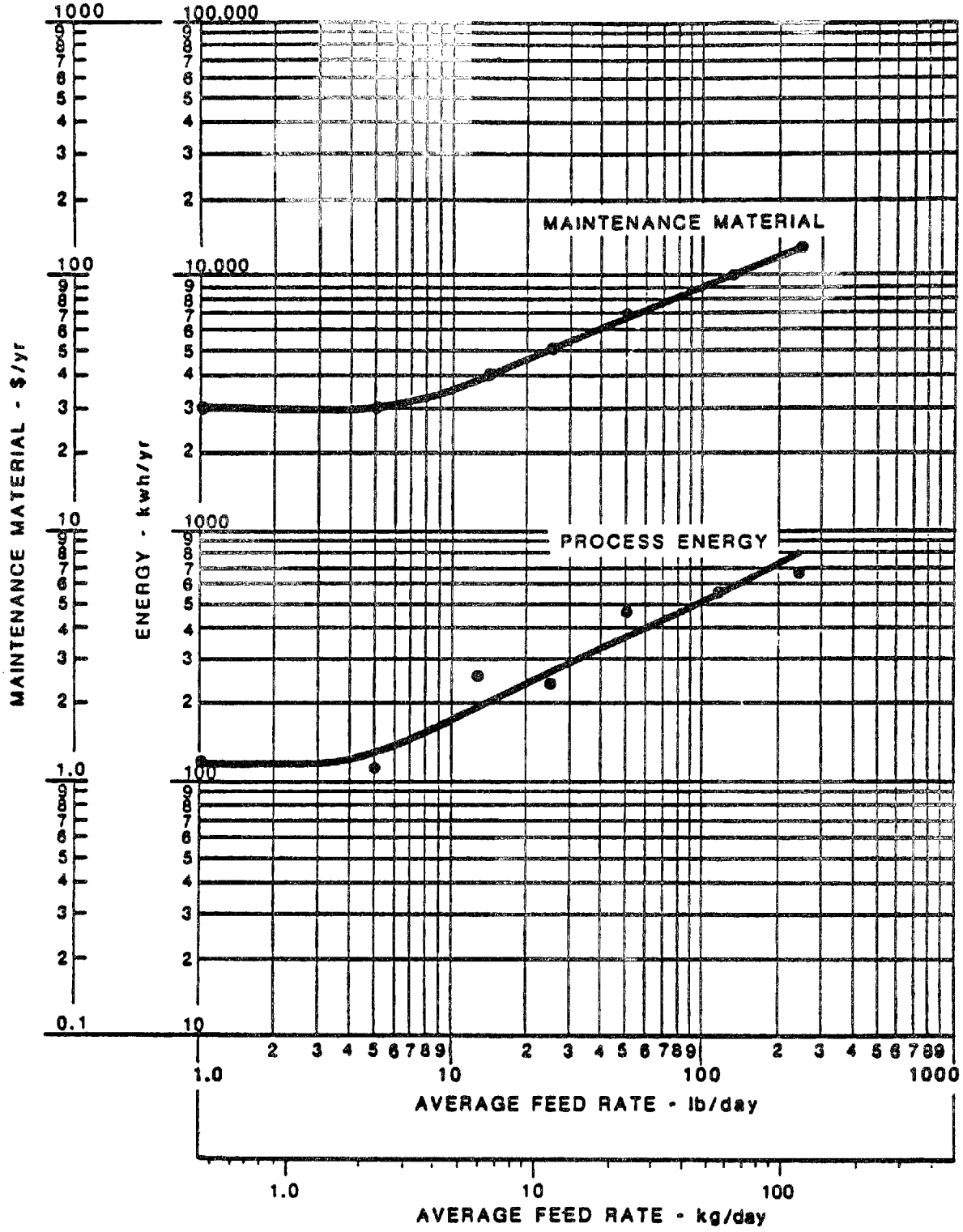

Figure 41. Operation and maintenance requirements for potassium permanganate feed systems -- process energy and maintenance material (Gumerman et al., 1986).

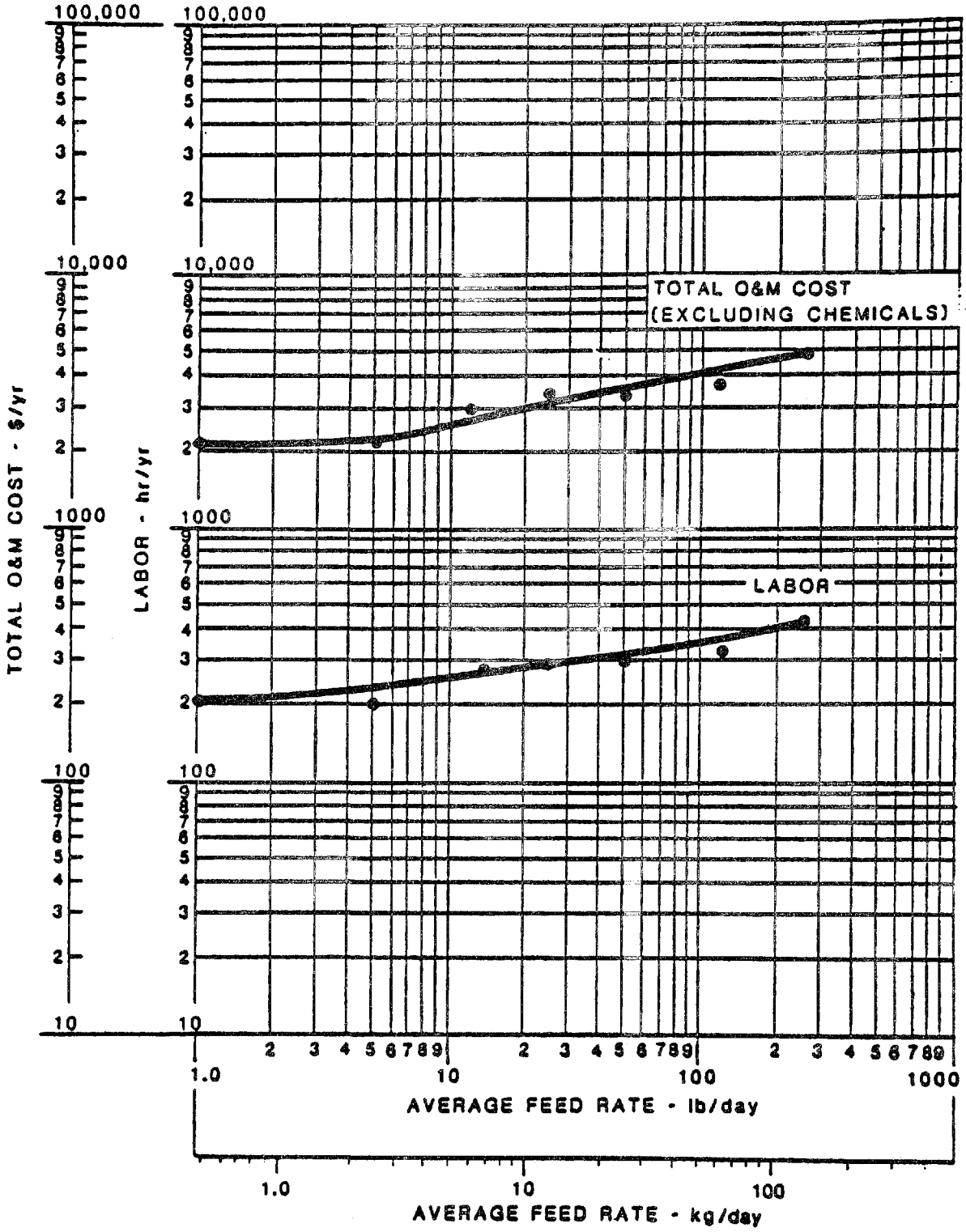

Figure 42. Operation and maintenance requirements for potassium permanganate feed ststems -- labor and total O&M cost (Gumerman et al., 1986).

VIII. CASE EXAMPLES OF EMERGING TECHNOLOGIES

Several examples of the use of disinfectants other than chlorine are presented in this section. The objectives of the different approaches described are (1) to attain the desired degree of disinfection and (2) to minimize the formation of disinfection by-products. Some of the examples illustrate changes in disinfection/oxidation techniques to cope with problems in addition to disinfection by-products, e.g., taste and odor, color, algae, etc.

Case histories presented include examples of the use of ozone as a primary disinfectant for controlling Giardia lamblia cysts at one plant and as a preoxidant for lowering THM levels at another.
Another case history involves a surface water treatment plant which has installed UV for primary disinfection, followed by chlorination for secondary disinfection.

Other examples involve uses of chlorine dioxide for preoxidation and for post-disinfection, of chloramines to lower THM concentration, and of combinations of chlorine dioxide and chloramine to lower THM concentrations.

A. OZONE CASE HISTORIES

1. North Andover, Massachusetts[1]

Ozone Disinfection for Giardia lamblia

a. The Problem

During early 1986, 18 cases of Giardiasis were reported in the North Andover area. On May 1, residents there were instructed to boil their tap water for at least five minutes while public health officials sought to locate and correct the problem.

North Andover's water supply, Lake Cochichewick, was found to contain Giardia cysts in samples taken in April 1986. Local officials confirmed that the lake's watershed has a large muskrat population, and there has been concern that residential septic systems were not working well enough to prevent harmful effects in the lake.

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[1]The author is indebted to Messrs. Ross Hymen and Paul Anderson of the Massachusetts Department of Environmental Quality Engineering, Mr. Tom Boshar of Lally Associates, the consultants on this project, and to Bill Nezgod and Dr. Carl Nebel, of PCI Ozone Corporation, suppliers of the ozonation equipment, for providing information for this case history.

At the time of the Giardiasis outbreak, treatment of North Andover water supply involved pumping of Lake Cochichewick water through two pumping stations into the distribution system without filtration, but with chlorination. Over the years, high humic concentrations have resulted in the formation of a significant scale in the pipes, containing a significant amount of biofilm as well.

Heavier chlorination overcame the immediate Giardia problem, but caused a second water quality problem. Descaling in the old distribution system piping released coliform organisms into the water supply. The presence of coliforms caused the State DEQE to continue the "boil water" notice until the coliform organisms could be shown to be absent.

In addition, THM levels of the heavily chlorinated water rose to above 200 μg/L. Also, residents began complaining about high chlorine concentrations. Ozonation was investigated and was found to have promise.

Total coliforms in Lake Cochichewick raw water normally are between 50 and 500 per 100 mL; raw water turbidities normally are between 1 and 2 NTU.

b. The Interim Solution

In early October, 1986, two ozonation systems (ozone generators, contactors, and exhaust gas destruction) began operating at the two Lake Cochichewick pumping stations in response to the emergency situation. Two discrete ozonation systems, one capable of generating 50 lbs/day of ozone, the second capable of generating 150 lbs/day, were rented from the ozonation equipment supplier for a period of time. Later, when the efficacy of ozonation was proven, the town purchased and installed two 150-lb/day ozonation systems in the two pumping stations.

Therefore, as an interim solution, the lake water is being treated with ozone at the two pumping stations. Each pumping station handles 2.5 to 3 mgd. At four points in the distribution system, chlorine is added to provide a residual disinfectant.

The state DEQE provided emergency funding of $2.5 million, which provided for the ozonation systems, for connecting pipelines to the three neighboring communities, for relining pipes with cement, and replacing water mains.

Rental fees for the two ozonation systems totaled approximately $90,000. The two 150-lb/day ozonation systems were purchased for $325,000. This fee included the air preparation system, ozone generation, diffuser contactors, and ozone destruction equipment, plus the appropriate instrumentation, including a monitor for measuring residual ozone at the outlet of the contact chamber.

These two ozonation systems were installed as a stop-gap measure to control Giardia cysts until a proposed $10.5 million water 12-mgd plant is designed and constructed, and which will provide complete treatment, including filtration and ozonation (in mid-1989).

The two ozone contacting chambers (each 10 ft wide x 20 ft long, with a 16-ft water depth) are designed with baffles, to provide each contactor with five complete mix ports, with ozone being applied equally in each section. Thus, there is plug flow throughout the ozone contactors. Applied ozone dosages are 5 mg/L.

At the outlet of each contact chamber, the concentration of ozone lies between 0.9 and 1.0 mg/L. System designers assume that the average ozone concentration in each contactor is 0.5 mg/L. Total residence time of water in the ozone contact chamber is 10 minutes at full pumping rate (summer time). During winter, with lower water demand, pumping rates are reduced by 50%, thereby doubling the residence time in the contactors to 20 minutes.

Water temperatures of the lake vary from about 5°C in winter to just under 20°C during summer. Therefore, the appropriate CT values listed in Table IIA for 99.9% inactivation of Giardia lamblia range from 3 to 1.5 mg/L-min. Assuming the average dissolved ozone concentration of 0.5 mg/L carried through the 10 minute contact period, the summertime CT value attained is 5 mg/L-min.

During winter, when the contactor residence time is 20 minutes, the CT value attained is 10 mg/L-min. Both of these CT values are well in excess of the 3 to 1.5 mg/L-min required to guarantee 99.9% inactivation of Giardia lamblia and 99.99% inactivation of viruses.

No filtration is provided during the current interim period. Instead, the community is placing total reliance on ozone for primary disinfection plus secondary disinfection with chlorine.

c. The Results

After approximately 90-days of ozone treatment, the State DEQE unconditionally lifted the boil water order, which had been in effect for nine months. Not only are Giardia cysts absent from the North Andover water supply, but also coliform organisms.

In addition, several additional benefits have been obtained as a result of installing ozonation. Prior to ozonation being installed, THM values were in the range of 8 to 120 μg/L. Since ozonation has been installed, THM values now are in the range of 1.1 to 2 μg/L. In addition, the color of the treated water has improved significantly (65% to 95% lower). Finally, taste and odor levels in the finished waters are greatly improved.

d. For The Future

As indicated earlier, a new 12-mgd conventional treatment plant, including ozonation and granular activated carbon adsorption, has been designed. Preozonation will be applied before the rapid mix. After dual media filtration, GAC adsorption is incorporated, followed by post-chlorination for residual. In addition to providing an adsorption capability, the GAC step

also will allow biological decomposition of the easily biodegraded organic fractions of the water present at that treatment point.

Bids were let for this plant in the summer of 1987; the plant is scheduled to be on-line by mid-1989.

e. Note - Sturgeon Bay, WI

A second plant is installing ozone specifically for controlling Giardia lamblia contamination in Sturgeon Bay, WI. This is a groundwater plant, without filtration, located on a Lake Erie shore, which has been shown to contain Giardia cysts. Water flow at this treatment plant is 100,000 gal/day. Water temperature is about 10°C the year round.

Two 4-minute residence time ozone contactors are being installed through which the water flows sequentially. After contacting, the ozone-containing water will be stored in a filling well. Thus, the total ozone contact time is estimated to be 10 minutes. Dissolved ozone concentrations at the outlet of both contactors will be adjusted to 1 mg/L.

Thus the CT value in the second ozone contact chamber will be 4 mg/L-min (4 minutes times 1 mg/L), plus a conservatively estimated 2 mg/L-min in the first chamber (0.5 mg/L times 4 minutes), plus an additional 1 mg/L-min in the filling well, during ozone decay from 1 mg/L. The total CT value designed is 7 mg/L-min. Table IIA requires a CT value of only 2.5 mg/L-min for 10°C.

The retrofitted ozonation system is expected to be operating in April/May 1988.

2. **Kennewick, Washington** (Cryer, 1986) - **Preozonation For THM Control**

a. The Problem

Prior to 1977, the City of Kennewick had been drawing essentially all of its municipal water supply from a system of five Ranney collectors located along the Columbia River, followed by chlorination. When initially installed, these were capable of producing approximately 20 mgd; however, their output had deteriorated to about 15 mgd by 1977. By 1978, the maximum daily system demand essentially had reached the capacity of the Ranney system. It was determined that direct utilization of the Columbia River would be the only reliable source of supply for long term development.

A consequence of this decision was the need to provide consider-ably more treatment to achieve the same or better finished water quality. Thus a pilot plant study was undertaken to test alternative water treatment processing steps. This study included the use of preozonation and of post-filtration GAC adsorption, in addition to conventional and direct filtration procedures.

Average values of the water quality parameters of the raw Columbia River are:

TTHM	1	µg/L
TTHMFP*	136	µg/L
TOC	2.4	mg/L
No. Particles	11,650	/mL
Particle Volume	160,700	nanoL/L
Turbidity	1.7	NTU

* Chlorine contact time: 1 week

b. Pilot Plant Study Results

Both the preozonation and coagulation/filtration steps provided approximately 30% reduction in levels of TTHM formation potential and 10% reduction in TOC levels. The combined processes gave approximately 60% reduction in levels of TTHMFP and 20% reduction in TOC levels. The preozonation/coagulation/filtration processes was determined to be operationally equivalent to activated carbon adsorption for the removal of THM precursors; it was also determined to be the most cost-effective method of treating organics in the Columbia River water supply.

c. Plant Design

Approval was given for a 30 mgd water treatment plant to be constructed in four stages of 7.5 mgd each, based on the following processing sequence: preozonation/flash mix/coagulation/flocculation/filtration and post-chlorination. Design criteria for the preozonation facilities are given in Table XXXIII.

At the point of application, ozone dosage rates were 1.5 mg/L (average) and 4.0 mg/L maximum. The contactors provide 10 minutes of detention time. Raw water total coliform levels are consistently less than 50 per 100 mL. Raw water turbidities are in the range of 1.5 to 2.0 NTU.

d. Operational Experiences

i. **General**

The new 7.5 mgd treatment plant currently is operated from May through October of each year, when system demand exceeds 10 mgd. For the balance of the year, water demand is about 8 mgd. This can be satisfied by the Ranney collector system, which operates at lower cost than the new treatment plant.

TABLE XXXIII. DESIGN CRITERIA FOR KENNEWICK WATER TREATMENT PLANT PREOZONATION FACILITIES (Cryer, 1986)

Item	U.S. Units	Initial	Ultimate	Metric Units	Initial	Ultimate
Plant Capacity						
Design Flow	mgd	7.5	30.0	m^3/day	28,300	113,300
	cfs	11.6	46.41	m^3/sec	0.33	1.33
	gpm	5,200	20,800	m^3/min	19.70	78.62
Ozone Contact Basins						
No. of basins		4	16		4	16
Detention time @ design flow	min	10	10	min	10	10
Basin dimensions-inside	ftxft	14x8	14x8	m x m	4.2x2.4	4.2x2.4
Av. water depth	ft	16	16	m	4.8	4.8
Basin volume	ft^3	1,792	1,792	m^3	50.75	50.75
	gal	13,400	13,400			
Total basin volume	ft^3	7,168	28,672	m^3	203	812
Chemical Feed Rate (Max. Dosage @ Design Flow)						
Ozone plant influent	lb/day	250	1,000	kg/day	113	454
Chemical Feeders						
Ozone	lb/day	2 x 125	3 x 250 2 x 125	kg/day	57	3 x 113 2 x 57
Chemical Storage Capacity (Max. Dose @ Design Flow)						
Ozone	No. O_3 generators	2	5	No. O_3	2	5
	Total lbs	250	1,000	Total kg	113	456

ii. Water Quality

Kennewick's new Columbia River Water Treatment Facilities came on-line in 1980. Generally, the City and the service area customers have been satisfied with the quality of water provided. Treated river water has a higher customer acceptance, judging by the limited number of complaints, than Ranney collector water alone.

THM analyses of the new treated water and chlorinated Ranney collector water indicate that the plant has been able to maintain the TTHM concentration below the current 100 μg/L standard, while the quality of water from the Ranney collector system remains very similar to the levels determined during pilot plant studies for raw Columbia River water. The City's Ranney collector waters have had an average THM concentration of approximately 107 μg/L, while the ozone treatment plant water has averaged approximately 14 μg/L.

iii. Applied Ozonation Dosages - Dissolved Ozone Residuals

Applied ozone dosage rates have ranged from 1.7 to 2.5 mg/L. Until 1983, ozone residual levels were maintained at approximately 0.5 mg/L exiting the contactor. In 1983, the City installed a dissolved ozone analyzer to control the ozone dosage, which has resulted in lowering the dissolved ozone residual concentrations to 0.1 mg/L, thus saving ozone, and still control biological growth in the filters and basins prior to chlorination.

iv. Ozone Equipment Operational Experience

Operationally, the ozone generation equipment has performed very well. The compressors have required only preventive maintenance. The ozone generators have required the replacement of only three burned out tubes during the first six years of operation. The major maintenance problem appears to be tube fouling which was found to be a result of high moisture in the feed gas. This situation was caused by two extenuating circumstances. After several years of operation, it was discovered that the refrigerant air dryer unit had developed a small leak which reduced the effectiveness of the air preparation system. It was then determined that the absorptive medium in the desiccant drier must be replaced when its regeneration capacity is reduced to 40% of its originally specified capability. Cleaning of dielectric tubes has become an annual maintenance procedure.

The only other significant operational problems concerned the ozone contactors. Excess foaming and scum production can occur during spring and late summer (algae destruction, primarily). This may require the installation of surface skimmers and froth spray equipment. In addition, the stainless steel tubes holding the ceramic diffusers corrode after about two to three years of use, and must be checked and occasionally replaced when the diffusers are cleaned.

v. Costs Of Ozonation

The Kennewick facility is able to produce ozone at approximately $0.20/lb. However, Cryer (1986) notes that the ozonation system has never been operated at 100% of the high voltage output, and that ozone generation efficiency has averaged approximately 16-17 kWh per pound of ozone produced.

Based upon the City's very limited experience in operating the facility during periods of time when the ozonation system has been off-line, the plant operator believes that the addition of ozone prior to flocculation/filtration results in a savings in flocculation chemicals of approximately 10%.

Currently, the treatment plant is producing finished water at a cost of approximately $14.10 per million gallons ($0.141/1,000 gallons).

e. Implications of Proposed Surface Water Treatment Rule Disinfection Conditions

During the May/October period of plant operation, the temperature of the waters treated is approximately 20°C. With a 10 minute ozone contacting time, and assuming an average residual ozone concentration of 0.5 mg/L (as was the case until 1983), the CT value of 5 mg/L-min was being obtained, compared with a value of 1.5 mg/L-min required (Table IIA) by the proposed SWTR for 99.9% inactivation of Giardia lamblia cysts and 99.99% inactivation of enteric viruses at 20°C. On the other hand, because the Kennewick plant filters (thereby providing 2-logs of Giardia inactivation), only a single log of additional Giardia inactivation is required. This means (Table IIB) a CT value of less than 0.7 mg/L-min, which corresponds to an ozone contact time of only 1.4 minutes at the same residual ozone concentration.

After filtration, gaseous chlorine is added. A residual of 0.6 mg/L free chlorine is maintained for 60 minutes at pH of approximately 8.0. The contribution of chlorination to the required disinfection CT value thus is 36 mg/L-min. From Table IIA, the CT value for chlorine at pH 8.0 and 20°C is 101 mg/L-min.

Therefore, maintenance of the 0.5 mg/L ozone residual for 10 minutes provides over 300% of the required disinfection capability, without reliance on the post-chlorination. In addition, post-chlorination provides a supplemental 36% disinfection credit (36/101).

However, since 1983 the ozone residual concentration leaving the ozone contact chambers has been reduced to 0.1 mg/L. Assuming this ozone concentration is present throughout the 10 minutes of ozone contacting, a CT value of only 1 mg/L-min is obtained, versus the 1.5 mg/L-min required by Table IIA. This means that only 67% of the disinfection capability is provided by the preozonation step to achieve 99.9% inactivation of Giardia, but 130% of the inactivation required to obtain 90% additional inactivation because of the filtration capability. The 60 minute chlorine contact time at pH 8.0 (0.6 mg/L) provides an additional 36% of the required disinfection.

This means that the plant currently provides at least 100% of the amount of disinfection stipulated under the proposed Surface Water Treatment Rule, disregarding the contribution of filtration.

B. UV RADIATION CASE HISTORY

1. Ft. Benton, Montana [2]

UV Radiation for Primary Disinfection

a. The Problem

The City of Ft. Benton, MT takes water from the Missouri River and treats it in a 20-30 year old filtration plant. This plant needed to be upgraded. Costs for installing a new filtration plant were deemed to be excessive.

b. The Solution

A new 2 mgd peak flow treatment plant was installed in mid-1987. Water is drawn through Ranney collectors installed 20-25 feet below the river bed. This allows the river bed to filter the raw water. Turbidities of water entering the treatment plant average 0.08 NTU. No Giardia cysts have been found in the filtered river water.

Plant intake water is treated with UV radiation for primary disinfection, then chlorinated for residual. If chlorination were to be relied on for primary disinfection, a 2-hour contact time would be required by the State authorities. Even a 30-minute contact time would require two-stage pumping with long concrete pipes to provide sufficient contact time.

After primary UV disinfection, the water is chlorinated to a 1 mg/L residual with no contact time. The water being chlorinated is quite clean, in that the applied chlorine dosage is just over 1 mg/L. The pH is about 7.4 and the water temperature is approximately 20°C year around.

The entire water treatment process is housed in a 32 x 32 ft building.

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[2]The author is indebted to Fred Zinnbauer of Aquionics, Incorporated, Erlanger, KY (supplier of the UV radiation equipment) and to Gary Swanson, Project Engineer at Robert Peccia Associates, Helena, MT, consultants for this project, for information on this plant.

c. UV Radiation Conditions

The UV disinfection system consists of six irradiation chambers, two control cabinets with alarms, chart recorders, relays, hour-run meters, lamp and power on-lights, six thermostats, electrical door interlocks, mimic diagrams, and six UV intensity motors measuring total UV output.

Four irradiation chambers are on-line at all times, with two chambers reserved for backup. The alarm system is tied into the automatic butterfly valves to provide for a fully automatic backup system. Each irradiation chamber contains one 2.5 kW mercury vapor, medium pressure arc tube, generating UV radiation at 253.7 nm.

The initial UV dosage is 41,000 μW sec/cm^2 at maximum water flow (1,650 gal/min) through each irradiation unit. Expected arc tube life is 4,500 operating hours providing a minimum UV dosage of 25,000 μW sec/cm^2. These conditions are designed to reduce concentrations of E. coli organisms by a minimum of 5-logs (10^5 reduction).

The UV irradiation system is interfaced with the telemetry control system activated when the low tank pump start set-point is activated on the set-point controller. Sufficient warmup time is maintained before pump startup is initiated. The UV system is deactivated once the high tank stop set-point is activated on the set-point controller and the pump stops running. Sufficient time delay is built into the system to ensure that water flow is completely stopped before the UV system is deactivated.

A fully automated backup system is provided. Each bank of three irradiation chambers has two units on-line at all times, with the third unit serving as backup. In the event that the UV intensity drops below acceptable limits (20,000 μW sec/cm^2) in any of the chambers, the automatic butterfly valve will close, stopping flow through the chamber; the automatic butterfly valve on the standby unit will open. The alarm system also is activated if UV intensity drops below acceptable limits in any of the chambers. The UV alarm system is interfaced with the automatic dialer and alarm system. Replacement of the UV lamps is quite simple, requiring no more than a few minutes.

d. Costs

Total equipment costs for the 6-unit UV irradiation system with butterfly valves was $74,587.

e. Operating Experience

The new Ft. Benton water treatment plant started up in July 1987; no operational data are yet available.

C. CHLORINE DIOXIDE CASE HISTORIES

1. Evansville, Indiana (Lykins & Griese, 1986) Predisinfection for THM Control

a. The Problem

Because of the November 1979 amendment to the National Interim Primary Drinking Water Regulations (U.S. EPA, 1979), the Evansville (Indiana) Water and Sewer Utility was faced with reducing the levels of trihalomethanes in their finished drinking water. At the time, raw water was being prechlorinated and treated with alum prior to primary settling, treated with lime (to pH = 8), passed through secondary settling, fluoridated, rapid sand filtered, then post-chlorinated before passage into the clearwell. The treatment process was conducted in two separate 30 mgd treatment lines (total production 60 mgd), and THM levels exceeded the THM standard of 100 μg/L. Prechlorination doses averaged 6 mg/L. Distribution system residence time averages three days.

b. Pilot Plant Study

With the assistance of a cooperative agreement from the Environmental Protection Agency (CR811108 - Sept. 1983), the Evansville utility initiated research to evaluate the use of chlorine dioxide in a 100-gal/min pilot plant adjacent to the full-scale plant. One train of the full-scale treatment plant served as the control for the pilot plant study.

The pilot plant study was conducted in two phases, optimization, and long-term. Chlorine dioxide was substituted first for prechlorination, then for post-chlorination. GAC adsorption also was evaluated prior to the post-chlorination step.

i. Optimization Phase

When predisinfection was eliminated and the pilot plant effluent was disinfected and stored three days (to simulate distribution system residence time), TTHM concentrations averaged 141 μg/L with chlorine post-disinfection (2.5 mg/L residual chlorine concentration), and 1.2 μg/L with chlorine dioxide post-disinfection (1.9 mg/L residual).

Predisinfection with chlorine dioxide to maintain a residual through the pilot plant did not increase the THM concentration and provided adequate disinfection. The ClO_2 residual decreased from 4 to 0.3 mg/L through the pilot plant.

ii. Long-Term Evaluation

In this phase the pilot plant procedures were evaluated during each season of the year to determine the extent of seasonal effects. In this phase of

the study, predisinfection with chlorine dioxide (1.1 mg/L average applied dosage) reduced the amount of THMs formed during post-chlorination by approximately 60%. The concept of post-disinfection with chlorine dioxide was abandoned because of the difficulty in maintaining a disinfectant residual in the distribution system (three days average residence time), keeping in mind that the current EPA recommendation is that total oxidants from application of chlorine dioxide should not exceed 1 mg/L in the distribution system. The average chlorine residual concentration in the clearwell was 2.1 mg/L.

c. The Full-Scale Plant

Based on data obtained from the pilot plant study, Evansville utility officials concluded that the MCL for TTHMs would be exceeded if the then-current treatment was not altered. Changing the primary disinfectant from chlorine to chlorine dioxide was judged to be the most effective procedure for control at the least cost. A separate building was constructed to house the chlorine dioxide generation facility, One portion contains the ClO_2 generator, a second portion houses two 1-ton cylinders of chlorine.

This installation is capable of generating 14.24 lbs of ClO_2 per hour, which can be divided in any proportion between the two halves of the treatment plant. Gaseous chlorine and 25% $NaClO_2$ solution are delivered to the chlorine dioxide reactor under partial vacuum generated by an eductor. Both reagent flows are controlled by flow-rate meters, and the system is designed to shut down if the eductor water supply fails or if chemical feed lines break.

This production rate has been achieved with over 95% conversion to ClO_2 over the first 18 month period of operation.

d. Operating Experience

Chlorine dioxide began being added as a predisinfectant prior to any additional chemical treatment in August 1983. The ClO_2 produced is divided evenly between the two treatment lines. During the first five months of use, various ClO_2 dosage levels were used to determine the resultant reductions in THM concentrations, to gather data on what percentage of the ClO_2 dosage would appear as total oxidant residuals in the finished water, and to review the general operation of the entire system.

During this period, only one major problem was encountered. Brass corporation cocks used to connect the PVC ClO_2 feed lines to the raw water influent piping were oxidized by the concentrated disinfectant. This oxidation and subsequent leaking of ClO_2 solution resulted in temporary disruption of the new treatment technique. The problem was resolved by sliding a section of PVC pipe through new corporation cocks into the main stream of the raw water lines. This modification permitted the PVC piping to serve as an inductor while preventing direct contact of the brass corporation cocks with concentrated ClO_2 solution.

Since the implementation of the treatment change, total oxidant levels from chlorine dioxide have been maintained consistently below the 1.0 mg/L recommended by the U.S. EPA. With an average applied ClO_2 pretreatment dosage of 1.2 mg/L, total oxidant concentrations in the finished water have averaged 0.5 mg/L. These data show that approximately 42% of the ClO_2 dosage is present as total oxidant.

Since the installation of predisinfection with chlorine dioxide at Evansville, annual TTHM levels in the distribution system have been maintained between 50 and 80 μg/L.

e. Implications of the Proposed Surface Water Treatment Rule

Raw water total coliform levels at Evansville are in the range of 3,400 to 5,400 per 100 mL. The filtration system provides 2-logs of Giardia and virus inactivation. However, because of the higher raw water total coliform levels, EPA recommends (U.S. EPA, 1987d) that primary disinfection be provided to attain 99.9% inactivation of Giardia and 99.99% inactivation of viruses, in addition to those provided by filtration.

Chlorine dioxide predisinfection at Evansville employs a dosage of 1.2 mg/L, followed by chlorination in the clearwell at an average concentration of 2.1 mg/L. Although the contact time after adding ClO_2 is not stated in the reference, attainment of the required CT value of 21 mg/L-min at 20°C (Table IIA) and an average ClO_2 concentration of 1.0 mg/L means that a 21 minute contact time would provide 99.9% inactivation of Giardia cysts and 99.99% inactivation of viruses, independently of the added degree of disinfection which can be credited to post-chlorination. Since the average total oxidant (from chlorine dioxide) concentration in the plant finished water is 0.5 mg/L, an actual CT value of 10.5 mg/L-min would be expected in a 21 min contact time. This represents about 50% of the required degree of primary disinfection.

With respect to post-chlorination, at an average 2.1 mg/L chlorine residual in the clearwell at pH 8 (CT value = 101 mg/L-min at 20°C) means that a contact time of 48 minutes would be required to provide 99.9% inactivation of Giardia cysts and 99.99% inactivation of viruses. If only a 30-minute clearwell contact time is provided, still 63% of the required disinfection is provided by chlorine in the clearwell. Therefore, it is likely that the required amount of disinfection, even with the high level of raw water total coliforms present, is attained from both the chlorine dioxide and chlorine disinfection steps.

2. **Hamilton, Ohio** (Augenstein, 1974; Miller et al., 1978; U.S. EPA, 1983)

Primary/Secondary Disinfection With Chlorine Dioxide

a. The Problem

In 1956 a 15 mgd lime softening plant began operating in Hamilton, OH treating groundwater (18 wells, 200 ft deep). Chlorine was used as the sole disinfectant when the plant started operating. However, because of customer complaints of chlorinous tastes and odors, a change was deemed necessary. Chlorine dioxide was tested, and in 1972 this material was substituted for chlorine for primary and secondary disinfection.

b. The Treatment Process

Hamilton's treatment process in 1987 is as follows: aeration, lime addition, flash mixing, sedimentation, recarbonation (with food grade CO_2), filtration, fluoridation (sodium silicofluoride), disinfection (with ClO_2), clearwell storage. Raw water turbidities are below 1 NTU, and raw water total coliforms are less than 1 per 100 mL.

c. Generation of Chlorine Dioxide

Chlorine dioxide is generated by mixing 37% aqueous sodium chlorite and aqueous chlorine in a ratio of 1:1 by weight (2 lbs of each reagent per million gallons of water to be disinfected). This provides an applied ClO_2 dosage of 0.25 mg/L. Chlorine gas is delivered to the site in 150-lb cylinders. Aqueous $NaClO_2$ solution (37%) is delivered in 200-lb drums.

The chlorine dioxide generation system consists of one plant-fabricated reactor vessel for ClO_2 production, one peristaltic pump for $NaClO_2$ solution, two chlorinators (one serves as standby). Two 150-lb liquid chlorine cylinders are positioned next to the chlorinators. The weight of the cylinder contents is measured by a scale. Switchover from one cylinder to the other is manual. PVC tubing is specified between the chlorinator and ClO_2 reactor vessel; heavy Tygon tubing transports the $NaClO_2$ solution from the drum to a small plastic day-tank and to the reactor vessel. This Tygon tubing loses its rigidity and must be replaced after about a month of use. The semi-transparent day tank allows visual inspection of the level of liquid $NaClO_2$ and thereby enables the operator to maintain an acceptable suction head on the peristaltic pump.

The chlorine dioxide reactor vessel is constructed of Schedule 80 PVC piping, 18 inches high and approximately 6 inches in diameter. The vessel is filled with PVC rings, 1-inch in diameter. The chamber is opaque except for the sight glass mounted in-line on the discharge piping. A white card is positioned behind the sight glass for better observation of the ClO_2 color.

Applied dosage of ClO_2 in the clearwell is 0.25 mg/L. The residual leaving the clearwell is approximately 0.15 mg/L, and is 0.10 mg/L at the extremities of the distribution system.

d. Effects of Installation of Chlorine Dioxide

Prior to installation of ClO_2, customers had complained about brown stains (iron) during washing of clothes. When ClO_2 treatment was initiated, brown slimes were loosened from the mains. Plant personnel then flushed the distribution system. Shortly thereafter, the brown stain problems disappeared, and complaints ceased. Plant personnel attributed the source of the problem to crenothrix and leptothrix bacteria (iron bacteria) that had been present in the extremities of the distribution system before introduction of chlorine dioxide.

Since 1972, ClO_2 has been the sole disinfectant in Hamilton's drinking water.

e. Costs for Chlorine Dioxide

In 1977, the costs for ClO_2 in Hamilton were determined (Miller et al., 1978) to be about 3.6¢/capita/year. Chlorine and $NaClO_2$ together cost $6,540/yr (1977). Total chemicals costs in 1977 for the finished water averaged 19¢/1,000 gal; the fraction due to ClO_2 was considered negligible. The operating and maintenance costs for ClO_2 generation at Hamilton were estimated to be less than $50/yr in 1977. The plant-fabricated ClO_2 reactor, piping, hardware, and installation were estimated by the plant supervisor to cost around $400 in the 1977 market. Installation was done by plant personnel. The peristaltic pump for $NaClO_2$ solution cost less than $200 (1977). To this must be added the cost of the two chlorinators ($600), which were already on line at the plant.

f. Implications of the Proposed SWTR CT Values

Although the Hamilton raw water is groundwater, and therefore probably will not be subject to the requirements of the proposed Surface Water Treatment Rule (U.S. EPA, 1987a), it is interesting to consider the effects if such disinfection requirements as listed in Table IIA were to be levied on this water supply system.

Chlorine dioxide is added to the Hamilton water in applied doses of 0.25 mg/L as it enters the clearwell. The water temperature is about 20°C year round, and the pH is 9.4 to 9.5. Hamilton's first customer is located about 0.5 mile from the plant. Thus there is very little contact time in the distribution system.

The plant filters efficiently, and therefore only 1-log additional inactivation of Giardia cysts and 2-logs inactivation of viruses need be provided by the chlorine dioxide. Table IIB shows that at 15°C, a CT value of 9 mg/L-min will provide the required degree of disinfection.

The Hamilton clearwell holds 500,000 gallons. During periods of high water use, water is produced at the rate of 19 mgd. In periods of low water use, only 8 mgd are produced. Thus the contact time in the Hamilton clearwell ranges from 30 to 90 minutes, at the high and low production rates, respectively. Assuming that the average concentration of ClO_2 in the clearwell is 0.2 mg/L, then the CT values provided are 6 and 18 mg/L-min, respectively.

Thus the current disinfection conditions using chlorine dioxide meet the proposed CT requirements, except at the most rapid production of water, when only two-thirds of the disinfection capability is provided by ClO_2 in the clearwell. However, simply increasing the ClO_2 dosage by one-third (i.e., to 0.32-0.33 mg/L) during periods of highest flow will provide the additional amount of disinfection required by the proposed SWTR.

3. Galveston, Texas (Myers et al., 1986)

Preoxidation With ClO_2
Post-Disinfection With ClO_2 + Chloramine

a. The Problem

The Galveston County Water Authority (GCWA) owns and operates an 18 mgd capacity water treatment plant in Texas City, TX, currently (1986) producing 12 mgd of finished water from the Brazos River. Raw water characteristics include high color, variable turbidities (68-111 NTU), high organic contents, high iron (2.7-3.8 mg/L), and seasonally high algae content, sometimes reaching levels of 5,000 blue/green algae/mL. Such high algae and organic contents create the potential for unpalatable tastes and odors to develop during treatment and distribution.

Total trihalomethane formation potentials for Brazos River water, measured periodically during September 1983 through April 1984 (20-day chlorination period), were in the range of 400 to 650 μg/L. Finished water THM concentrations measured during the same period were in the range of 180 to 350 ug/L. During periods of intermittent raw water algae blooms and associated high organic carbon contents, numerous consumer complaints were received regarding tastes and odors.

These problems prompted an investigation of alternative disinfectant strategies.

b. The Original Treatment Process

The treatment process included addition of cationic polymer for primary coagulation, lime for pH adjustment, prechlorination for taste and odor control, and ferric sulfate as a flocculant aid prior to upflow reactor/-clarifiers. These provide the dual functions of flocculation and sedimentation. Dual media filtration follows, then disinfection (chlorination

to a 2.4-5.0 mg/L total available chlorine residual in the finished water), and fluoridation.

c. Study of Alternatives

Chloramines and chloride dioxide were selected for further study and pilot plant testing. Ozone was eliminated from further study because of implementation considerations. Also, ozone does not maintain a residual during distribution, and therefore would require the use of a secondary disinfectant anyway. Chlorine dioxide for both preoxidation and post-disinfection achieved the goals of GCWA better than did chloramines (poor preoxidant).

Preoxidation/post-disinfection combinations were studied in the following sequences:

Phase 1) Chlorine/chlorine

Phases 2a & b) Chloramine/chloramine

Phase 3) Chlorine dioxide/chlorine

Phase 4) Chlorine dioxide/chlorine dioxide

Phase 5) Chlorine dioxide/combined chlorine + chlorine dioxide, and

Phase 6) Chlorine dioxide/combined chloramine + chlorine dioxide.

i. Study Results

Phase 1: Chlorine - Chlorine

Finished water exhibited intermittent algae-related taste and odor, and THM levels were in excess of federal standards (350 μg/L); however bacterial quality was excellent. This approach was abandoned.

Phases 2a and 2b: Chloramine - Chloramine

Phases 2a and 2b employed chlorine:ammonia weight ratios of 3:1 and 7:1, respectively. Although THM levels were lowered to about 60 μg/L, bacterial counts for coliforms demonstrated that confluent growth was occurring on several cultures, indicating that inadequate residual was being maintained in the distribution system (3:1 chlorine:ammonia ratio). This approach was abandoned.

The experiments were repeated using the 7:1 chlorine/ammonia ratio. Acceptable bacterial quality was achieved, but numerous taste and odor complaints were received during this period. This approach was abandoned.

Phase 3: Chlorine Dioxide - Chlorine

Chlorine dioxide was installed in May 1984, using a generator with a conversion efficiency (chlorite ion to ClO_2) of approximately 80%. After ClO_2 preoxidation, the clarified water showed no traces of THMs. No taste and odor complaints were received, despite very high raw water algae counts (up to 5,000 blue/green algae/mL). However, finished water THM levels sometimes persisted above 100 μg/L.

In November 1984, a chlorine dioxide generator with a 98+% conversion efficiency was installed, and this phase was continued for an additional two months. THM levels averaged 102 μg/L), and no taste and odor complaints were received. This approach was abandoned.

Phase 4: Chlorine Dioxide - Chlorine Dioxide

This approach of using chlorine dioxide both as the preoxidant and post-disinfectant was authorized on an interim basis by the Texas Department of Health in early March 1985 with the stipulation that a maximum ClO_2 residual of 1.0 mg/L be maintained and that finished water quality be monitored throughout the distribution system.

Finished water THM concentrations during the test period averaged 60 μg/L, and finished water turbidities were the lowest of any of the alternative disinfectant scenarios. Bacterial counts generally were excellent, but intermittent elevated counts were noted at three different points in the distribution system: at the clearwell, and at locations 2 and 5 miles from the plant.

Additionally, the bacterial species distribution also changed upon ClO_2 disinfection, both at the plant and in the distribution system. Bacterial counts displayed a shift from orange to yellow-staining gram negative (-) rods to white-staining gram positive (+) rods, similar to slime-forming Bacillus (sp.).

This approach, although promising, also was abandoned.

Phase 5: Chlorine Dioxide - Combined Chlorine + Chlorine Dioxide

Phase 4 was repeated except that chlorine was applied in conjunction with ClO_2 until the bacteria could be identified. Excellent bacterial quality was obtained. The bacterial plate counts remained at or below the guideline of 500 colonies per 100 mL for all monitoring locations. The shift in bacterial species distribution continued as the plate counts decreased, so that over 95% of all colonies examined were either yellow gram (-) rods or white gram (+) rods.

Finished water THM levels rose to an average of 81 μg/L. This approach was rejected, in favor of Phase 6.

Phase 6: Chlorine Dioxide - Combined Chloramine + Chlorine Dioxide

This phase was implemented on December 6, 1985. With this post-disinfection combination, finished water THM levels averaged 68 μg/L, and the bacteriological quality remained excellent. No coliforms were found in the clearwell or in the distribution system during this phase, and bacterial counts have ranged from < 1 to 30 colonies per 100 mL. Of those colonies identified, over 95% were the white-staining, gram (+) Bacillus (sp.) variety with less than 1% belonging to the orange-staining gram (-) type.

d. The Results

Preoxidation with chlorine dioxide and post-disinfection with ClO_2 in combination with either chlorine or chloramines has provided effective taste and odor control, maintained an active disinfectant residual and mitigated THM formation (to a current level of about 68 μg/L).

Chlorine dioxide preoxidation has proven to be an excellent algicide and biocide. The effectiveness of ClO_2 in removing algae in flocculation/-sedimentation has been demonstrated in a decrease in filter fouling and improved finished water turbidities since implementing its use.

Odors experienced at the flocculating clarifiers and taste and odor complaints in the distribution system have been reduced. The unexpected benefit of improved treatment plant performance has been maintained for at least the first seven months of operation of the treatment modifications. Finished water turbidities decreased from an average range of 0.3 to 0.65 NTU during 1983 (chlorine pre- and post-treatment) to 0.09 to 0.2 NTU in 1986.

Bacterial counts using the membrane filter method for coliforms have declined to excellent levels. Since the advent of ClO_2 post-disinfection, all bacterial counts obtained from samples collected at the GCWA distribution point have been below 30 colonies/100 mL, and all but two samples have been below 10 colonies/100 mL. This indicates a substantial residual present at that distribution system point. The bacterial counts obtained from the GCWA distribution system continually are below the guideline of 500/mL, and often are below 5 colonies/100 mL, indicating the maintenance of a good, active residual.

The Galveston County Water Authority has successfully implemented the first chlorine dioxide disinfection program in the State of Texas.

C. CHLORAMINE CASE HISTORIES

1. Bloomington, Indiana (Singer, 1986)

Prechlorination, Post-Chloramination

a. The Problem

Bloomington takes its water from a lake having TOC levels of 4-6 mg/L. This water is treated by conventional coagulation with alum, flocculation, sedimentation, and filtration through pressure filters. Prior to September 1984 the utility applied chlorine to the raw water and again ahead of the pressure filters. Average chlorine dosages were 1.8 and 1.0 mg/L, respectively. Typical average TTHM concentrations reported by the utility as part of its quarterly compliance monitoring program were as follows:

March 1983	77 μg/L
June 1983	168 μg/L
Sept 1983	142 μg/L
Dec 1983	50 μg/L
March 1984	79 μg/L
May 1984	113 μg/L

It is clear that the current 100 μg/L TTHM running annual average standard was being exceeded.

b. The Solution

In September 1984, the Bloomington water utility changed from post-chlorination to post-chloramination. An average 0.54 mg/L of ammonia was applied along with 1.5 mg/L of chlorine ahead of the pressure filters. The desired residual chlorine concentration leaving the plant of 1.0 mg/L of free chlorine was changed to 1.5 mg/L of combined chlorine.

c. Performance

Quarterly compliance monitoring data for TTHMs subsequent to the changeover are as follows:

Sept. 1984	47 μg/L
Dec. 1984	24 μg/L
Feb. 1985	43 μg/L
April 1985	56 μg/L
Aug. 1985	57 μg/L

Clearly, TTHM concentrations have been brought down to about 50 μg/L from well over 100 μg/L.

Table XXXIV summarizes THM and TOX (Total Organic Halide) data for samples collected as major points in the treatment system when chlorine

alone was used for pre- and post-treatment. The data show that TOX levels increased in parallel with increases in TTHM levels. Table XXXV summarizes similar data taken using combined chlorine residuals. These data show that although the TTHM formation ceases after the addition of ammonia, the production of TOX continues, although at a greatly reduced rate. This illustrates that as EPA sets MCLs for additional halogenated organic materials other than THMs, utilities opting for post-chloramination must plan to determine the makeup of their TOX fraction.

TABLE XXXIV. SUMMARY OF THM DATA AT BLOOMINGTON, INDIANA WITH FREE CHLORINATION 8/16/84 (Singer, 1986)

Sampling Point	Residual Free Chlorine, mg/L	TOC mg/L	TTHM μg/L	TOX μg/L
Raw Water	---	4.3	1	23
Settled Water	0.25	3.6	48	127
Filtered Water	1.0	2.4	81	205
Dist. System #1	1.8	---	110	291
Dist. System #2	0.65	---	151	363

TABLE XXXV. SUMMARY OF THM DATA AT BLOOMINGTON, INDIANA WITH POST-CHLORAMINATION 8/26/85 (Singer, 1986)

Sampling Point	Residual Chlorine, mg/L	TOC mg/L	TTHM μg/L	TOX μg/L
Raw Water	---	4.1	0	17
Settled Water	Trace, Free	2.8	53	94
Filtered Water	1.2 Combined	2.8	55	91
Dist. System #1	1.0 Combined	---	52	115
Dist. System #2	0.9 Combined	---	57	116

Since switching to post-chloramination, the utility has experienced no adverse effects in operations or in finished water quality. According to distribution system monitoring records, the microbiological safety of the water has been maintained.

2. **Philadelphia, Pennsylvania** (McKeon et al., 1986)

Pre-Chlorine Dioxide + 1-Hour Prechlorination
Post-Chloramination

This is a case history which is still evolving, but one which has resulted in modifications to attain current regulatory and water quality objectives. However, the types of studies which have been conducted by the Philadelphia Water Department point to the directions this utility probably will take in response to continued tightening of federal regulations and changes in water quality.

a. The Problems

The Baxter Water Treatment Plant (formerly called Torresdale), was built in 1960 on the site of a slow sand filtration plant that had been in service since 1903. The current plant is rated at 282 mgd, and supplies potable water to over 800,000 people, from the Delaware River by conventional treatment.

Chemicals fed routinely include chlorine, ferric chloride or ferrous sulfate, lime, fluoride, and ammonia. Powdered activated carbon is fed on demand for control of taste and odor events, and chloride dioxide is fed currently for control of THMs and tastes and odors. The ClO_2 feed system was incorporated in the original plant design in the 1950s to oxidize phenolic compounds found in the watershed. Since that time, the sources of phenol have been eliminated and the ClO_2 feed system has found use as part of the program to reduce concentrations of trihalomethanes.

Prior to 1976, the Baxter plant practiced breakpoint chlorination at the raw water basin and maintained free chlorine in the distribution system. From raw water chlorination to the consumer, a total of 96 hours of free chlorine contact time normally elapsed.

Initial analyses for THMs in 1978 showed peak concentrations above 300 μg/L with a running annual average of 140 μg/L. In light of these results, the Philadelphia Water Department began to reevaluate its disinfection strategies. The selection of an alternative disinfectant strategy at the Baxter plant not only must take into consideration bacterial kills, but taste and odor control, suppression of algae, corrosion control, residual duration, and economics.

This case history reviews Philadelphia's experiences over ten years in modifying chlorination practices, and the problems which surface with reduction of chlorine contact time.

b. Process Modifications

Initial efforts to reduce formation of THMs concentrated on reduction in free chlorine contact times. From the original 96-hour free chlorine contact time, today (1986) chlorine contact time has been reduced to 1-hour.

i. Chloramination of Finished Water (Reduction of Free Chlorine Contact Time from 96-hours to 24-hours)

Chloramination of the finished water was initiated in 1976. Ammonia was added to convert free chlorine to monochloramine, to yield a longer lasting residual in the distribution system, to improve the organoleptic properties of the water, and to reduce the corrosion rates associated with the use of free chlorine. Adequate disinfection was assured by maintaining a 2-3 mg/L free chlorine residual throughout the plant treatment process.

Trihalomethane formation within the treatment process was reduced by 40% under summertime conditions in comparison to the ultimate (96-hour) THMFP reached previously (from 231 to 174 μg/L).

ii. Reduction in Chlorine Treatment at Raw Water Basin

A gradual phasing out of chlorine addition at the raw water basin inlet took place from 1976 through 1979. Whereas in 1975, 60 lbs of chlorine per million gallons of chlorine was added at the intake, by the end of 1979, chlorine addition was limited to 20-30 lbs/million gallons of water. From 1977 to 1979, the marginal chlorination of the intake followed by five hours of free chlorine contact time in the floc/sedimentation basins and filters produced summertime average THM concentrations of 200 μg/L and yearly averages of 140 μg/L. While this treatment regimen produced positive results in the control of algae blooms in the raw water basin and minimization of taste and odor events, its debit was high formation of THMs. The decreased use of chlorine in the raw water basin also had the effect of reducing the amount of chlorine loss due to evaporation, and thus the quantity of chlorine used.

iii. Utilization of Chlorine Dioxide at Raw Water Basin Inlet (5 Hours Free Chlorine Contact Time)

Beginning in 1980, routine use of chlorine at the raw water intake basin was abandoned. In its place, chlorine dioxide was added in dosages between 0.5 and 1.0 mg/L. Summertime THM values thus were reduced from 200 μg/L to 140 μg/L. This treatment was sufficient to control algae, and thus tastes and odors, at all times except during the spring algae bloom. For that period of time, breakpoint chlorination of the intake water and/or 100-200 lbs of powdered activated carbon per million gallons is required to eliminate vegetative tastes and odors.

iv. Installation of a New Chlorine Application Point (One Hour Free Chlorine Contact Time)

In the fall of 1980, a chlorine application point was installed in the "applied to filters" channel which allowed for increased flexibility in the use of chlorine. Free chlorine contact time was reduced from five hours to one.

Chlorine was added at the rapid mix to barely achieve breakpoint and provide a residual which dissipated within a few minutes. Chloramines were carried across the floc/sedimentation basins. Sufficient chlorine then was added at the new application point to achieve a free chlorine residual of 1.5-2.0 mg/L. This residual was converted to chloramines one hour later as the water flow left the filter building.

This treatment regimen gave adequate control of taste and odor, except for the previously mentioned outbreaks associated with spring algae blooms, which forced reversion back to free chlorine at the intake. THM levels, with only one hour free chlorine contact time, resulted in summertime values averaging 100 μg/L with a yearly running average of 60 μg/L.

v. Ten Minutes Free Chlorine Contact Time

A plant trial was carried out in November 1982 utilizing a 10-minute chlorine contact time. Results indicated that satisfactory disinfection could be achieved with only chloramines carried through the floc/sedimentation basins when water temperature was below 60°F. This strategy was initiated on a plant-scale in December 1982. Adequate disinfection was achieved, but periodic taste and odor results were less than satisfactory. Medicinal and chemical taste complaints were received and several large taste and odor events occurred following storms.

THM results under the reduced chlorine treatment reduced running annual average concentrations from 60 to 50 μg/L.

The trial was terminated in December 1983 because the disinfection scheme did not adequately address the taste and odor qualities of the water. Treatment regimen returned to 1-hour free chlorine contact time.

c. Economics

Realization of 70% reduction in THM concentrations over the ten year period was obtained at minimum cost. The 1978 disinfection cost was $5.01/million gallons; in 1986 the cost was $9.53. Converting the 1986 costs into 1978 dollars, the 1986 adjusted cost is $5.52/million gallons. Cost increases were minimized because the reduced chlorine contact times resulted in less evaporative losses of chlorine, which netted a 20% decrease in the amount of chlorine utilized. This partially offset the increased costs incurred by the use of chlorine dioxide.

d. Operational Improvements

Free chlorine contact times at the Baxter plant have been reduced from 96-hours in 1975 to 1-hour in 1986. Trihalomethane concentrations in the finished water have been reduced from an estimated annual average of 220 μg/L in 1975 to 60 μg/L in 1986. Treatment strategy is most critical during the spring and summer months when vulnerability to taste and odor events is

high and THM formation within the treatment process is accelerated due to warm water temperatures.

e. For the Future

The near term goal of the Philadelphia Water Department is to reduce the annual running THM concentration average below 50 μg/L, a 15% reduction from current (1986) levels. This can be achieved at minimum expenditure by installation of a pH adjustment point at post-treatment. The existing treatment scheme calls for raising the raw water pH to 8.4 at the rapid mix and carrying this high pH through the distribution system for corrosion protection. Addition of a pH adjustment point at post-treatment will allow for a pH of 7.5 to be used through the floc/sedimentation basins and filters, with pH adjustment to 8.4 after chloramination. Plant scale trials using this treatment regimen yielded a 20% reduction in THM formation (to about 40 μg/L).

If EPA lowers the THM MCL to below 50 μg/L, ozone and/or granular activated carbon become the likely alternatives at the Baxter plant. Extensive laboratory and pilot plant evaluations (Neukrug et al., 1984) have developed conceptual full-scale plant designs incorporating these two treatment techniques.

Estimated annual amortized capital and operating costs for ozone at the Baxter plant, spread over the lifetime of the equipment, are estimated to be about $50/million gallons. The associated costs for GAC post-contacting (15-minute empty bed contact time) with a 75-day regeneration frequency would be about $212/million gallons. This design configuration is capable of producing THM concentrations of less than 10 μg/L.

IX. SUMMARY RECOMMENDATIONS FOR DISINFECTION STRATEGIES AND FOR THE CONTROL OF DISINFECTION/OXIDATION BY-PRODUCTS

Consideration of all of the preceding discussions, including the case studies, leads to the following general and specific conclusions and recommendations:

A. For Disinfection

1. From review of EPA's proposed Surface Water Rule (U.S. EPA, 1987a) and the National Academy of Sciences recommendations (NAS, 1987), ozone and chlorine should be viewed as the primary disinfectants of choice for surface waters and ground waters directly influenced by surface waters. However, chlorine can be used only when the THM and TOX formation potentials are sufficiently low to meet current and projected disinfection by-product regulations, and to insure that no other halogenated products are formed in quantities sufficiently high that they will be subject to regulation. UV radiation can be used as a primary disinfectant, but for groundwater only, since it does not provide the required amount of inactivation of Giardia cysts for surface water treatment.

2. For groundwater disinfection, ozone, chlorine, and UV radiation are the primary disinfectants of choice, with the same restrictions on chlorine as noted above.

3. Monochloramine is not recommended by EPA or by NAS as a primary disinfectant because of its very high CT values with respect to Giardia cysts and because inactivation of Giardia cysts with chloramine does not guarantee inactivation of viruses.

4. NAS also recommends against the use of preformed monochloramine and against marginal chlorination as methods of introducing chloramines. Organic N-chloramines, which are even weaker disinfectants than monochloramine, and which cannot be distinguished from inorganic chloramines by current field analytical techniques, are formed by these chloramination techniques.

5. For surface or groundwater, chlorine is the most effective secondary disinfectant, provided the water is sufficiently clean that significant quantities of THMs and other halogenated organic compounds are not produced.

5. If an MCL is set for chlorine dioxide at 1.0 mg/L, this material can be considered for primary disinfection, and definitely can be employed as a secondary disinfectant. A ClO_2 dosage of 1.2-1.4 mg/L will produce residual oxidant (ClO_2 + chlorite ion + chlorate ion) levels of ~ 1 mg/L.

6. On the other hand, if an MCL for chlorine dioxide is set at 0.2 mg/L (Table VII), use of ClO_2 as a primary disinfectant will be severaly restricted to exceptionally clean waters, because the maximum applied dosage then would be equivalent to about 0.3 mg/L. Its use as a secondary disinfectant also will require a high quality finished water in order to provide a stable, detectable residual throughout the distribution system.

7. If an MCL is set for monochloramine at 2.5 mg/L, it can be used as a secondary disinfectant. However, if an MCL is set at 0.29 mg/L (Table VII), its use as a secondary disinfectant, while not eliminated, will be limited to high quality finished waters.

8. If EPA sets low MCLs for both ClO_2 and chloramine, then chlorine may become the only practical secondary disinfectant available. In this event, the water will have to be pretreated more efficiently in order to lower TOX precursor levels.

9. The National Academy of Sciences (1987) recommends that when chloramine is used as the secondary disinfectant, chlorine should be added first to produce a slight residual of free chlorine above that required to oxidize nitrogen, followed by addition of ammonia to form monochloramine and limit THM formation.

10. CT values for different disinfectants employed in a treatment process are additive. For example, preoxidation with ozone or chlorine dioxide for a

non-disinfection application nevertheless provides some CT benefit which can be added to that obtained in the primary and secondary disinfection steps. When attempting to take disinfection credit for ozone, a measurable residual of dissolved ozone must be maintained for a specific contact time in the treatment plant. Preferebly, dissolved ozone should be monitored at two points, and the detention time between then should be known as accurately as possible. This will allow more accurate depiction of CT values than those calculated from measurement of residual ozone at a single point.

11. When using ozone for disinfection, contact time must be defined in terms of detention time in the ozone contacting chamber or subsequent ozone reaction chamber. This is because ozone residuals dissipate rapidly after application of ozone to water ceases. To calculate the disinfection credit of ozone under such conditions requires making assumptions regarding the period of time over which the ozone residual concentration is established and maintained (if only a single ozone contactor is employed). Satisfying the ozone demand of the water and attaining the desired residual of ozone in a first contact chamber, followed by a second chamber in which the desired residual ozone is maintained, is a more quantitative and reliable disinfection design approach.

12. Changing disinfection procedures usually must be made with attention being paid to overcoming other water quality problems, such as control of color, taste and odor, iron and manganese, synthetic or volatile organic contaminants, etc.

13. Whenever ozone is employed, for oxidation or disinfection purposes, it should be added in the absence of chlorine, chlorine dioxide, or chloramine. This is because ozone oxidizes these three chemicals (very rapid oxidation of ClO_2), and both reagents are mutually destroyed, to no benefit to the water treatment process. When primary disinfection with ozone is followed by chlorine, chlorine dioxide, or chloramine as the secondary disinfectant, it is important that no residual ozone be present, particularly in the case of chlorine dioxide, for the same reason.

B. For Controlling Disinfectant/Oxidant By-Products

14. Currently, halogenated by-products are the only compounds being regulated or selected for regulation in the next few years.

15. Attention to minimizing the use of chlorine during disinfection will also minimize the production of disinfection by-products.

16. Conventional physical water treatment processes (e.g., coagulation, flocculation, sedimentation, filtration) should be improved to remove or minimize concentrations of organic precursors of disinfection by-products prior to the addition of chlorine. Preoxidation and activated carbon adsorption are treatment steps which can be effective in this regard. Ozone, potassium permanganate, hydrogen peroxide can be effective

preoxidizing agents. Chlorine dioxide also is an effective preoxidant, if its use at 1.2-1.4 mg/L applied dosages continues to be allowed.

17. When relying on monochloramine as the secondary disinfectant, close attention should be paid to the TOX levels and the halogenated organic products which are contained in this group parameter. TOX levels are known to increase slowly in distribution systems employing chloramine as the secondary disinfectant.

18. Most current preoxidation applications of ozone are designed to provide only a trace residual of ozone at the exit of the contact chamber. In plants currently employing ozone for preoxidation using a single contactor, simply increasing the dissolved ozone residual to the level appropriate for the designed ozone contact time and the water temperature can provide at least the major portion, if not all, of the primary disinfection required to guarantee inactivation of Giardia cysts and enteric viruses.

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DISINFECTION / BY-PRODUCTS WORKSHOP

SURFACE WATER PROBLEM

I. RAW WATER PARAMETERS

Source	:	Unprotected Watershed
Turbidity	:	5 - 10 NTU
Total Coliforms	:	500 - 5,000 per 100 mL
THMFP	:	350 μg/L
TOXFP	:	500 μg/L
TOC	:	5 - 10 mg/L (mostly humics)
$[NH_4^+]$	:	0.1 mg/L
[organic-N]	:	0.5 mg/L
$[Br^-]$	:	0.1 mg/L
Cl_2 Demand	:	7 mg/L
ClO_2 Demand	:	2 mg/L
$KMnO_4$ Demand	:	4 mg/L
Ozone Demand	:	3 mg/L

II. TREATMENT OBJECTIVES

Disinfection

TTHMs	:	100 μg/L

III. REGULATORY FACTORS

$(ClO_2 + ClO_2^- + ClO_3^-)$ MCL	:	1.0 mg/L
Chloramine MCL	:	2.5 mg/L
[Residual Disinfectant]	:	detectable residual

SURFACE WATER TREATMENT PROBLEM

Modification # 1

I. RAW WATER QUALITY - Same

II. TREATMENT OBJECTIVE - TTHMs = 50 μg/L

III. REGULATORY FACTORS

(ClO_2 + ClO_2^- + ClO_3^-) MCL : 0.5 mg/L

Chloramine MCL : 1.0 mg/L

[Residual Disinfectant] : detectable residual

SURFACE WATER TREATMENT PROBLEM

Modification # 2

I. RAW WATER QUALITY - Same

II. TREATMENT OBJECTIVE - TTHMs = 25 μg/L

III. REGULATORY FACTORS

(ClO_2 + ClO_2^- + ClO_3^-) MCL : 0.2 mg/L

Chloramine MCL : 0.25 mg/L

[Residual Disinfectant] : detectable residual

3/30/88

DISINFECTION / BY-PRODUCTS WORKSHOP

GROUNDWATER PROBLEM

I. RAW WATER PARAMETERS

Source	:	Aquifer - Not Directly Influenced by Surface Water
Turbidity	:	0.3 NTU
Total Coliforms	:	0 - 100 per 100 mL
THMFP	:	200 μg/L
TOXFP	:	300 μg/L
TOC	:	3 - 5 mg/L
$[NH_4^+]$	:	0.1 mg/L
[organic-N]	:	0.5 mg/L
$[Br^-]$	:	0.1 mg/L
Iron	:	0.6 mg/L
Manganese	:	0.30 mg/L
Cl_2 Demand	:	4 mg/L
ClO_2 Demand	:	1.3 mg/L
$KMnO_4$ Demand	:	2 mg/L
Ozone Demand	:	3 mg/L

II. TREATMENT OBJECTIVES

Disinfection

TTHMs	:	100 μg/L

III. REGULATORY FACTORS

$(ClO_2 + ClO_2^- + ClO_3^-)$ MCL	:	1.0 mg/L
Chloramine MCL	:	2.5 mg/L
[Residual Disinfectant]	:	detectable residual

GROUNDWATER TREATMENT PROBLEM

Modification # 1

I. RAW WATER QUALITY - Same

II. TREATMENT OBJECTIVE - TTHMs = 50 μg/L

III. REGULATORY FACTORS

(ClO_2 + ClO_2^- + ClO_3^-) MCL : 0.5 mg/L

Chloramine MCL : 1.0 mg/L

[Residual Disinfectant] : detectable residual

GROUNDWATER TREATMENT PROBLEM

Modification # 2

I. RAW WATER QUALITY - Same

II. TREATMENT OBJECTIVE - TTHMs = 25 μg/L

III. REGULATORY FACTORS

(ClO_2 + ClO_2^- + ClO_3^-) MCL : 0.2 mg/L

Chloramine MCL : 0.25 mg/L

[Residual Disinfectant] : detectable residual

3/30/88

Technical Session: Organics

John E. Dyksen, *Senior Project Manager, Malcolm Pirnie, Inc., Paramus, NJ*

WORKSHOP ON
EMERGING TECHNOLOGIES FOR
DRINKING WATER TREATMENT

ORGANICS TREATMENT TECHNIQUES
OVERVIEW

Conducted by:

United States Environmental Protection Agency

and

Association of State Drinking Water Administrators

Presented By:

John E. Dyksen
Senior Manager, Water Treatment
Malcolm Pirnie, Inc.
Paramus, New Jersey

WORKSHOP ON
EMERGING TECHNOLOGIES FOR
DRINKING WATER TREATMENT

ORGANICS TREATMENT TECHNIQUES
OVERVIEW

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I. INTRODUCTION

A. Purpose and Scope

The June 1986 Amendments to the Safe Drinking Water Act (SDWA) require the United States Environmental Protection Agency (EPA) to set maximum contaminant levels (MCLs) for several contaminants found in drinking water. The MCLs are to be established based upon:

1. Health goals
2. Effectiveness of treatment technologies in removing the contaminants
3. Level of treatment that is affordable for the water supply systems

EPA is currently establishing MCLs for radon and a number of organic chemicals occurring in contaminated water supplies. According to the Amendments, all public water systems will be required to come as close as possible to meeting the MCLs by using the Best Available Treatment (BAT) technology.

The purpose of this document is two-fold:

1. To assist water utilities in selecting appropriate treatment methods to meet the regulations.
2. To assist the regulatory agencies in assessing the feasibility of treatment methods proposed by the water utilities.

Provided in this document is a review of all the emerging treatment technologies for removing organic contaminants and radon from drinking water. Emphasis is given to treatment methods that have been proven effective for their removals. The discussion on these treatment methods includes the process selection criteria, treatability tests, design considerations, operational issues and facility costs.

II. AVAILABLE ORGANICS TREATMENT TECHNOLOGIES

A. Summary of Available Technologies

1. Most Applicable Technologies

   a. Granular activated carbon (GAC) adsorption
   b. Packed column aeration

2. Other Applicable Technologies

   a. Powdered activated carbon (PAC) and conventional treatment
   b. Diffused aeration
   c. Multiple tray aeration

3. Additional Technologies (Emerging)

   a. Ozone/UV
   b. Reverse osmosis
   c. Mechanical aeration
   d. Catenary grid (aeration)
   e. Higee (aeration)
   f. Resins

B. Other Applicable Technologies

1. Powdered Activated Carbon (PAC) and Conventional Treatment

   a. Based on the principles of adsorption, PAC is generally added at one or more application points in a conventional treatment train (coagulation, flocculation, sedimentation and filtration). Principal design considerations are:

      - Dosage
      - Contact time (at least 15 minutes)
      - Point(s) of application (1 to 3)

      A schematic of the PAC treatment process is shown on Figure 1.

   b. Typical performances of PAC and conventional treatment processes are presented in Table 1. As can be seen, PAC addition achieves higher removals than conventional treatment alone.

   c. Principal advantages of PAC:

      - Better organics removals than conventional treatment
      - Acts as coagulant aid
      - Taste and odor removal

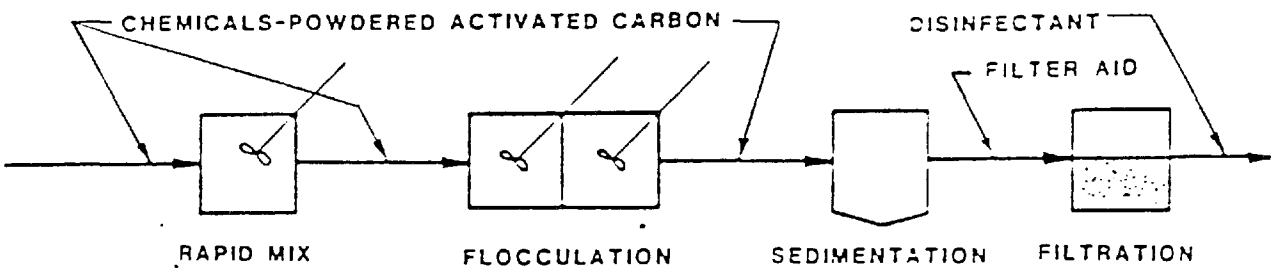


FIGURE 1 - SCHEMATIC OF P.A.C. ADSORPTION PROCESS

TABLE 1

TYPICAL PERFORMANCE OF PAC AND
CONVENTIONAL TREATMENT PROCESSES

	Conventional Treatment	PAC	
	Percent Removal	Dosage (mg/L)	Percent Removal
VOCs			
Carbon Tetrachloride	-	9.6 - 30	0 - 25
1,1,1-Trichloroethane	-	7	40 - 65
SOCs			
Acrylamide	5	8	13
Alachlor	<50	4 - 34	36 - 100
Carbofuran	54-79	9 - 25	45 - 75
o-Dichlorobenzene	-	8 - 27	38 - 95
2,4-D	0-3	11 - 306	69 - 100
Ethylbenzene	-	8 - 27	33 - >99
Heptachlor	64	11 - 97	53 - 97
Lindane	10-20	2 - 34	82 - 97
Monochlorobenzene	-	8 - 27	14 - >99
Toluene	-	8 - 27	0 - 67
2,4,5-TP	63	1.5 - 17	82 - 99
Toxaphene	-	1 - 44	40 - 99
Xylenes	-	8 - 27	60 - >99

Note:

(-) Information not available.

- Useful for short-term, emergency applications in conjunction with conventional treatment

d. Limitations:

- Excessive dosages may be required for certain contaminant removal.

- Limited applicability in locations which have certain constraints (e.g., hydraulic, space, sludge handling) and also where conventional treatment is not in place or is not required.

2. Diffused Aeration

a. Based on bubbling air into a water-filled contact chamber through a diffuser mechanism usually located at or near the bottom of the chamber. Principle design considerations are:

- Basin depth (5 to 10 feet)
- Diffuser type
- Air/Water ratio (5:1 to 15:1)
- Detention time (10 to 15 minutes)
- Basin geometry

A schematic of diffused aeration process is shown on Figure 2. A typical home diffusion aeration unit for radon removal is shown on Figure 3.

b. Typical performance of diffused aeration at an air to water ratio of 5:1 to 15:1 and a contact time of 10 to 15 minutes is presented in Table 2.

c. Principle advantage of diffused aeration:

- Existing basins such as a chlorine contact basin can be retrofitted with diffusers and converted to aeration basins.

d. Limitations:

- Less effective than packed column aeration (discussed later).

- Generally used only where existing basins are available.

3. Multiple Tray Aeration

a. Water falls over a series of trays with slats, perforations, or wire mesh. The counter-current flow of air (either from

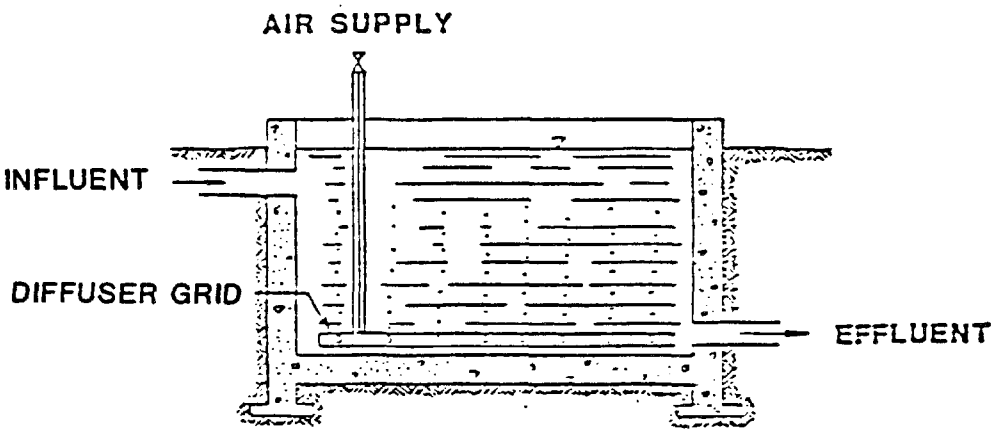


FIGURE 2- SCHEMATIC OF DIFFUSED AERATION PROCESS

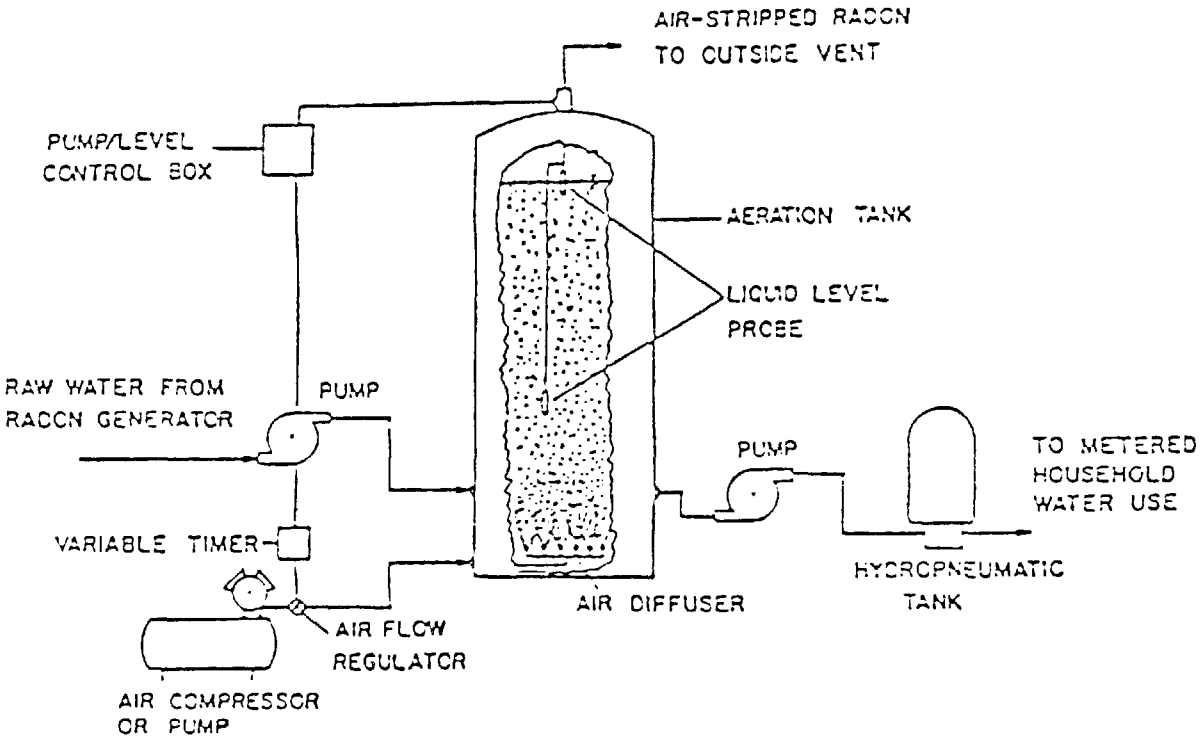


FIGURE 3 - HOME DIFFUSED AERATION SYSTEM

TABLE 2

TYPICAL PERFORMANCE OF DIFFUSED AERATION

	% Removal
VOCs	
Trichloroethylene	53-95
Tetrachloroethylene	73-95
1,2-Dichloroethane	42-77
1,1-Dichloroethylene	97
1,1,1-Trichloroethane	58-90
SOCs	
Carbofuran	11-20
1,2-Dichloropropane	12-79
cis-1,2-Dichloroethylene	32-85
trans-1,2-Dichloroethylene	37-96
o-Dichlorobenzene	14-72
Ethylbenzene	24-89
Monochlorobenzene	14-85
Toluene	22-89
Xylenes	18-89

blowers or natural ventilation) removes the volatile organics in the water. Principal design considerations are:

- Tray type (wood, plastic)
- Tray height (12 to 16 feet)
- Natural or forced draft
- Air/Water ratio (30:1)

A schematic of a slat tray aeration system is shown on Figure 4.

b. Typical performance of slat tray aeration at an air to water ratio of about 30:1 and tray height of 12 to 16 feet is presented in Table 3.

c. Principle advantages of multiple tray aeration:

- Less susceptible to clogging, from iron and manganese precipitation, than packed column aeration.

- Readily available as package units from manufacturers.

d. Limitations:

- Not as effective as packed column aeration (discussed later)

- Control of biological growth and corrosion may be required.

B. Additional Technologies (Emerging)

1. Ozone/UV

a. Ozone provides organics removal by acting as an oxidant, generally breaking down unsaturated bonds within the molecules. Ultra-violet (UV) radiation catalyzes this breakdown reaction. Principal design considerations are:

- Ozone dosage
- Contact time (15 minutes)
- Radiation intensity

A schematic of the ozonation process is shown on Figure 5.

b. Typical performance of the ozonation process at a contact time of about 15 minutes is presented in Table 4.

c. Principle advantages of Ozonation/UV process:

- Can combine organics removal with disinfection, and taste and odor control

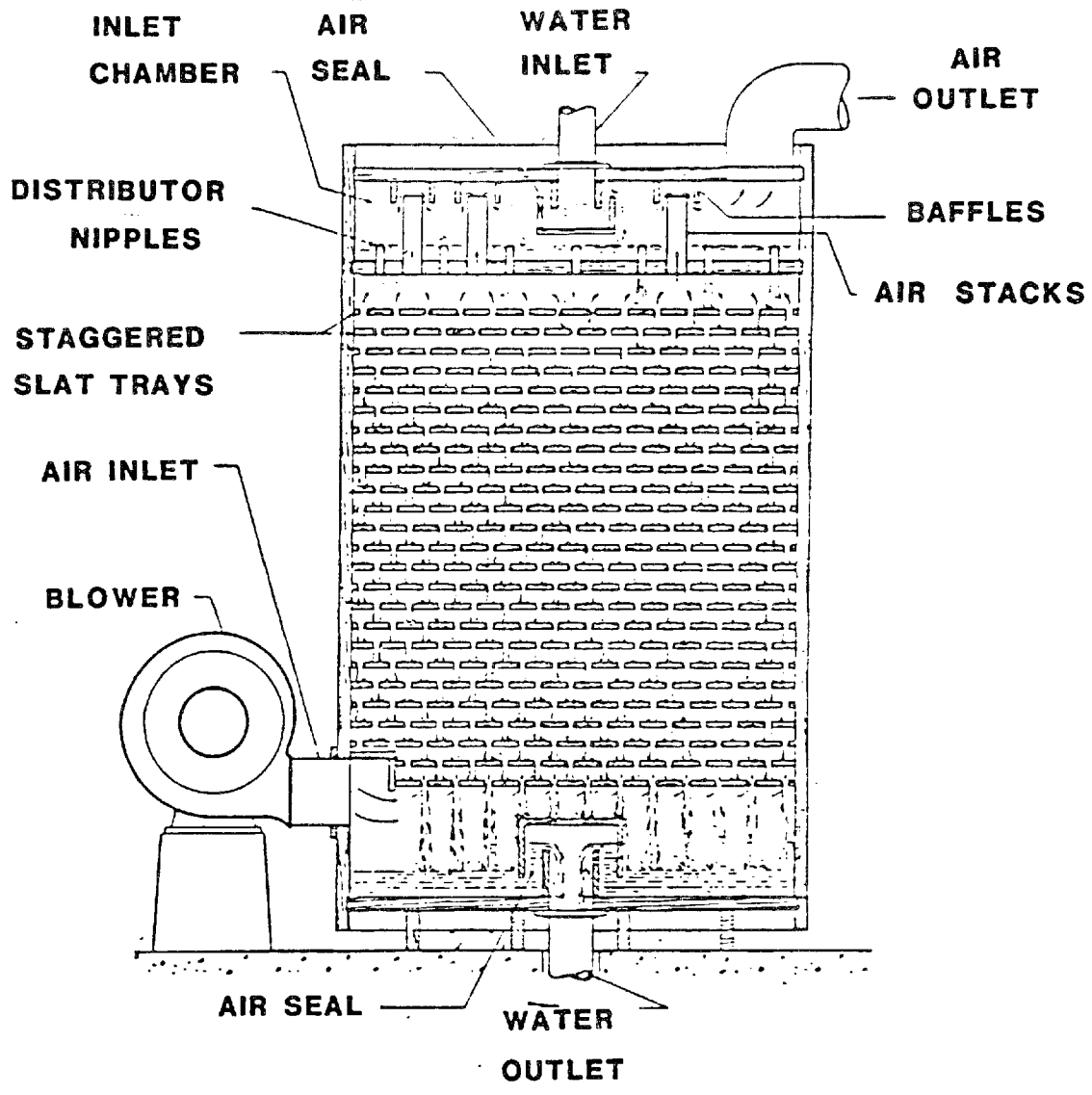


FIGURE 4- SCHEMATIC OF A REDWOOD SLAT TRAY AERATOR

TABLE 3

TYPICAL PERFORMANCE OF SLAT TRAY AERATION

VOCs	% Removal
Trichloroethylene	30-90
Tetrachloroethylene	20-85

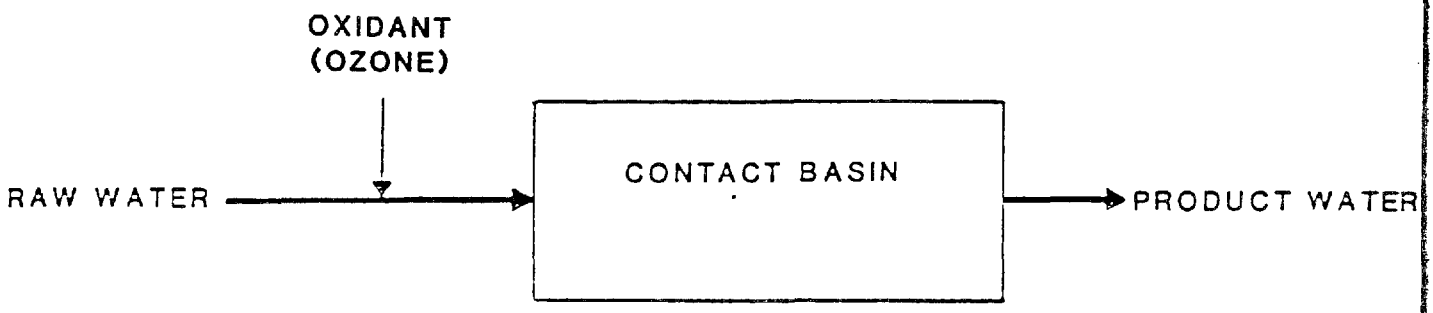


FIGURE 5 - SCHEMATIC OF OZONATION PROCESS

TABLE 4

TYPICAL PERFORMANCE OF OZONATION PROCESS

	Dosage (mg/L)	% Removal
SOCs		
Carbofuran	9	100
1,2-Dichloropropane	0.9 - 6	8 - 22
cis-1,2 Dichloroethylene	2 - 10	87 - 93
trans-1,2 Dichloroethylene	0.9 - 6	100
o-Dichlorobenzene	9	88
Ethylene Dibromide	0.9 - 6	8 - 9
Ethylbenzene	1.5 - 9	47 - 95
Heptachlor	17	100
Heptachlor epoxide	17	26
Lindane	0.4 - 150	0 - 100
Monochlorobenzene	0.4 - 6	86 - 98
Toluene	1.5 - 12	49 - 98
Xylenes	1.5 - 12	54 - 98

- Waste disposal not required

- No THM formation

d. Limitations:

- May not achieve complete oxidation, concern about intermediate breakdown products.

- Background matrix and presence of other contaminants will impact effectiveness.

2. Reverse Osmosis

a. Based on the application of hydrostatic pressure to drive the feed water through a semipermeable membrane while a major portion of its impurity content remains behind and is discharged as waste. Principal design considerations are:

- Operating pressure (150 to 250 psi)
- Percent recovery (10 to 50 percent)
- Membrane type
- Pretreatment requirements

A schematic of the reverse osmosis process is shown on Figure 6.

b. Generally, reverse osmosis shows promise for removing low molecular weight, volatile organic contaminants and certain pesticides. Typical performance of reverse osmosis process at an operating pressure of about 200 psi is presented in Table 5.

c. Principal advantage of reverse osmosis process:

- It is a proven technology for inorganics removal and may, therefore, be very useful in situations where a dual inorganic/organic problem is present.

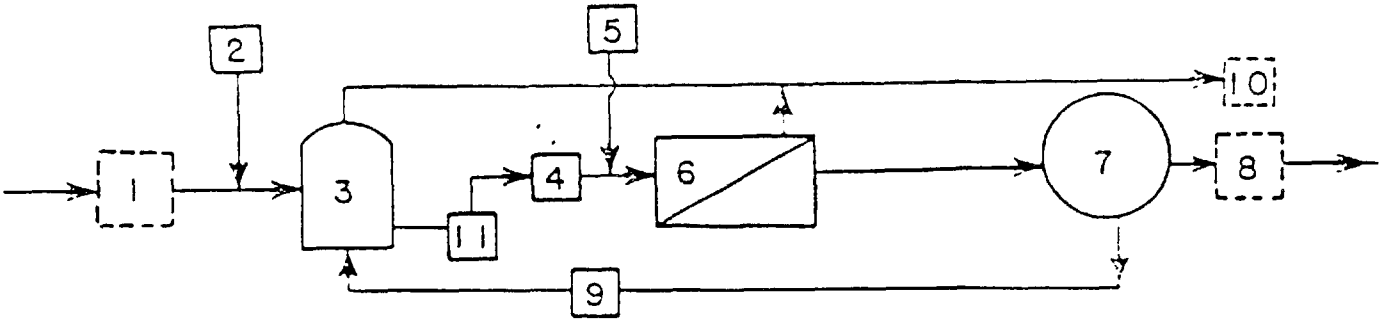
d. Limitations:

- Considerable pretreatment may be required, depending on the raw water quality.

- Low recovery.

3. Mechanical Aeration

a. Surface or submerged mechanical aerators are used to entrain atmospheric air into the water by creating a region of intense turbulence in the water. Volatile organics are removed by the dispersed air. Principal design considerations are:



LEGEND

1. SOURCE WATER PUMPING
2. POLYMER FEED SYSTEM
3. FILTRATION
4. HIGH PRESSURE PUMP
5. pH AND SCALE CONTROL
6. REVERSE OSMOSIS
7. FILTER WASH WATER STORAGE
8. DISINFECTION
9. FILTER BACKWASH
10. WASTEWATER DISPOSAL
11. CARTRIDGE FILTRATION

--- EXISTING FACILITIES

FIGURE 6- SCHEMATIC OF REVERSE OSMOSIS PROCESS

TABLE 5

TYPICAL PERFORMANCE OF REVERSE OSMOSIS PROCESS

	% Removal
VOCs	
1,2-Dichloroethane	15-70
1,1,1-Trichloroethane	15-100
Carbon tetrachloride	95
Trichloroethylene	0-75
Tetrachloroethylene	70-90
Benzene	2-18
p-Dichlorobenzene	0-10
SOCs	
Acrylamide	0-97
Aldicarb	94-99
Alachlor	100
Carbofuran	86-99
1,2-Dichloropropane	10-90
cis-1,2-Dichloroethylene	0-30
trans 1,2-Dichloroethylene	0-30
2,4-D	1-65
o-Dichlorobenzene	65
Ethylbenzene	30
Ethylene dibromide	37-84
Lindane	50-75
Methoxychlor	>90
Monochlorobenzene	50-100
PCBs	95
Xylenes	10-85

- Aerator type
- Detention time (1 to 2 hours)
- Energy requirements

Schematics of the two types of mechanical aerators are shown on Figure 7.

b. Performance of mechanical aerators for the removal of specific organics is not available.

c. Principal advantages of mechanical aerators appear to be:

- Simplicity of operation

- Applicable where there is a risk of chemical precipitation or biological growth that would tend to clog a packed column aerator

d. Limitations:

- High energy requirement
- Long detention time and, therefore, large area requirement
- Potential freezing of open aeration basins in cold climate
- Generally used for wastewater treatment

4. Catenary Grid Aeration

a. Based on bringing the raw water in contact with air and transferring the organics from water to air phase. Water flows down a column which is divided into sections by catenary grids. The shape of the catenary grid is designed so that a zone of turbulence is created above each grid section. Principal design considerations are:

- Air/water ratio
- Number of grids
- Hydraulic loading rate

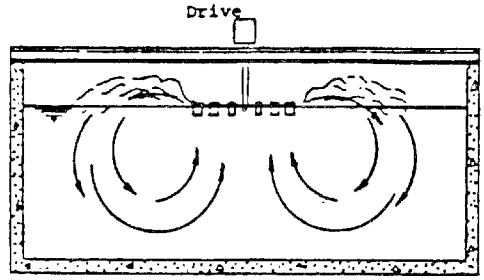
A schematic of the catenary grid aerator is shown on Figure 8.

b. Catenary grids can provide VOC removals that are comparable to packed column aeration. In general:

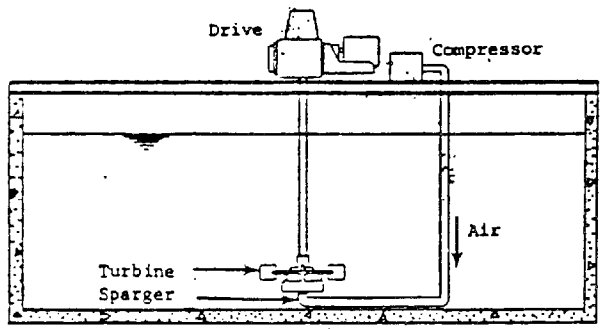
- Removal increases with increasing air/water ratio.

- Removal increases with increasing number of grids.

- Mass transfer coefficient decreases with increasing number of grids.



Mechanical Surface Aerator



Submerged Turbine Aerator

FIGURE 7- SCHEMATIC OF MECHANICAL AERATION PROCESS

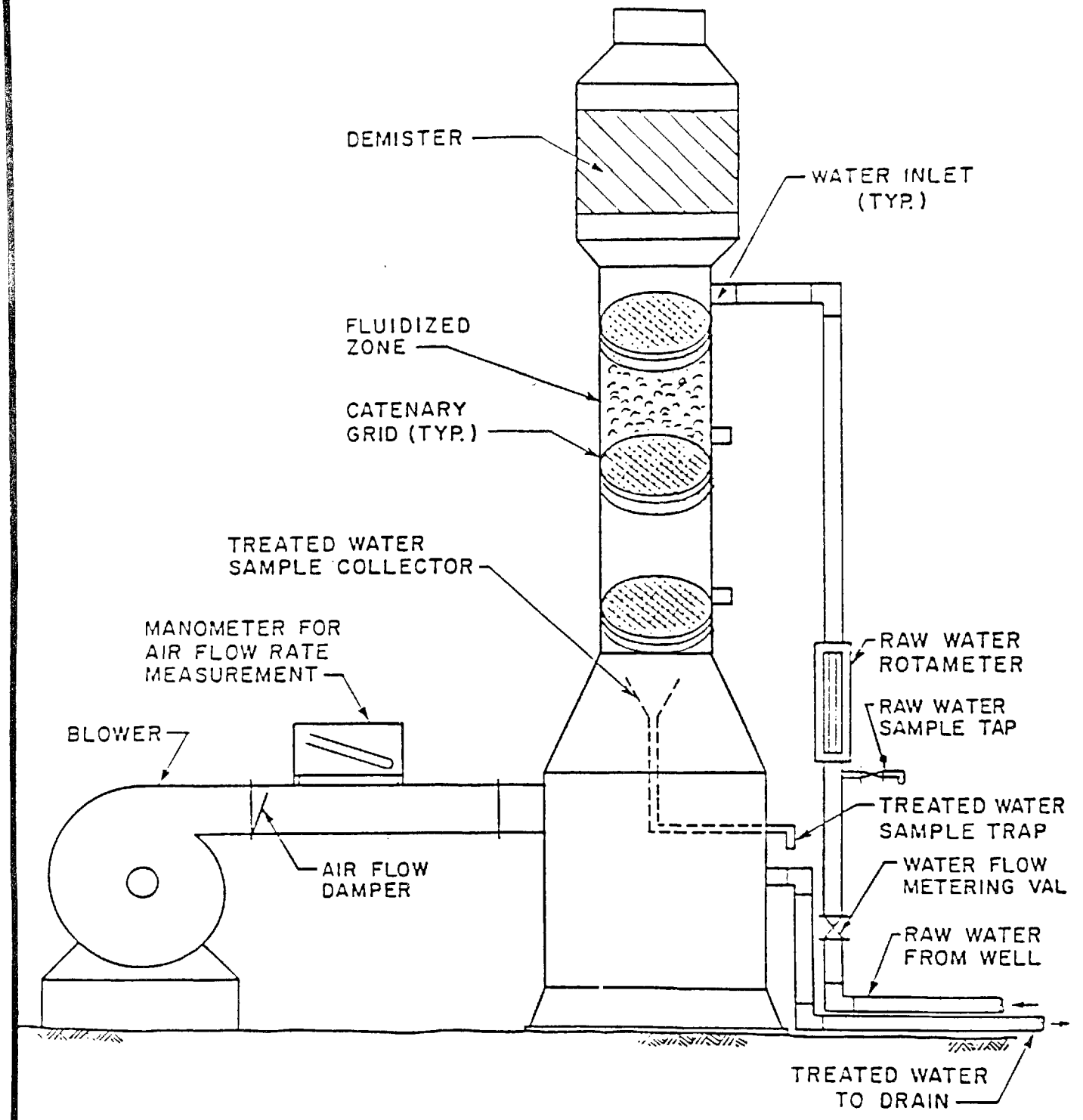


FIGURE 8- SCHEMATIC OF CATENARY GRID SYSTEM

c. Principal advantage of catenary grid aerator:

- Compact design: a smaller diameter and lower column height than packed column aeration.

- Lower capital cost than packed column because of more compact design.

d. Limitations:

- The scale-up procedure from pilot to full-scale is not fully understood and requires further development.

- The air flow pressure drop is relatively high, resulting in larger blowers and higher energy costs than packed column aeration.

- Limited treatability data are available for several organics.

5. Higee

a. The process uses a rotating bed of packing with a high surface area per unit volume. Air is forced into the rotating packing element while the contaminated water flows from the center of the packing outward in a counter current manner. Principal design considerations are:

- Air/Water ratio
- Pump (Higee) size

A schematic of the Higee system is shown on Figure 9.

b. Very little treatability data is currently available for organics removal.

c. Principal advantages of Higee system appear to be:

- Packing requirements are less than in packed column aeration for equal removal efficiencies.

- High liquid loading rates are possible with relatively compact equipment

- Air volumes required are reduced.

d. Limitations:

- Limited treatability data are available for organics removal.

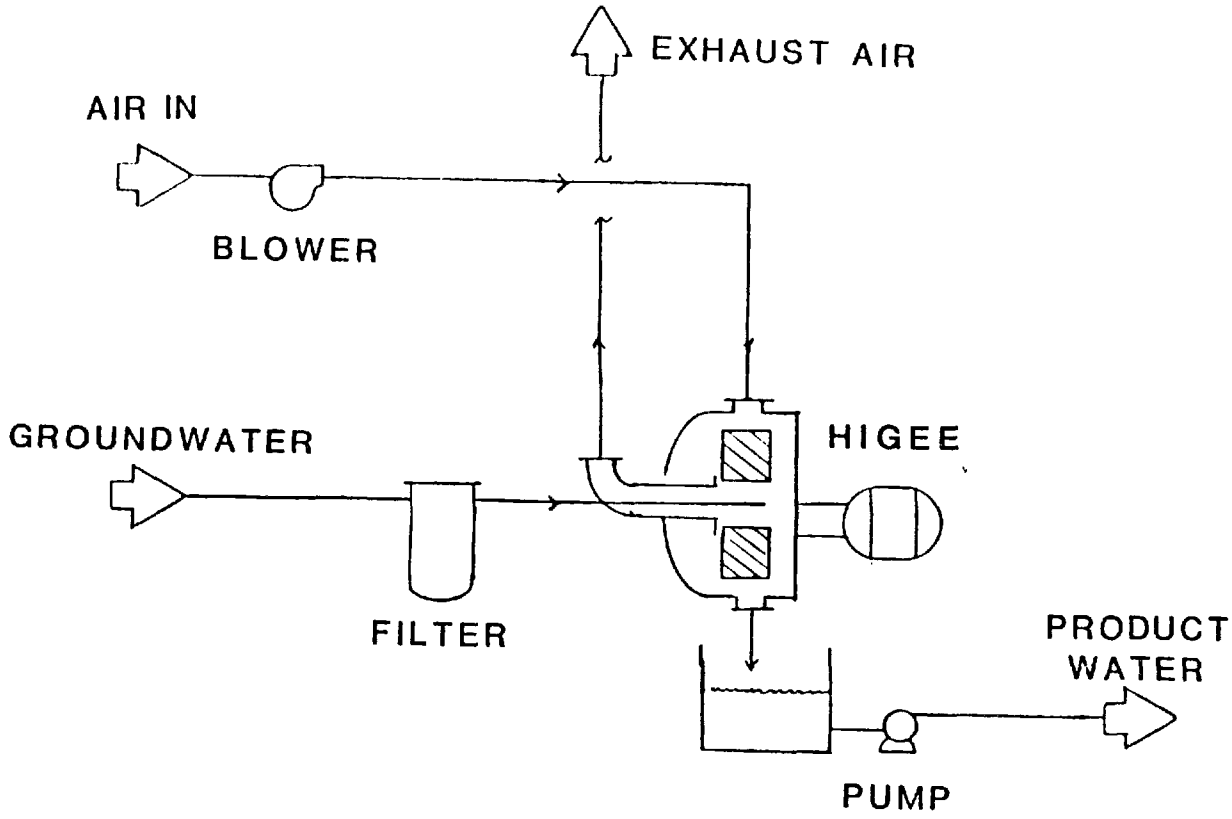


FIGURE 9 - SCHEMATIC OF HIGEE SYSTEM

- Generally considered only under special requirements such as space constraint, height limitations or exhaust air treatments.

- Currently, treatment cost is high. Appears to be cost-effective only for high organic concentrations (greater than 1,000 ppm) and low flow rates (less than 100 gpm).

6. Resins

a. Process uses special synthetic resins that have high adsorptive capacity for organic compounds. Principal design considerations are:

- Resin type
- Empty bed contact time (EBCT)
- Regeneration frequency

b. Studies indicate that Ambersorb XE 340 (made by Rohm and Haas) is effective in removing VOCs.

c. Principal advantages of synthetic resins appear to be:

- Shorter EBCT required than GAC
- Longer life than GAC
- Resin regeneration on site using steam

d. Limitations:

- High cost of resins - $10 per pound as compared to $.80 per pound for GAC.

- Disposal of highly concentrated regenerant water.

III. GRANULAR ACTIVATED CARBON

A. Process Description

1. Based on the principle of adsorption - the transfer of a dissolved contaminant (adsorbate) from a solvent (solution) to the surface of an adsorbent (carbon).

2. Factors Affecting Adsorption Process

   a. Type of contaminant (adsorbate) - Tables 6 and 7 present lists of readily adsorbed and poorly adsorbed organics, respectively.

      - branched-chain compounds more adsorbable than straight-chained compounds
      - increasing molecular weight increases adsorption
      - lower solubility increases adsorption
      - greater concentration, increased adsorbability

   b. Adsorbent

      - high degree of porosity
      - extensive internal surface area
      - affinity of adsorbate for absorbent (polar, nonpolar)

   c. Aqueous Solution

      - temperature
      - pH
      - dissolved solids
      - other adsorbates

B. Process Design Considerations

1. Key Parameters

   a. contaminant

   b. levels

   c. GAC type

   d. empty bed contact time

   e. carbon usage rate - pounds of carbon per 1,000 gallons of water treated

   f. surface loading rate (2 to 10 gpm/sf)

TABLE 6

READILY ADSORBED ORGANICS

- Aromatic Solvents

  Benzene, toluene, nitrobenzenes

- Chlorinated Aromatics

  PCBs, chlorobenzenes, chloronapthalene

- Phenol and chlorophenols

- Polynuclear Aromatics

  Acenapthene, benzopyrenes

- Pesticides and herbicides

  DDT, aldrin, chlordane, heptachlor

- Chlorinated non-aromatics

  Carbon tetrachloride, chloroalkyl ethers

- High MW Hydrocarbons

  Dyes, gasoline, amines, humics

TABLE 7

POORLY ADSORBED ORGANICS

- Alcohols
- Low MW Ketones, Acids, and Aldehydes
- Sugars and Starches
- Very High MW Or Colloidal Organics
- Low MW Aliphatics

g. carbon depth (10-30 ft)

h. radon removal

2. Contaminant and Levels

a. Effect of different organics on GAC design is shown on Figure 10.

b. Effect of contaminant levels on GAC design is shown on Figure 11.

c. Selected pretreatment can lower contaminant loading on carbon and thereby increase carbon life. Example:

- Packed column for volatile organic chemical (VOC) reduction.

- Coagulation/filtration for turbidity and total organic chemical (TOC) reduction.

3. GAC Type

a. Low cost GAC - low capital cost, but more frequent reactivation and, therefore, higher operating cost.

b. Total cost for different GAC types are shown on Figure 12.

4. Empty Bed Contact Time (EBCT)

a. Affects capital costs
b. Average - 10 minutes for most organics
c. Calculated based on flow rate and GAC volume

$$\text{EBCT (min)} = \frac{\text{GAC volume (cu ft)}}{\text{Flow rate (gal per min)}} \times 7.48 \frac{\text{gal}}{\text{cu ft}}$$

5. Carbon Usage Rate

a. Rate at which carbon capacity will be exhausted

b. Affects facility capital and operating costs of the facility

c. Carbon usage rates for several organics are shown in Table 8. In general, pesticides are better adsorbed than VOCs.

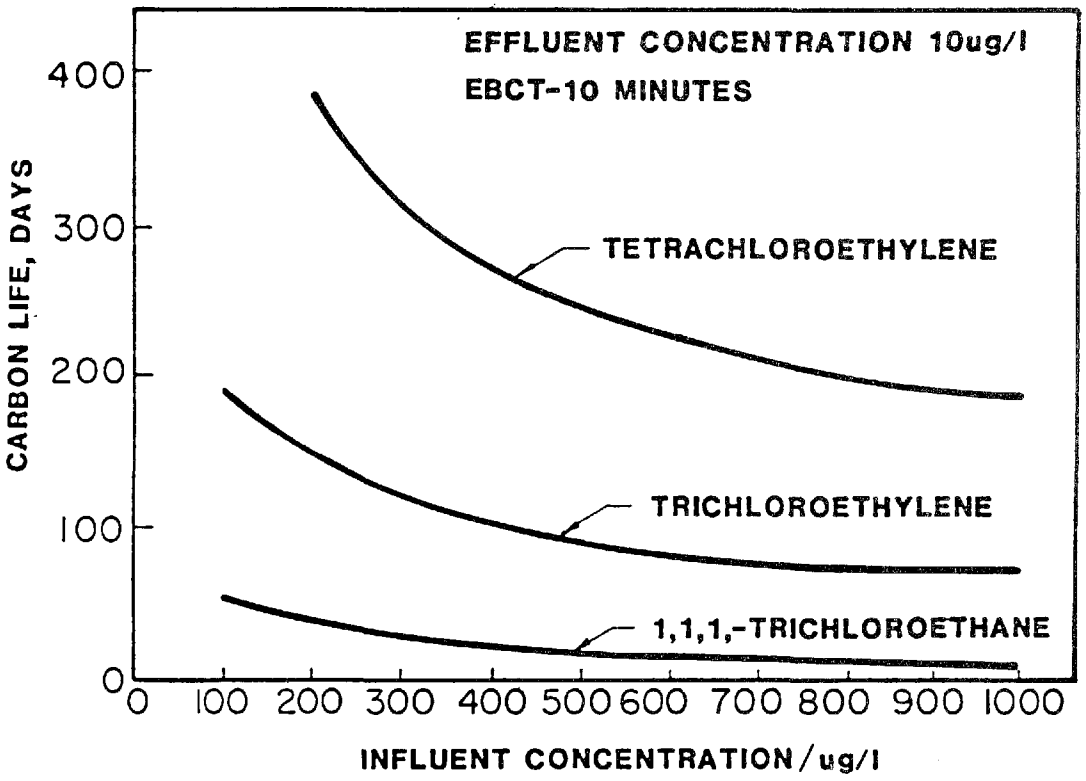


FIGURE 10- EFFECT OF TYPE OF COMPOUND ON CARBON LIFE

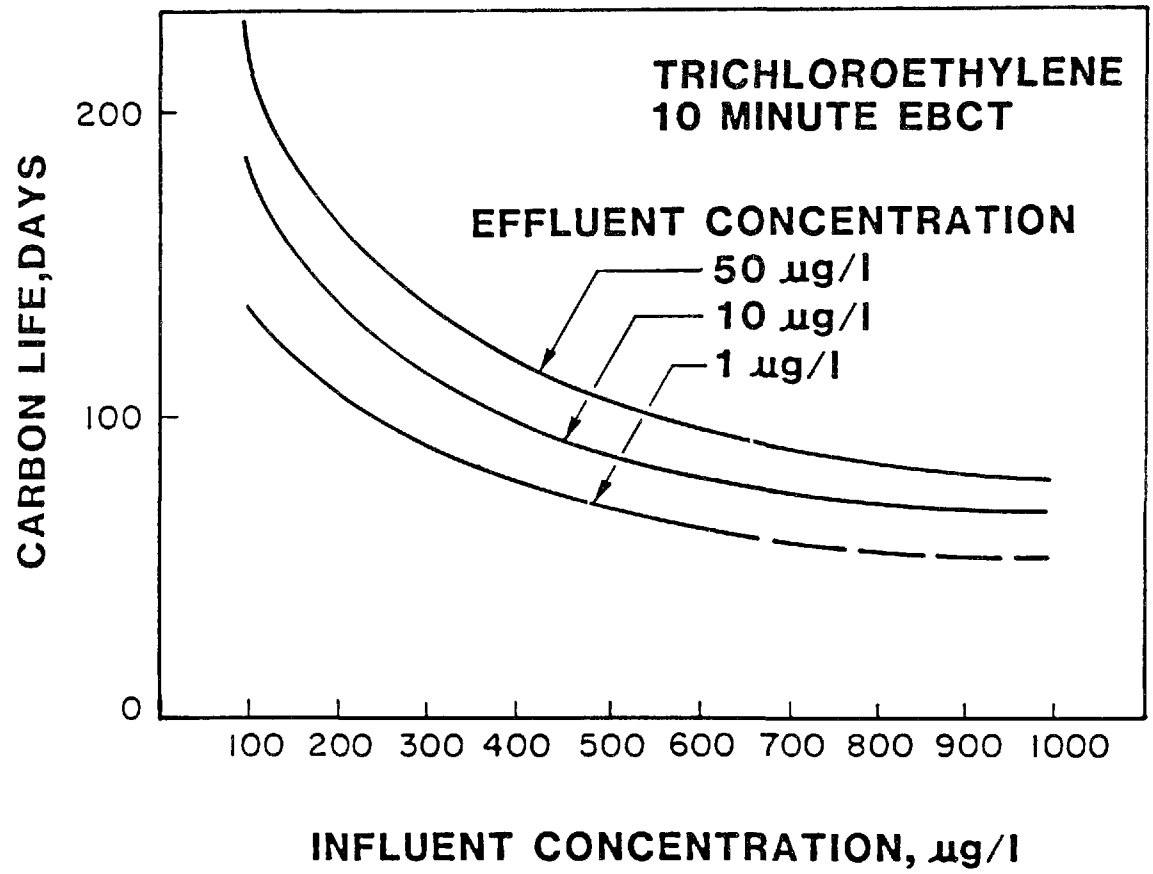


FIGURE 11- EFFECT OF CONTAMINANT LEVELS ON CARBON LIFE

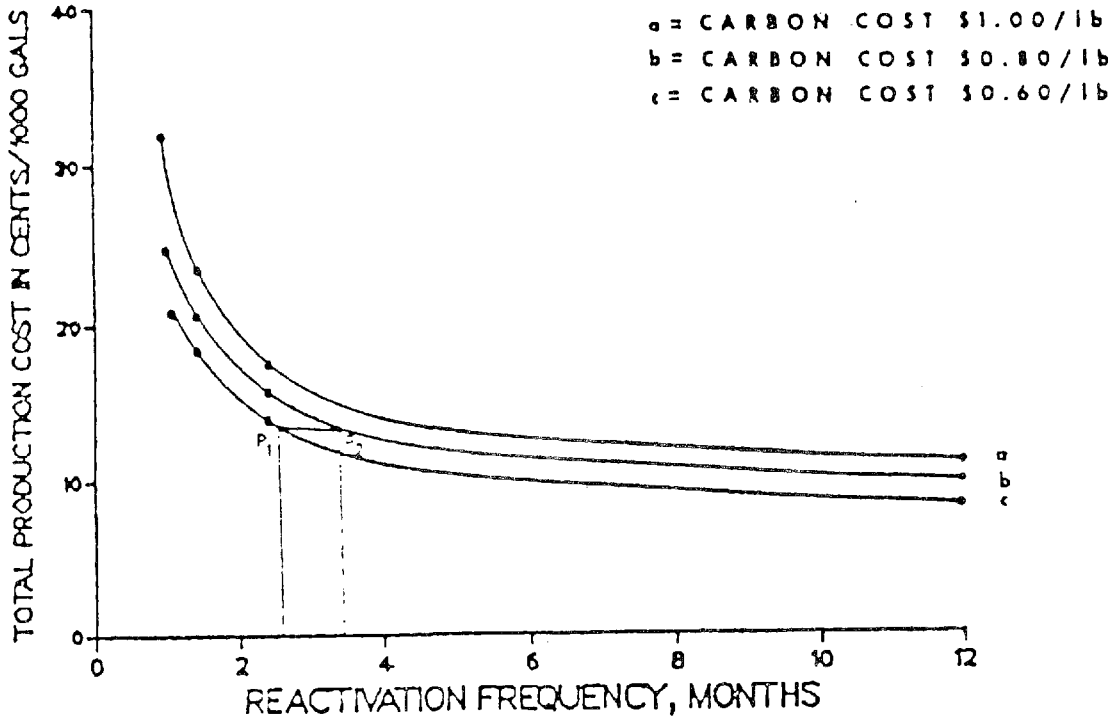


FIGURE 12- EFFECT OF CARBON TYPE ON FACILITY COST

TABLE 8

SUMMARY OF CARBON USAGE RATES

	Concentration (ug/L)		Carbon Usage
	Influent	Effluent	(lbs/1,000 gal)
Volatile Organic Chemicals (VOCs):			
Tetrachloroethylene (PCE)	100	2	0.08
Trichloroethylene (TCE)	100	2	0.16
Trichloroethane (TCA)	100	2	0.96
Pesticides:			
Chlordane	100	1	0.012
Dibromochloropropane (DBCP)	100	1	0.016
Aldicarb	100	1	0.02
Chlorinated Aromatics:			
Dichlorobenzene	100	2	0.01
PCB (Aroclor 1016)	100	2	0.015

6. Radon Removal

a. EBCT

- Requires large EBCT (100 to 200 minutes). EBCT required for various removals are presented on Figure 13.

b. Adsorption/decay

- Radon that is adsorbed on the carbon decays continuously

- Comparison of breakthrough curves for radon and a nondecaying adsorbate is shown on Figure 14.

- Decay of radon acts to continuously self-regenerate the carbon bed.

C. Testing to Evaluate Process Design Parameters

1. Isotherm Testing

a. Useful screening tool for:

- Determining preliminary carbon usage rates.

- Evaluating relative adsorbabilities of different contaminants.

- Evaluating the effects of temperature and pH on adsorption

- Comparing the performances of different carbons

- Evaluating the relative effects of other contaminants present in raw water

b. Procedure:

- Mix a measured weight of pulverized carbon in water of known organic concentration and agitate for a certain contact time.

- Measure resultant effluent organic concentration and calculate equilibrium capacity from the amount of organic adsorbed and the known weight of carbon in solution.

c. The relationship between equilibrium capacity and effluent concentration has been found to generally follow Freundlich isotherm relationship:

$$x/m = Kc^{1/n}.$$

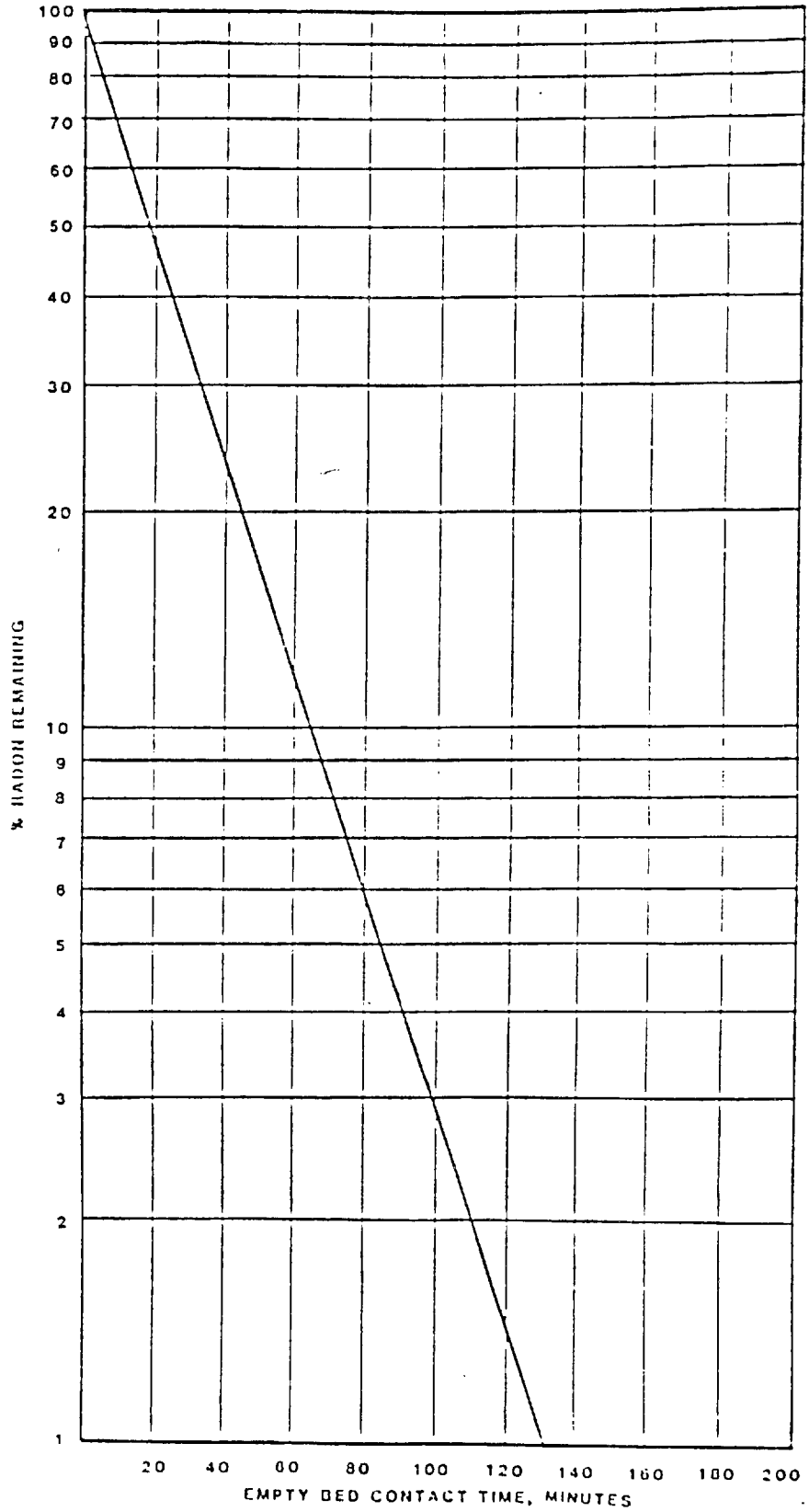


FIGURE 13- EMPTY BED CONTACT TIME VS PERCENT RADON REMAINING

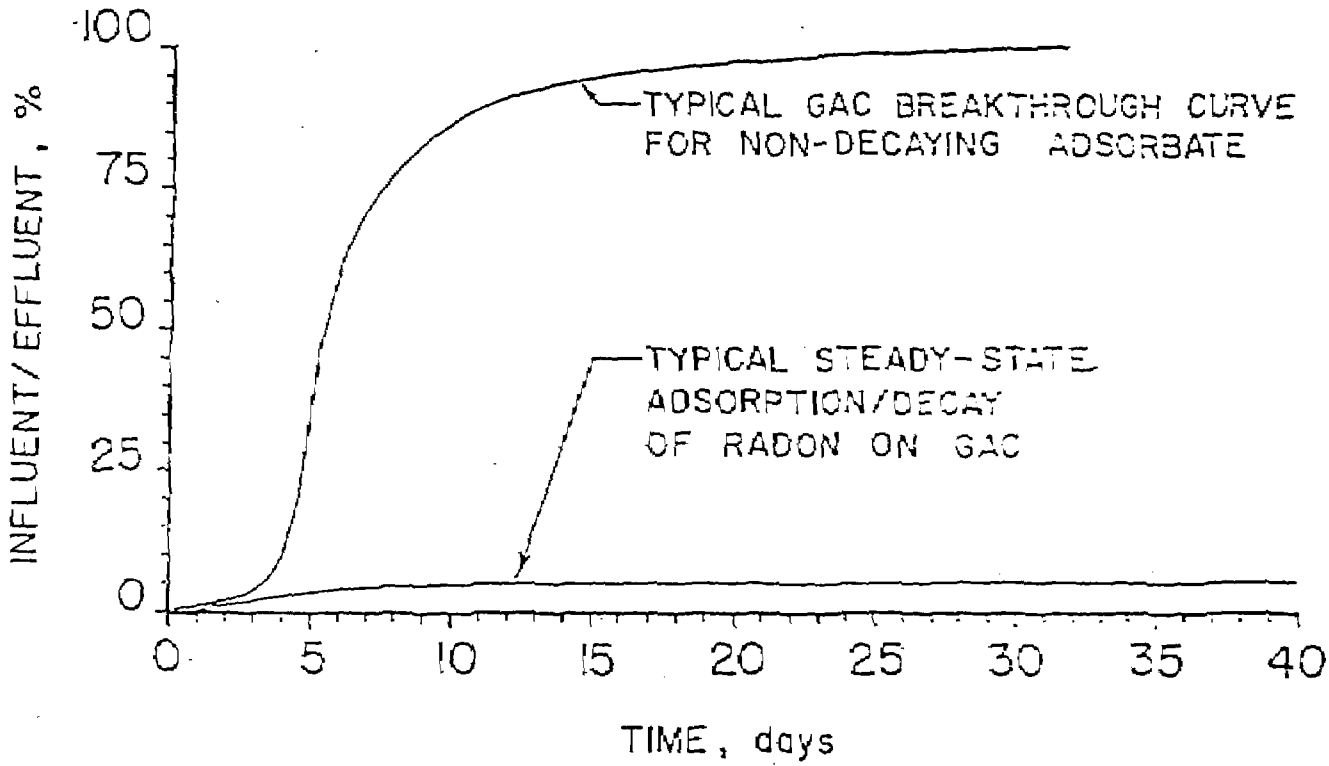


FIGURE 14- STEADY-STATE ADSORPTION/DECAY CURVE FOR RADON

where:

x/m = equilibrium capacity (mg organic/gm carbon)
c = organic concentration (mg/L)
K, 1/n = Freundlich constants

d. Isotherm constants for several organics have been reported by Dobbs and Cohen (Carbon Adsorption Isotherms for Toxic Organics, EPA-600/8-80-023, April 1980). Examples of the test results are shown on Figure 15 and in Table 9.

e. An approximate carbon usage can be calculated based on the isotherm equation. For example, assume:

Trichloroethylene (TCE) influent concentration (C_i) = 100 ug/L
Trichloroethylene (TCE) effluent concentration (C_o) = 5 ug/L
Safety factor (SF) = 0.75

Isotherm equation: $x/m = Kc^{1/n}$

Where:

$K = 28 \frac{(mg)}{(gm)} \left(\frac{(L)}{(mg)}\right)^{1/n}$ (From Table 9)

$1/n = 0.62$ (From Table 9)

Rearranging:

$$\text{Carbon Usage} \left(\frac{\text{lbs}}{1{,}000 \text{ gal}}\right) = \frac{Ci - Co}{K(C_i)^{1/n} SF} \times 8.34 \frac{(\text{lbs})}{(1{,}000 \text{ gal})} \frac{(L)}{(mg)}$$

$$= \frac{(100 - 5) \frac{ug}{L} \times \frac{1}{1{,}000} \frac{mg}{ug} \times 8.34 \frac{\text{lbs}}{1{,}000 \text{ gal}} \times \frac{L}{mg}}{28 \left(\frac{100}{1000}\right)^{0.62} \times 0.75}$$

$$= 0.16 \text{ lbs/1,000 gal}$$

2. Minicolumn Testing

a. Used to determine:

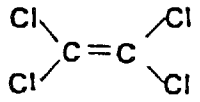
- Feasibility of carbon treatment for a given water
- Preliminary process design criteria
- Rough estimate of system economics

b. A typical setup for dynamic minicolumn test (DMCT) is shown on Figure 16. The procedure involves running a sample of raw water through a short GAC column (about 70 mm deep) and analyz-

TABLE 9
FREUNDLICH ISOTHERM CONSTANTS
FOR CARBON ADSORPTION

COMPOUND: Tetrachlorcethene (Tetrachloroethylene)

STRUCTURE:

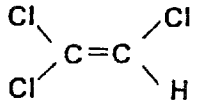


FORMULA: C_2Cl_4 MOL. WT. 165.83

FREUNDLICH PARAMETERS	pH		
	5.3		
K	50.8		
1/n	0.56		
Corr. Coef. r	0.96		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
1.0	51		
0.1	14.0		
0.01	3.9		
0.001	1.1		

COMPOUND: Trichloroethene (Trichloroethylene)

STRUCTURE:

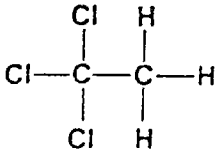


FORMULA: C_2HCl_3 MOL. WT. 131.39

FREUNDLICH PARAMETERS	pH		
	5.3		
K	28.0		
1/n	0.62		
Corr. Coef. r	0.99		
INITIAL CONC. mg/l	ADSORPTION CAPACITY, mg/gm		
1.0	28		
0.1	6.7		
0.01	1.6		
0.001	0.38		

COMPOUND: 1,1,1-Trichloroethane

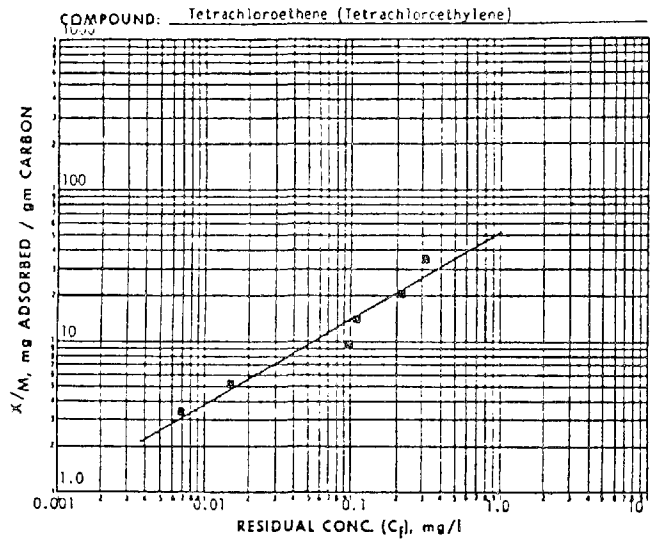
STRUCTURE:

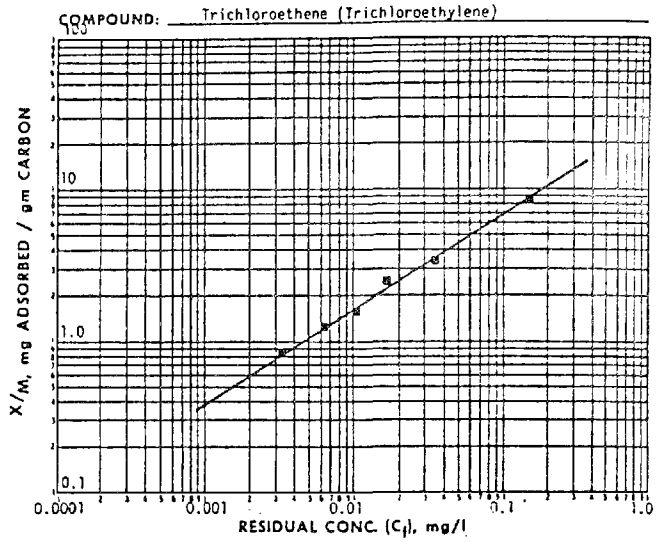


FORMULA: $C_2H_3Cl_3$ MOL. WT. 133.41

FREUNDLICH PARAMETERS	pH		
	5.3		
K	2.43		
1/n	0.34		
Corr. Coef. r	0.97		
INITIAL CONC mg/l	ADSORPTION CAPACITY, mg/gm		
1.0	2.5		
0.1	1.1		
0.01	0.51		
0.001	0.23		

REFERENCE: DOBBS AND COHEN (1980)





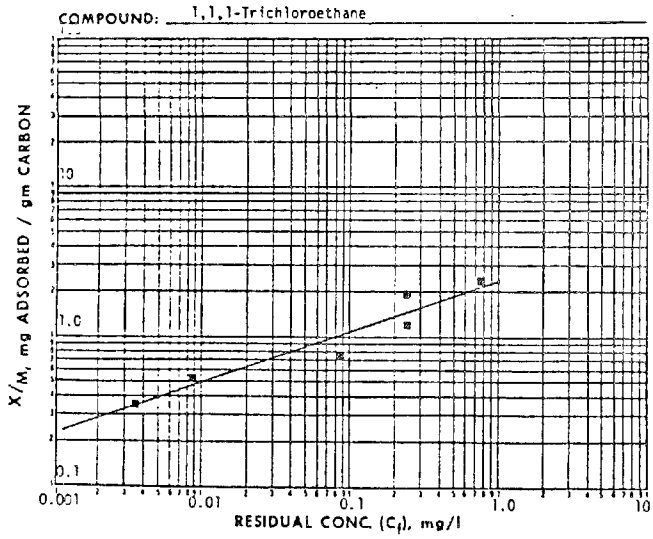


FIGURE 15- CARBON ISOTHERM TEST RESULTS

REFERENCE: DOBBS AND COHEN (1980)

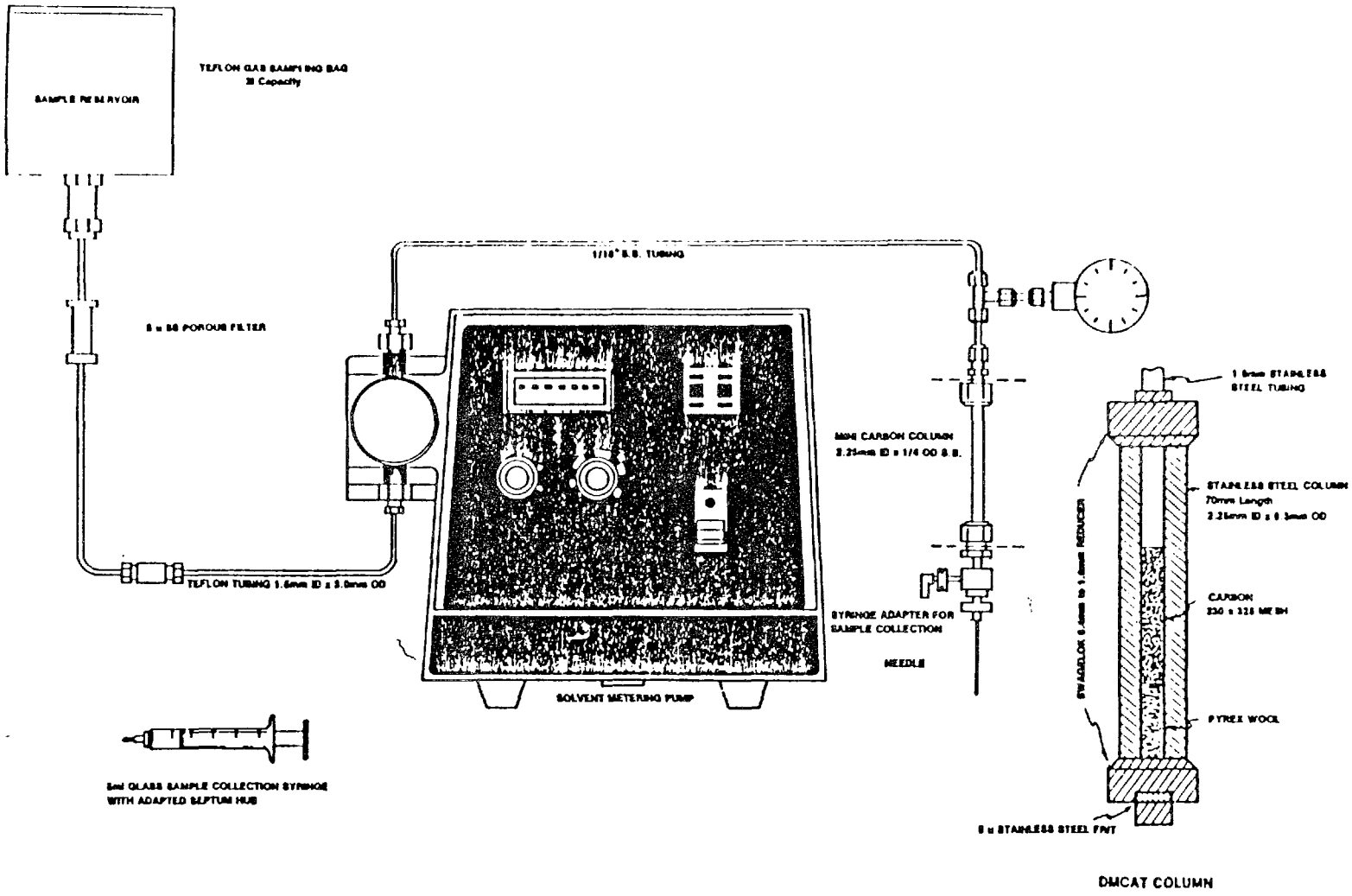


FIGURE 16- DIAGRAM OF DYNAMIC MINI-COLUMN ADSORPTION SYSTEM

ing the effluent concentration. Analysis of the test results is discussed in the following section.

3. Dynamic Column

   a. Used to simulate full-scale GAC facility operation and develop following design criteria:

      - Effect of various contact times
      - Optimum carbon bed depth
      - Effect of hydraulic loading
      - Number of vessels needed
      - Type of GAC needed
      - Carbon life/changeout frequency
      - Carbon exhaustion rate
      - Contaminant loading rates

   b. A typical set-up for pilot column test is shown on Figure 17. Raw water is run through GAC columns (about five-foot deep and 4-inch I.D.). Effluent is sampled to obtain the breakthrough curve (time versus concentration relationship).

D. Optimizing Design Criteria

1. Optimize key design parameters to minimize treatment costs. Cost components shown on Figure 18 indicate that key design parameters are:

   - EBCT
   - Carbon usage

2. Optimizing EBCT

   a. Plot breakthrough curves - examples of breakthrough curves for cis-1,2 dichloroethylene (DCE) and TOC are given on Figures 19 and 20, respectively.

   b. Calculate carbon usage rates:

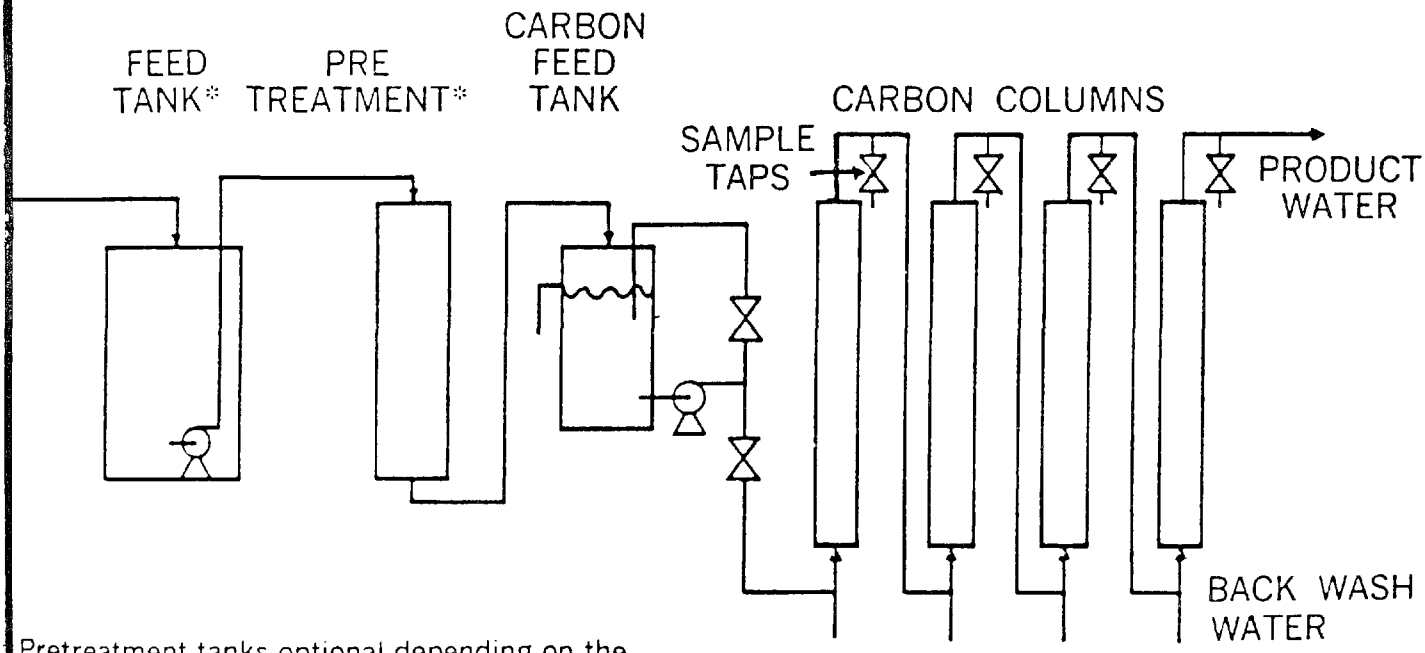
$$\text{CU (lbs/1000 gal)} = \frac{\text{Mass of Carbon (lbs) x 1,000 gallons}}{\text{Volume Treated to Breakthrough (gallons)}}$$

   c. Plot carbon usage versus EBCT - example for DCE and TOC are shown on Figures 21 and 22, respectively.

   d. Select optimum EBCT - 15 minutes for DCE, 20 minutes for TOC

3. Parallel versus series flow

   a. Parallel flow (shown on Figure 23) necessitates carbon replacement at breakthrough



Pretreatment tanks optional depending on the suspended solids concentration in feed.

FIGURE 17- DIAGRAM OF PILOT COLUMN TEST SYSTEM

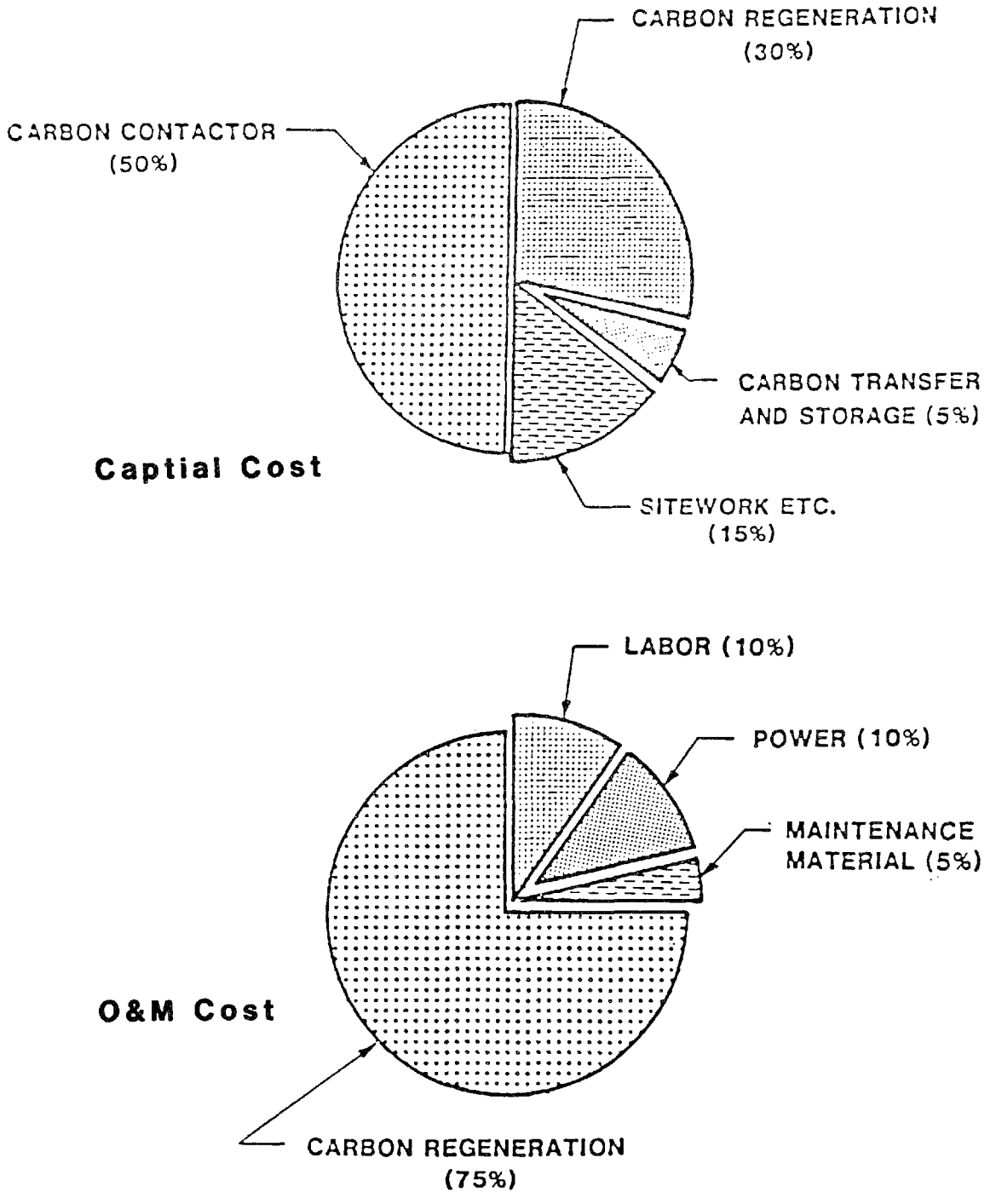
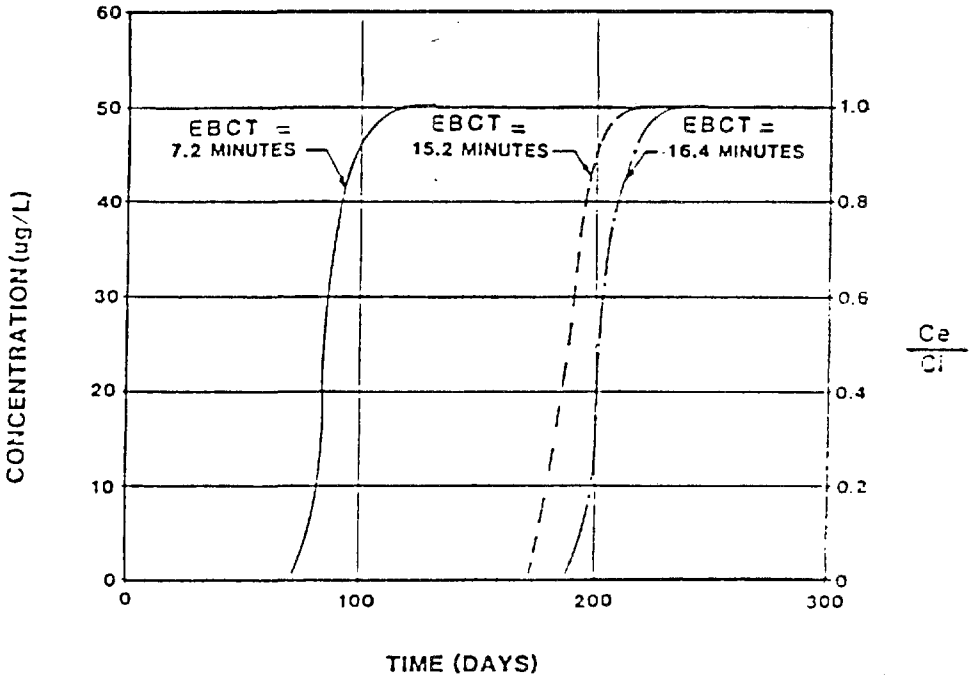
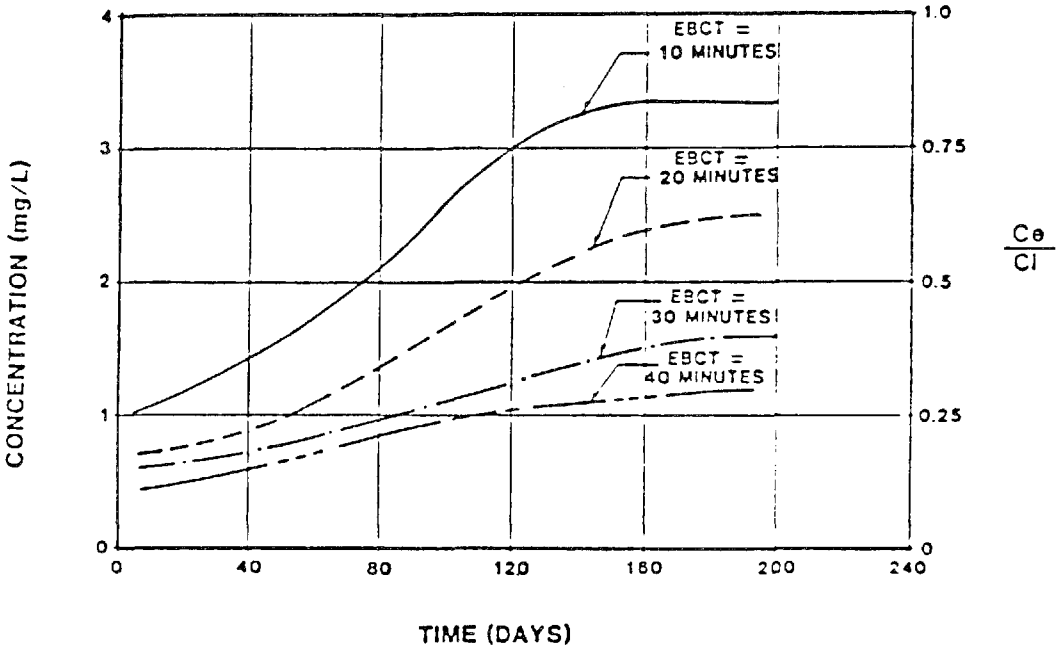


FIGURE 18- GAC FACILITY COST COMPONENTS



Note: Ci = Influent Concentration
Ce = Effluent Concentration

FIGURE 19- BREAKTHROUGH CURVES FOR c-1,2 DCE



Note: Ce = Effluent Concentration
Ci = Influent Concentration

FIGURE 20- BREAKTHROUGH CURVES FOR TOC

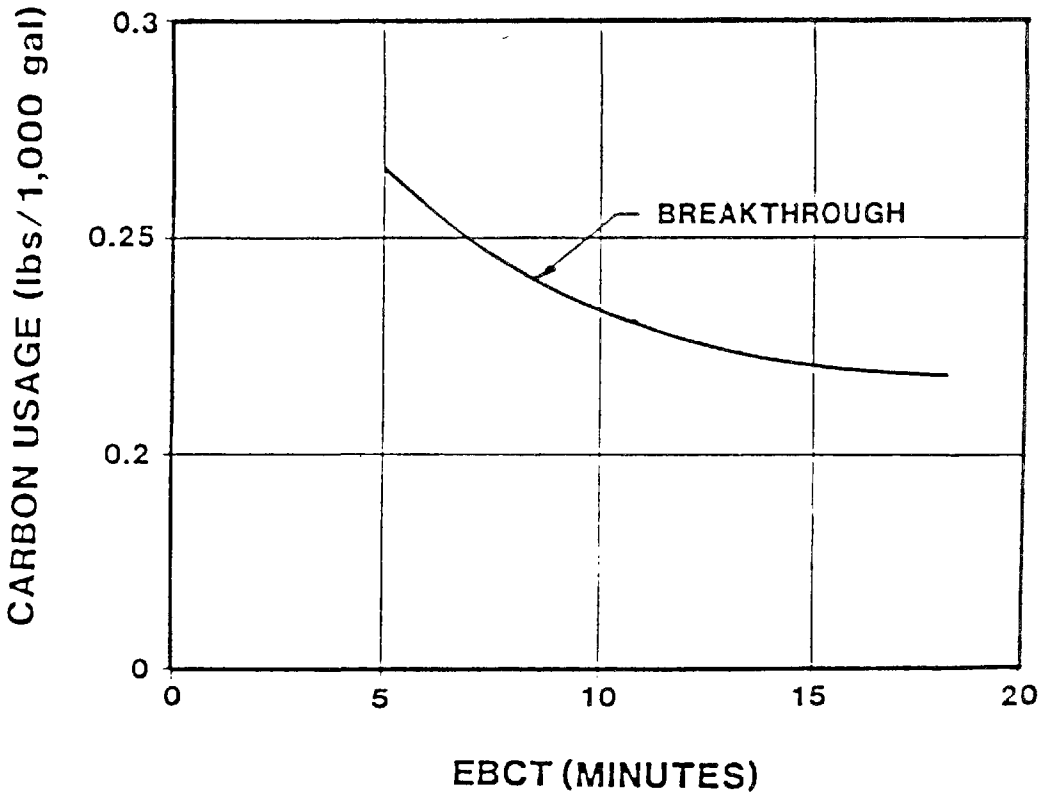


FIGURE 21- EBCT VERSUS CARBON USAGE FOR c-1,2 DCE

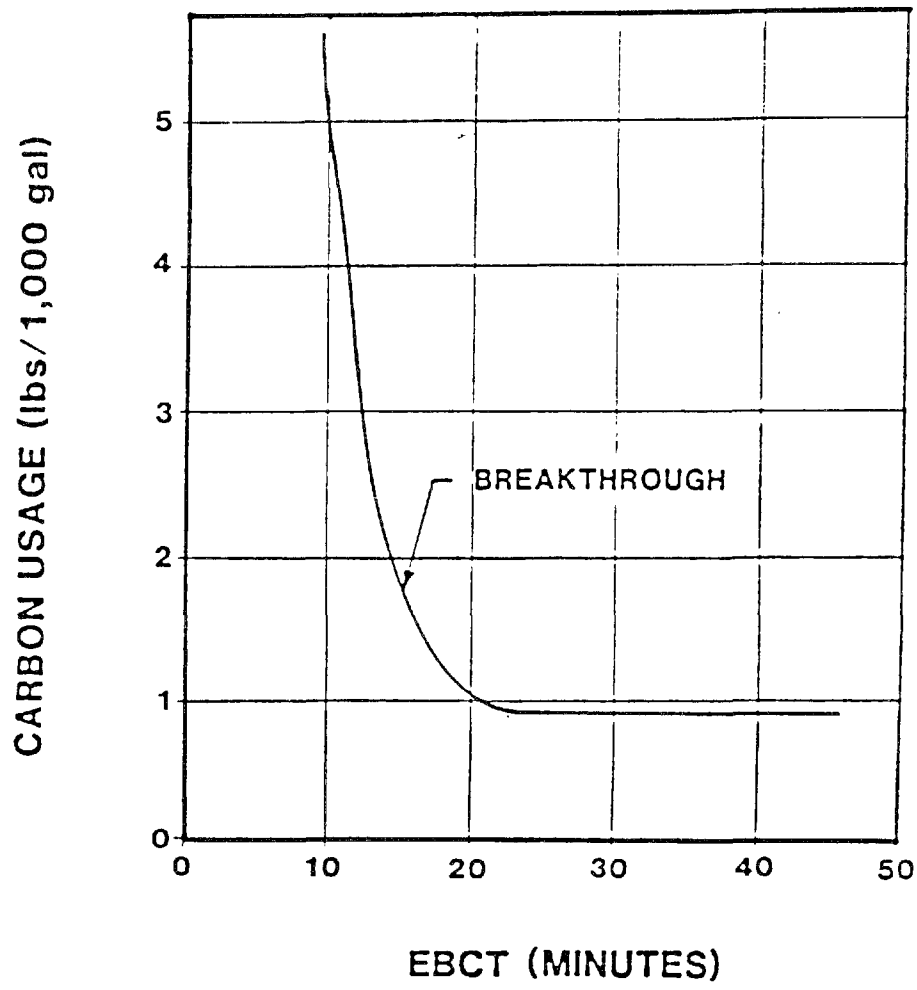
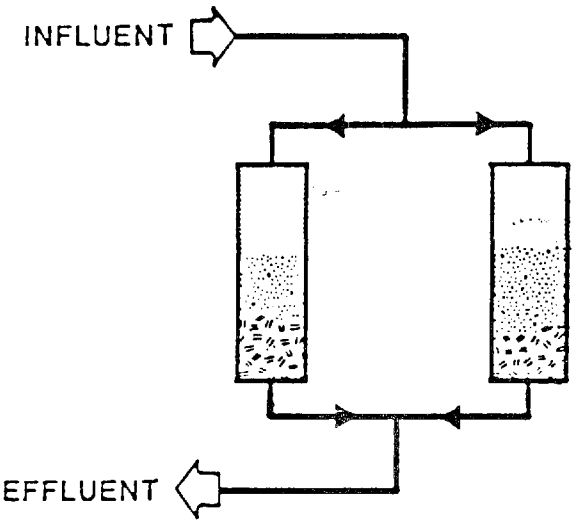


FIGURE 22- EBCT VERSUS CARBON USAGE FOR TOC



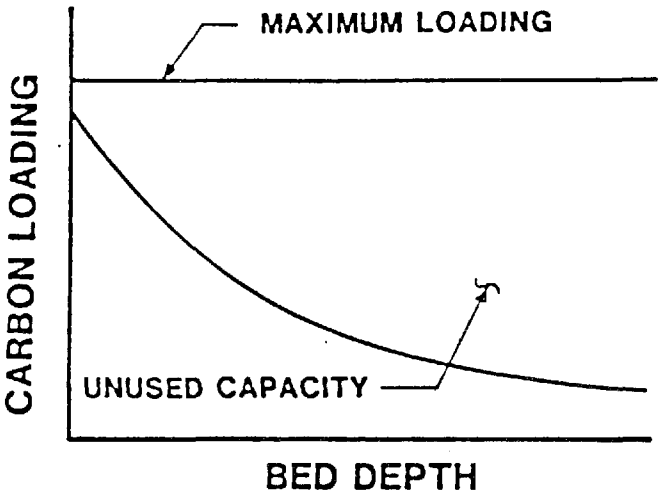


FIGURE 23- PARALLEL MODE OF OPERATION

b. Series flow (shown on Figure 24) provides for carbon replacement at exhaustion

c. Optimize between number of contactors (capital cost) and regeneration frequency (operating cost)

d. Cost comparison between the two modes are shown on Figures 25 and 26 for DCE and TOC, respectively.

E. Facility Design Considerations

1. Major Process Elements

a. Carbon contactors
b. Regeneration system

2. Carbon Contactor Configuration

a. Upflow

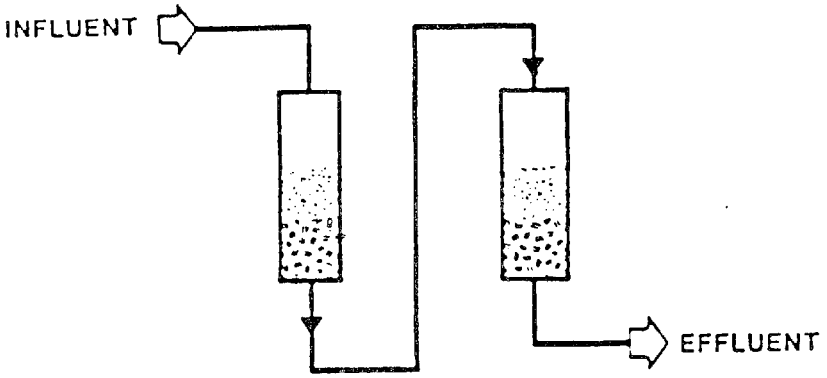
- Can be operated in parallel or series mode
- Bed allows suspended solids to pass without developing excessive pressure drop
- Release of carbon fines in effluent stream is of concern
- More widespread use for wastewater treatment

b. Downflow

- Can be operated in parallel or series mode
- Small amount of suspended matter can be handled by back-washing
- Can be operated in pressure or gravity mode
- Pressure contactor (shown on Figure 27) offers more flexibility as the system can be operated with higher head loss
- Gravity contactor (shown on Figure 28) are less expensive due to common wall construction

3. GAC regeneration:

a. On-Site Regeneration - economical where carbon exhaustion rate is greater than 1,500 pounds per day.



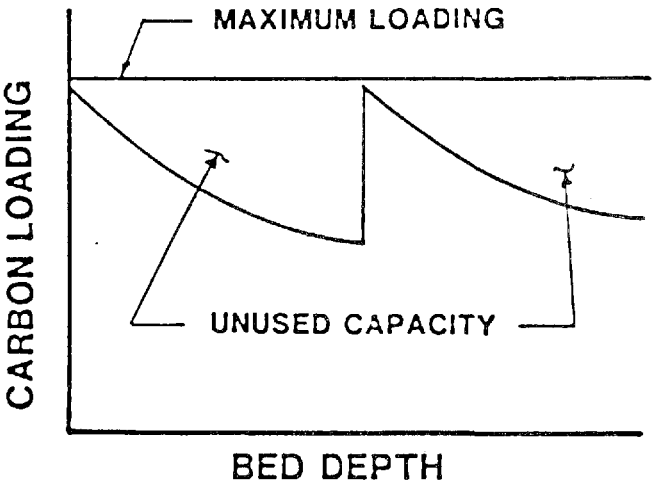


FIGURE 24- SERIES MODE OF OPERATION

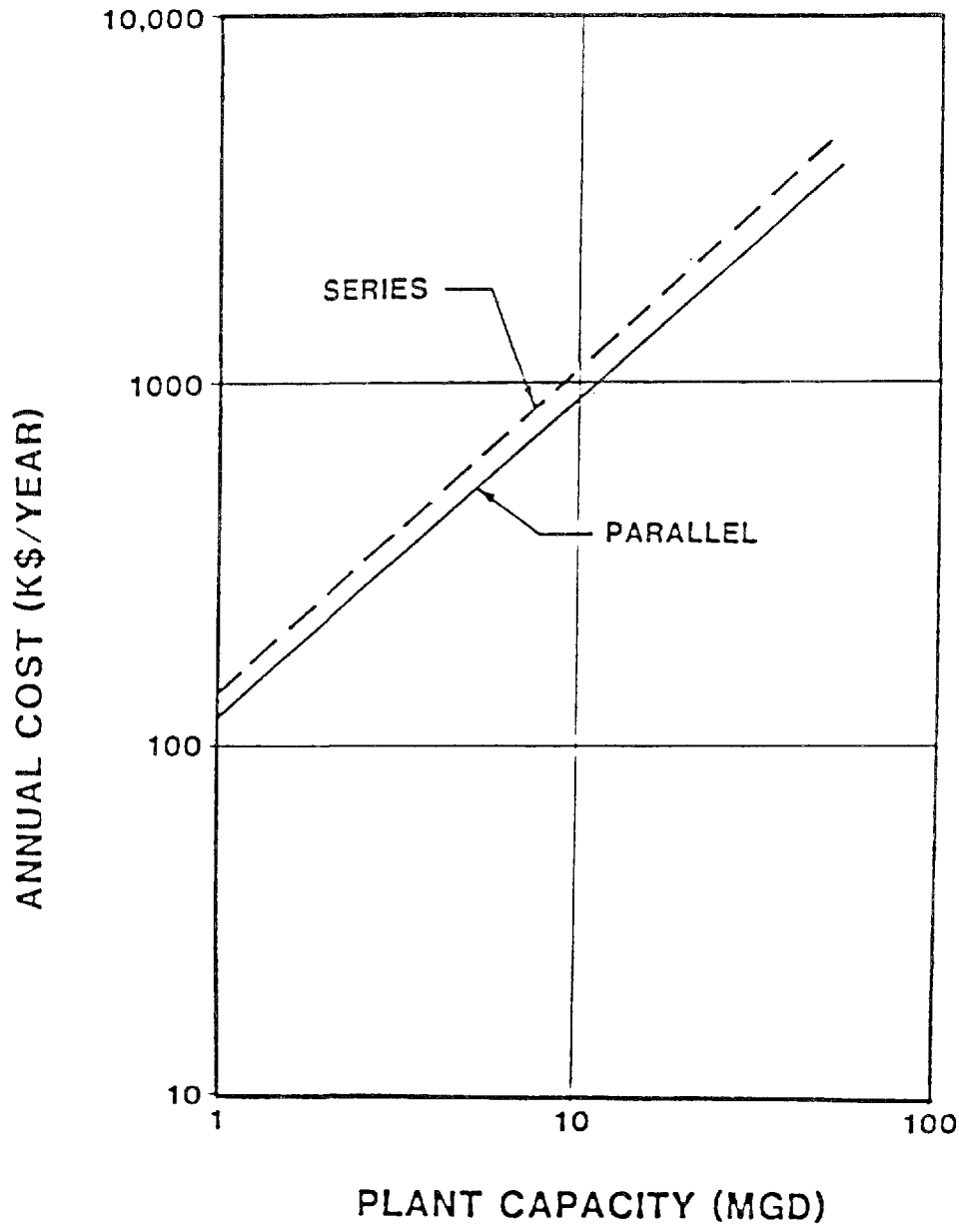


FIGURE 25- COST COMPARISON OF PARALLEL VERSUS SERIES FLOW FOR c-1,2 DCE

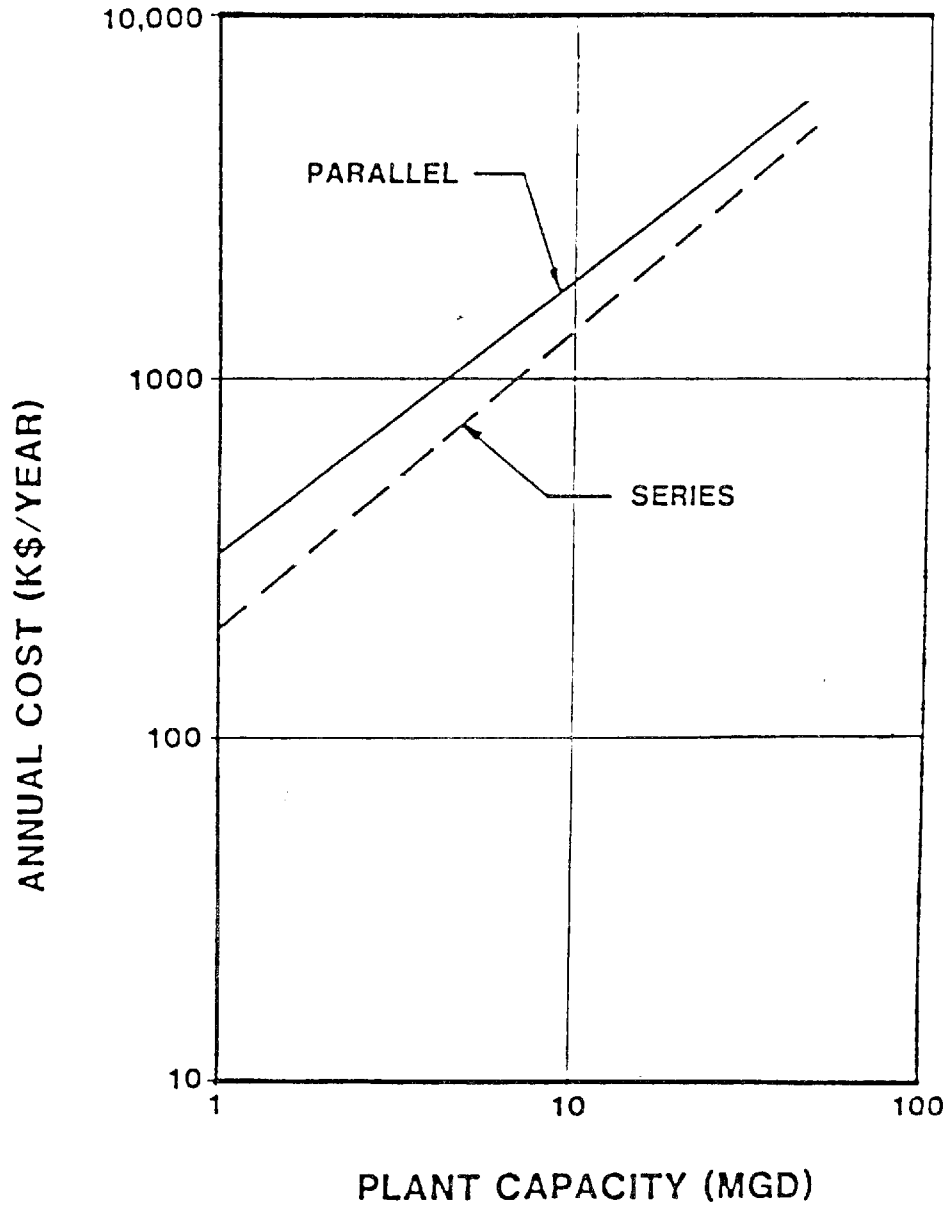


FIGURE 26- COST COMPARISON OF PARALLEL VERSUS SERIES FLOW FOR TOC

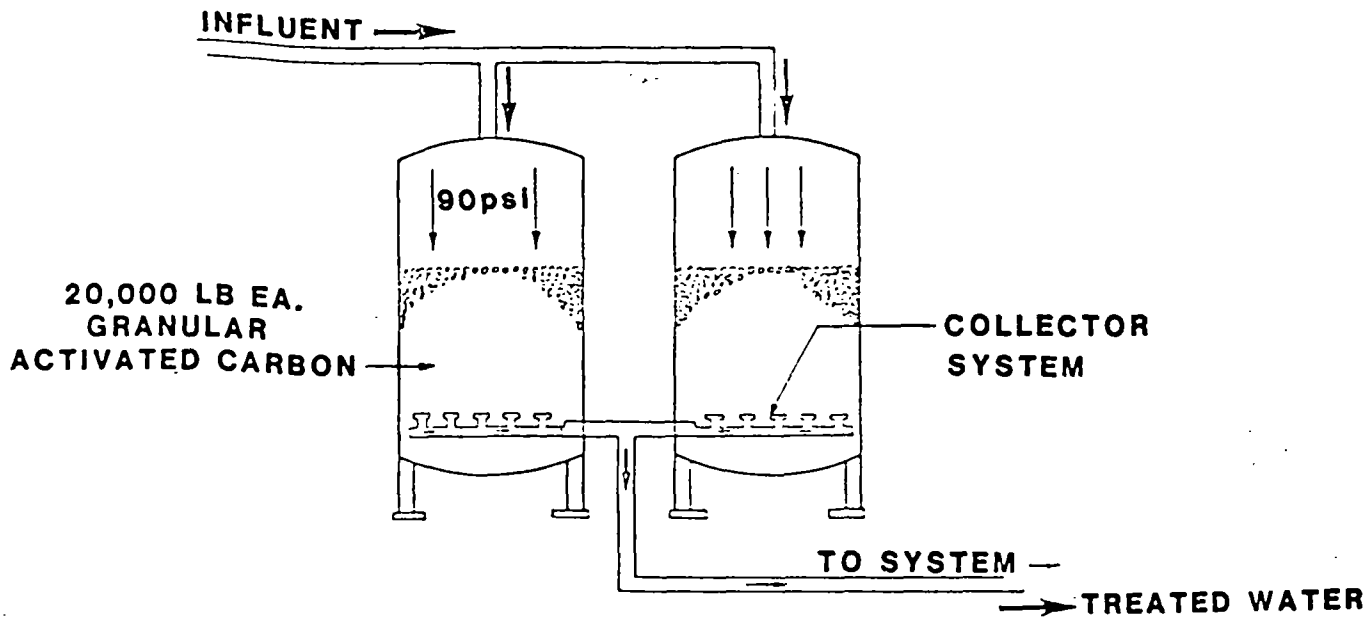


FIGURE 27- SCHEMATIC OF PRESSURE GAC CONTACTORS

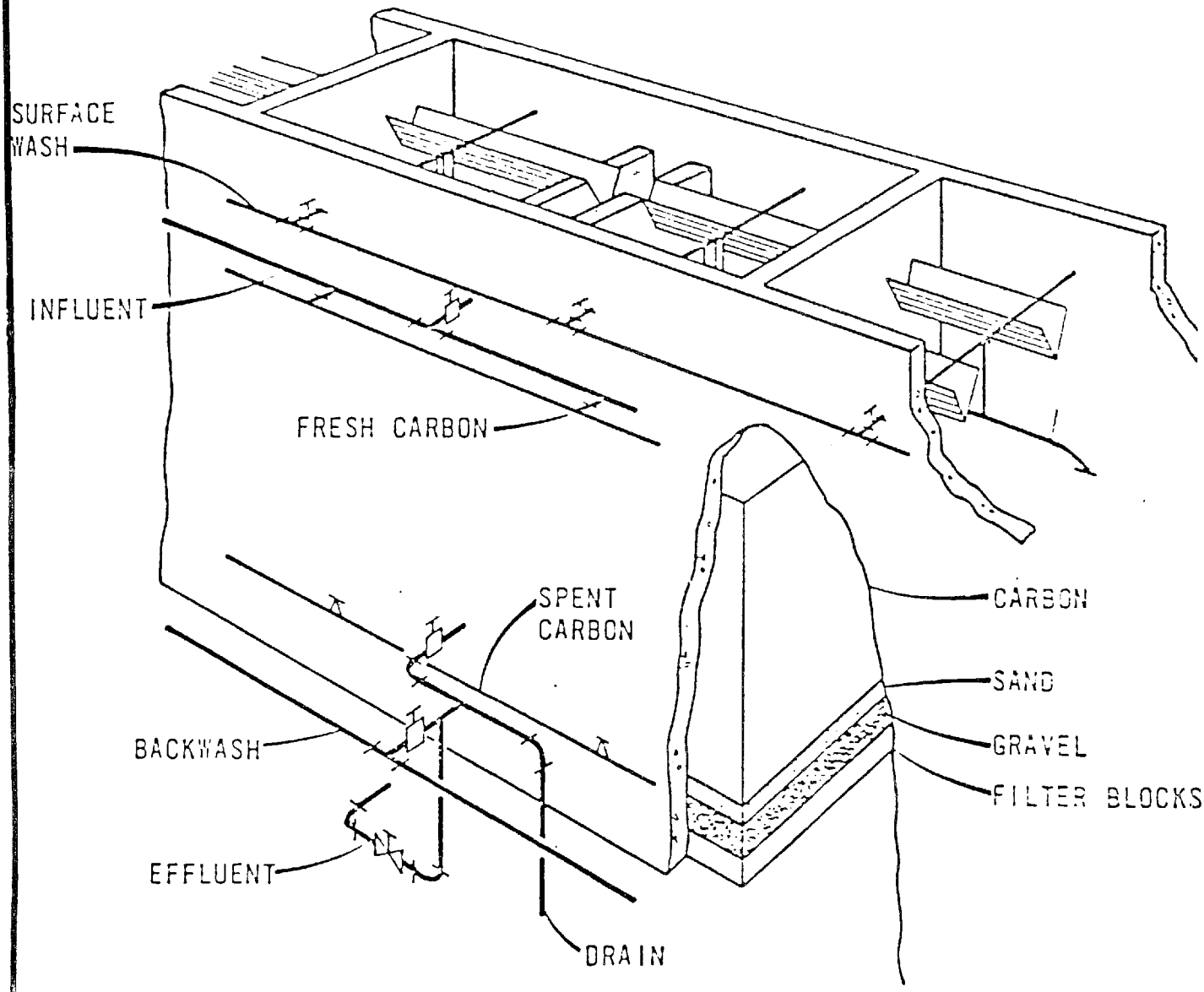


FIGURE 28- SCHEMATIC OF DOWNFLOW GRAVITY GAC CONTACTOR

b. Off-Site Regeneration - economical where carbon exhaustion rate falls between 500 and 1,500 pounds per day.

c. Off-Site Disposal - economical where carbon exhaustion rate is less than 500 pounds per day.

d. Cost comparison of different carbon recharge options are shown on Figure 29.

4. Operational Issues

a. Desorption

- Due to decrease in influent concentration

- Due to chromatographic effects (displacement of an organic compound by another that is more favorably adsorbed)

b. Bacterial growth

- Could enhance removals by biodegradation
- Causes clogging of the carbon bed
- Causes higher plant count in treated water

c. Backwash

- Minimized by providing adequate pretreatment. Backwashing should be gentle in order not to fluidize the carbon bed.

5. Waste Disposal

a. Backwash

- Carry-over of carbon fines during initial backwashing

b. Spent carbon

- Regeneration on-site or off-site
- Disposal in a hazardous waste landfill

F. Applicability to Various System Sizes

1. Organics Removal:

a. <1 mgd, package pressure contactors
b. 1 to 10 mgd, pressure contactors
c. >10 mgd, gravity contactors

2. Radon Removal:

a. Small systems, home GAC units - see Figure 30
b. Large systems, not economically feasible

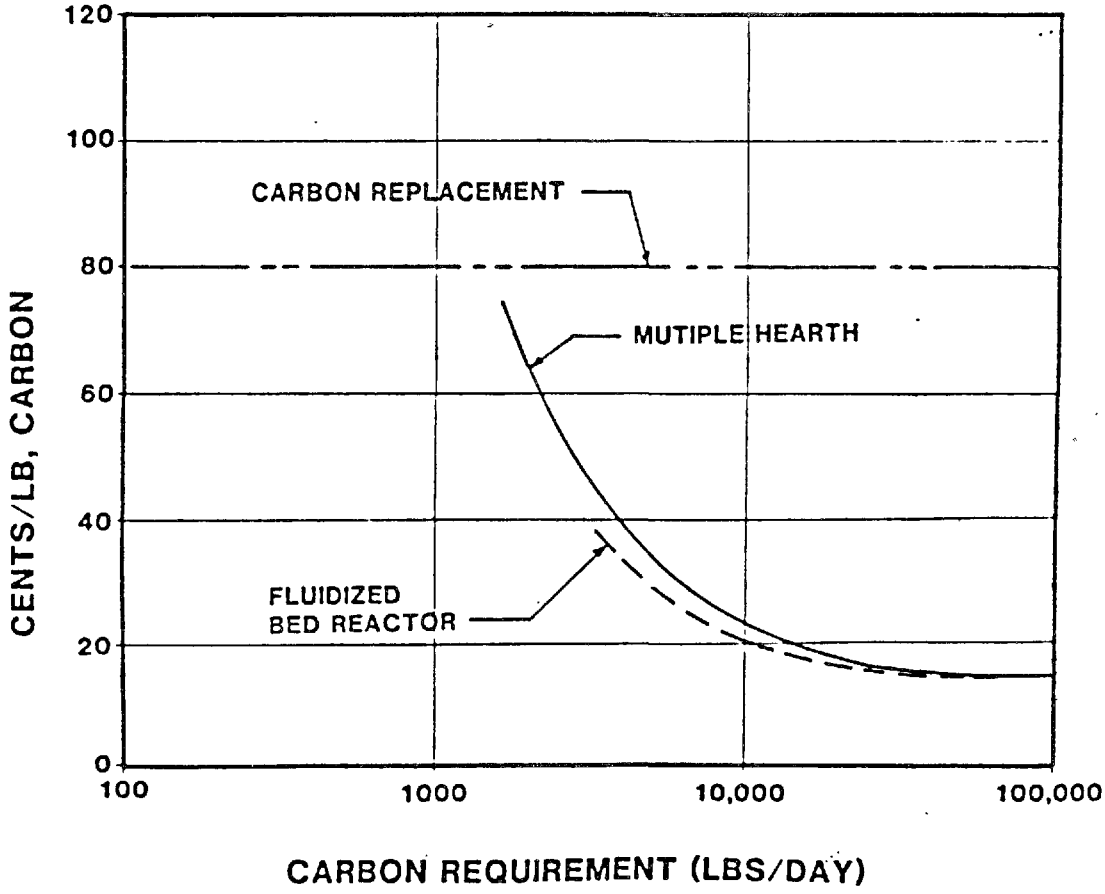


FIGURE 29- COST COMPARISON OF CARBON RECHARGE OPTIONS

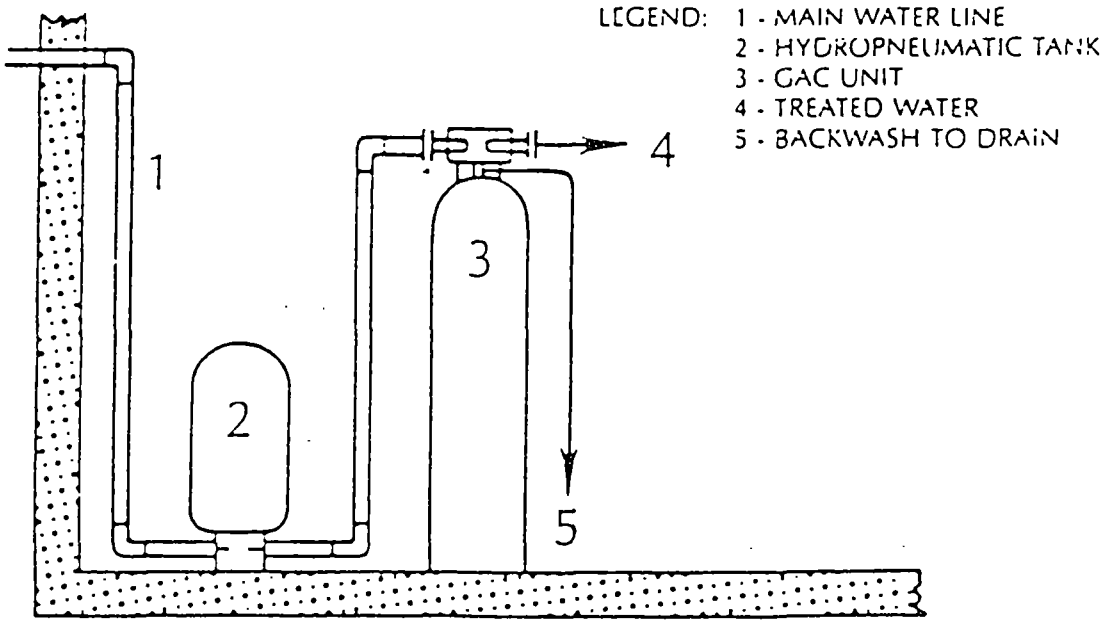


FIGURE 30- TYPICAL HOME GAC UNIT

G. Treatment Economics

1. Capital cost components include:

Basic	Site Specific
Contactors	Special sitework
Activated carbon	Raw water holding tank (for ground water systems)
Regeneration facility	New/restaged well pump (for ground water systems)
Carbon storage	GAC contactor building
Carbon transport facilities	Chemical facility
	Clearwell
	Finished water pump(s)
	Backwash storage

2. Operation and maintenance (O&M) cost components include:

- carbon make-up
- labor
- fuel
- steam
- power
- maintenance
- laboratory analyses

3. Cost curves for different contaminant groups are shown on Figure 31 (capital cost) and Figure 32 (O&M cost). In general:

Pesticides -
Chlorinated aromatics -
VOCs -
Radon -

least costly
↓
most costly

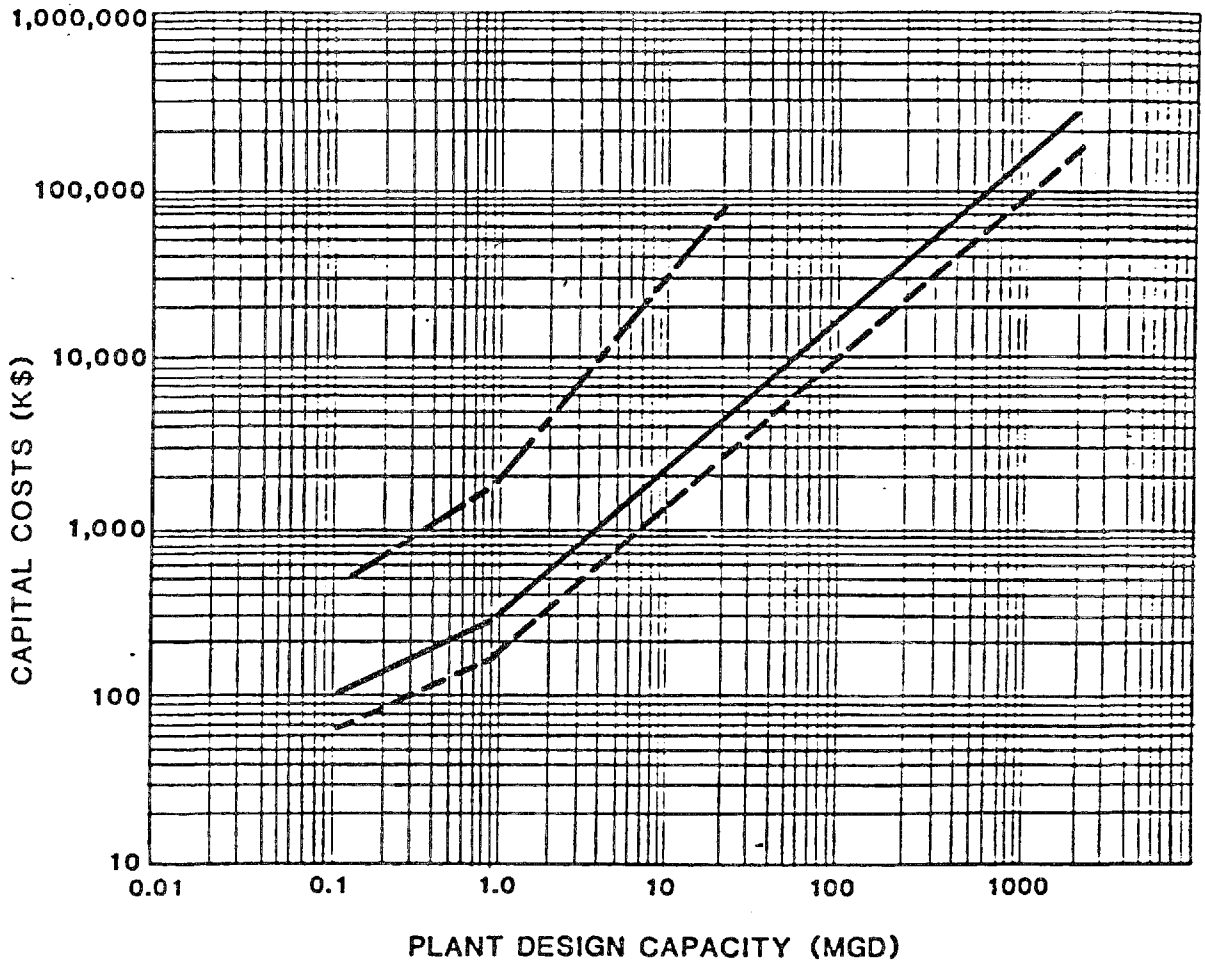


FIGURE 31 - CAPITAL COST CURVES FOR GAC FACILITIES

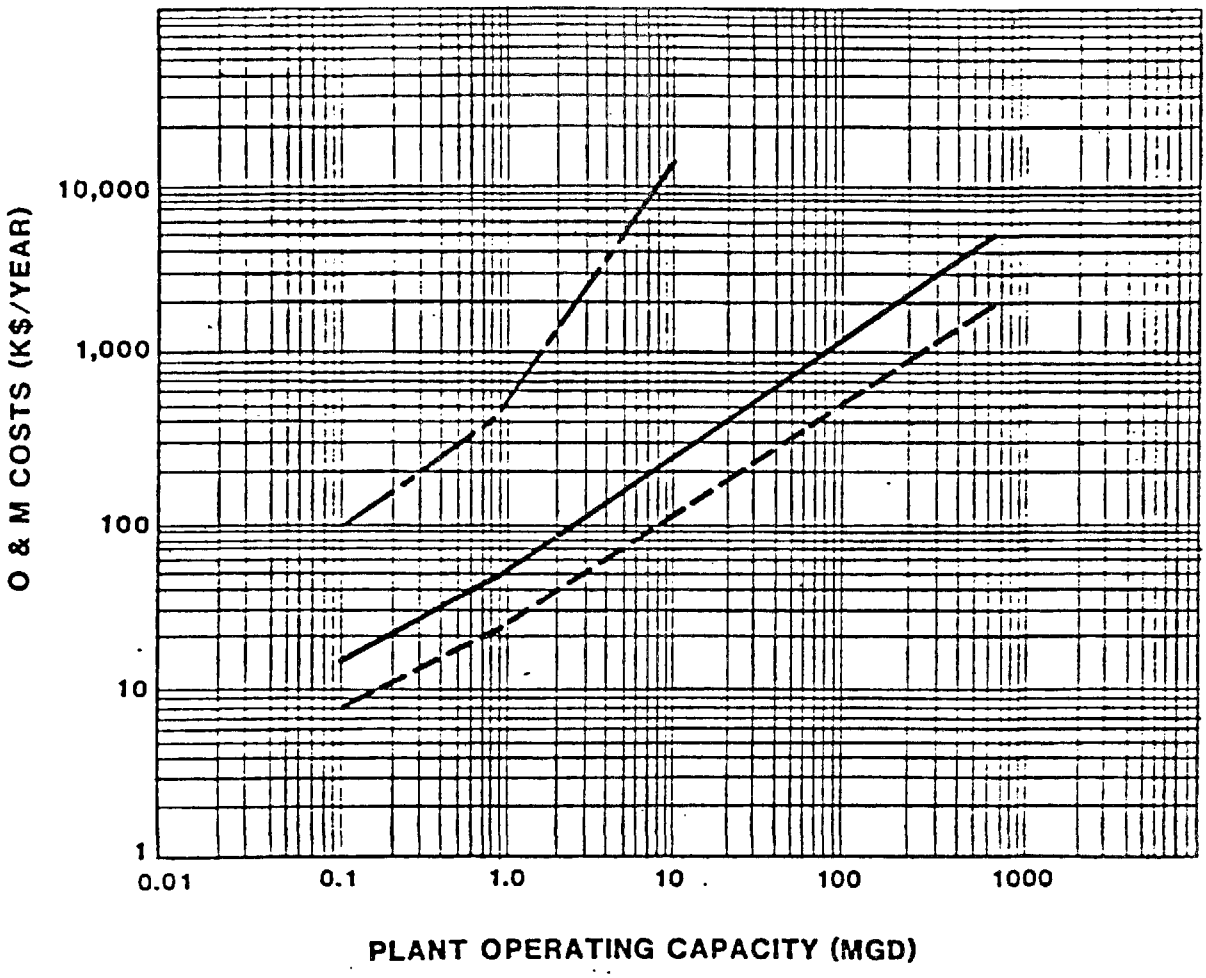


FIGURE 32 - O & M COST VURVES FOR GAC FACILITIES

IV. PACKED COLUMN AERATION

A. Process Description

1. Based on the principle of mass transfer from liquid phase to gas phase. Rate of mass transfer proceeds according to following equation:

$$M = K_L \, a \, \Delta P$$

Where: M = mass of substance transferred per unit time and volume (lb/hr/cf)

K_L = coefficient of mass transfer (lb/hr/sf)

a = effective area (sf/cf)

ΔP = concentration difference or driving force

2. Driving force is the difference between actual conditions in the air stripping unit and conditions associated with equilibrium between the gas and liquid phases.

3. Henry's Law

   a. Equilibrium concentration follows Henry's Law, which states that the amount of gas dissolves in a given quantity of liquid, at constant temperature and total pressure, is directly proportional to the partial pressure of the gas above the solution. Henry's constant calculated as follows:

$$H \text{ (dimensionless units)} = \frac{(16.04)\ (P)\ (M)}{(T)\ (S)}$$

   P = vapor pressure in mm
   M = gram molecular weight of solute
   T = temperature in degrees Kelvin
   S = solubility in mg/L

   b. A compound's Henry's Law constant indicates relative volatility of the compound; high Henry's Law constant - easily removed by air stripping.

   c. Henry's Constants for several chemicals (at 20 C):

VOCs	Henry's Constant (atm)
- Vinyl chloride:	2,985
- Trichloroethane (TCA):	286

- Tetrachloroethylene (PCE): 274
- Trichloroethylene (TCE): 155

Pesticides

- Chlordane: 5.35
- Dibromochloropropane (DBCP): 13.8
- Aldicarb: 2.32×10^{-4}

Chlorinated Aromatics

- Dichlorobenzene: 108
- PCB (Arochlor 1242): 78.6

Radon 2,260

4. A schematic of the packed column aeration system is shown on Figure 33.

B. Process Design Considerations

1. Key Parameters:

   a. contaminant

   b. levels

   c. type of packing material

   d. A:W ratio (cubic feet per cubic feet)

   e. Liquid loading rate (gpm/sf)

   f. Packing height (ft)

   g. water temperature

2. Contaminant and Levels

   a. Higher the volatility of a compound, the more easily it is stripped by aeration.

   b. Effect of different organics on packed column design is shown on Figure 34.

3. Type of Packing Material

   a. Packing materials are designed to provide:

      - maximum air-water contact area
      - low air pressure drop

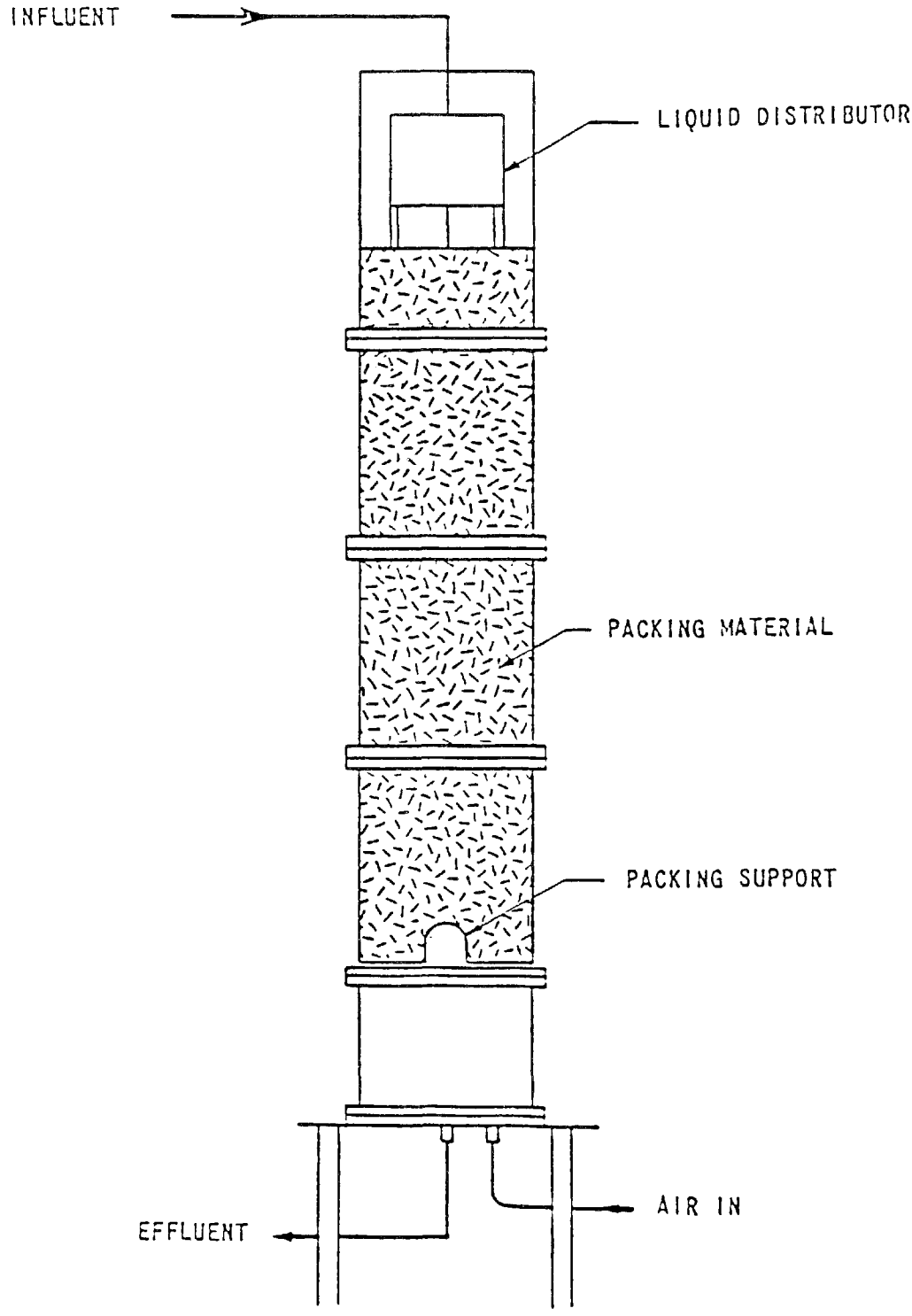


FIGURE 33- DIAGRAM OF PACKED COLUMN AERATOR

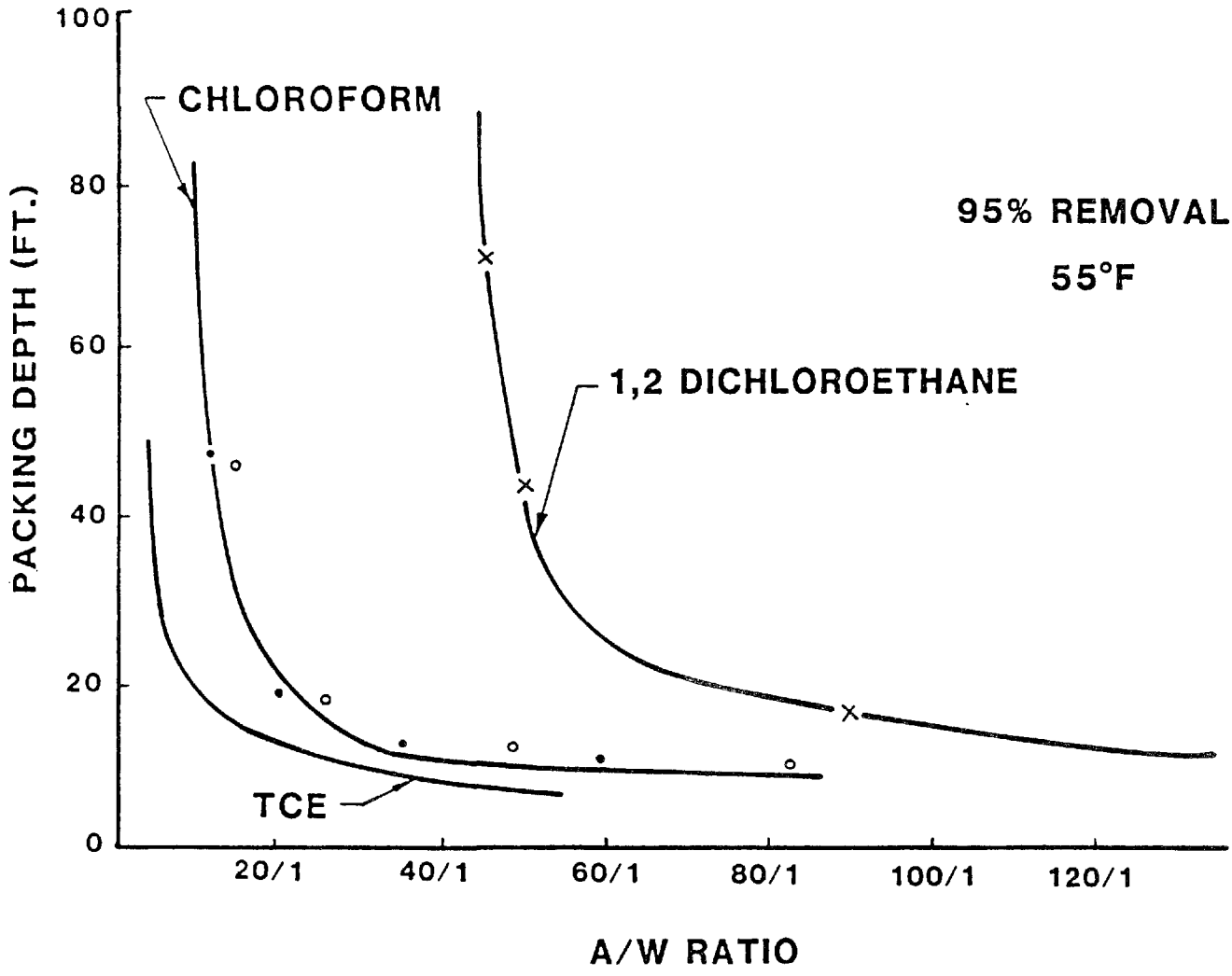


FIGURE 34- EFFECT OF COMPOUND ON PACKED COLUMN DESIGN

b. Generally made of plastic or ceramics, and vary in sizes (1/2 inch to 4 inches)

c. Commonly used packing materials include:

- Super intalox
- Tellerettes
- Tri-packs
- Pall rings
- Berl saddles
- Raschig rings

4. Air to Water Ratio

a. Function of:

- Contaminant type
- Water temperature

b. Determines the blower size and operating cost of the system

c. Typical range of air/water ratio are:

30:1 - Highly volatile compounds (e.g., TCE)
200:1 - Highly soluble compounds (e.g., DBCP)

5. Liquid Loading Rate

a. Determines the column diameter
b. Typically 25-30 gpm/ft^2

6. Packing Height

a. Function of:

- Air/Water ratio
- Required removal

b. Determines the capital cost of the system

7. Water Temperature

a. Solubility of organic compounds in water generally decreases with increase in temperature

b. Impact of water temperature on column design is shown on Figure 35.

C. Testing to Evaluate Process Design Parameters

1. A schematic of the pilot column used for testing packed column aeration is shown on Figure 36.

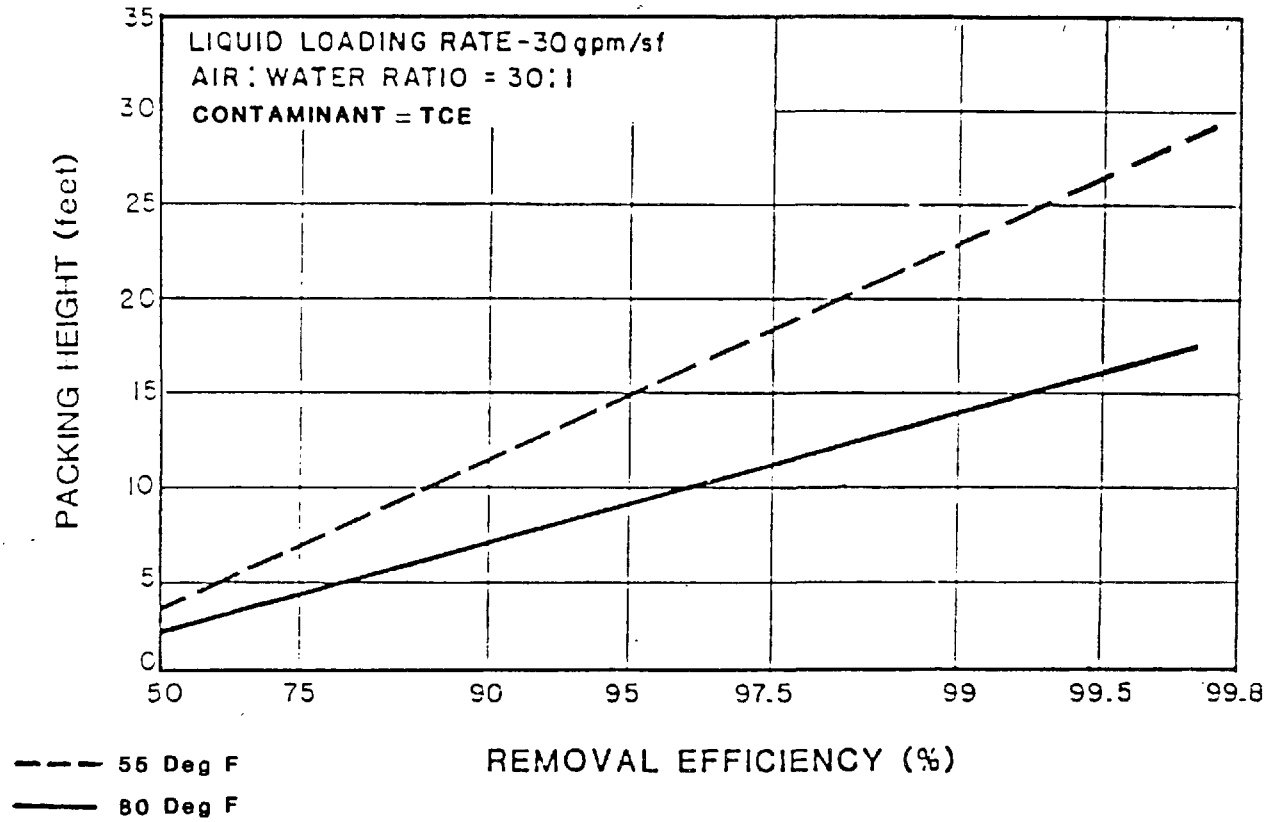


FIGURE 35- EFFECT OF TEMPERATURE ON PACKED COLUMN DESIGN

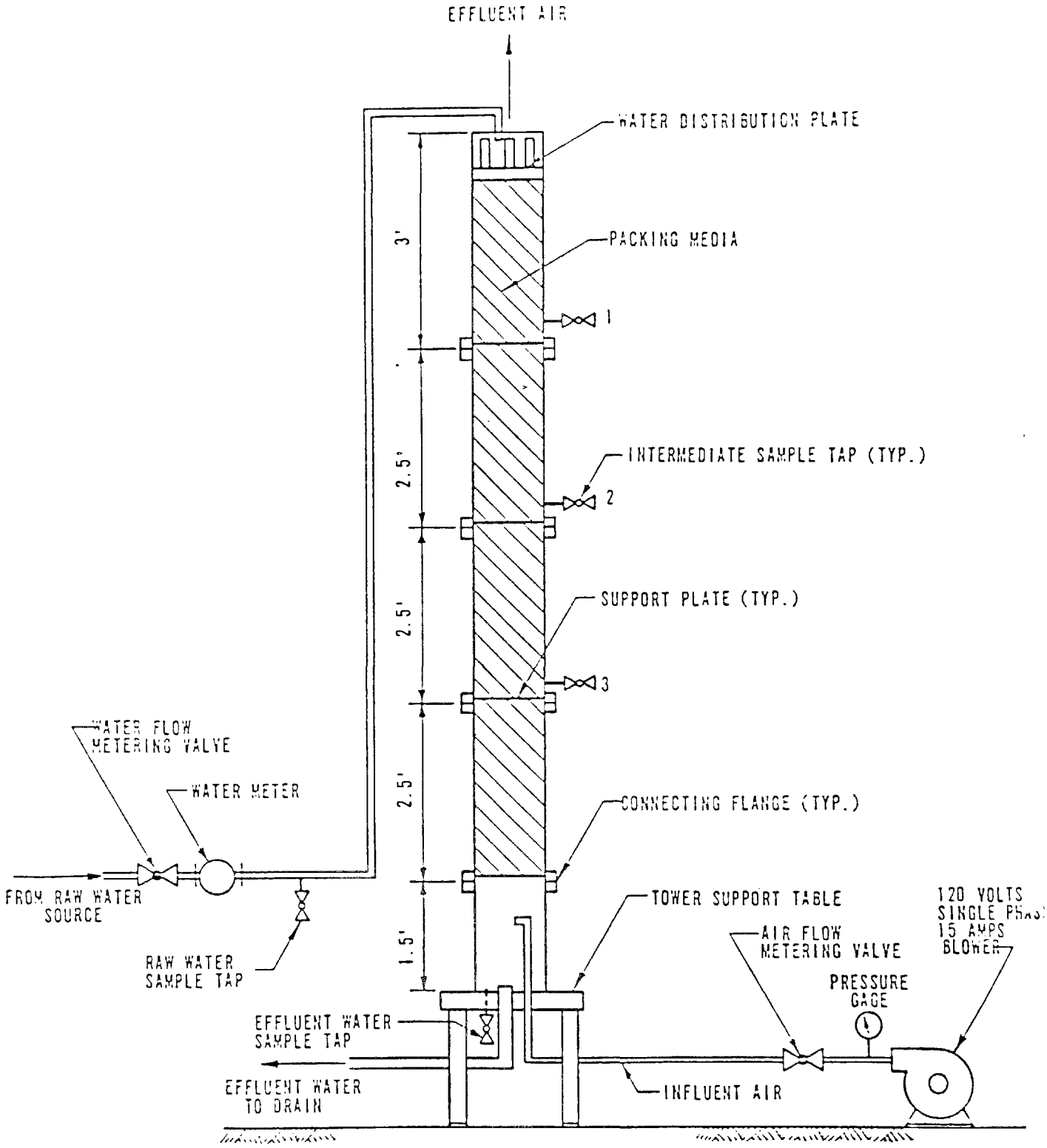


FIGURE 36- SCHEMATIC OF PILOT AERATION COLUMN

2. Test variables are:

   a. Hydraulic loading rate
   b. Air flow rate
   c. Air:Water (A:W) ratio
   d. Type of packing

3. Testing Procedure:

   a. Water and air flowrates are varied to obtain several A:W ratios. For each run, the column is operated for about 30 minutes to achieve steady state. Eight to twelve runs are recommended for each test.

   b. For each run, influent and effluent samples are collected, along with air and water flowrates, and air and water temperatures.

   c. The procedure is repeated for different packing materials.

   d. Precautions: In order to ensure reliable data from the pilot study, the following factors have to be considered:

      - Packing material should be dumped carefully to avoid channeling and void spaces in the column.

      - The pilot column should be on level ground to minimize channeling or wall effects.

      - Sampling points should be located so that the samples truly represent the process performance.

      - Samples should be collected in duplicates.

      - Accuracy of the laboratory analysis method should first be verified.

D. Development of Design Criteria

1. Design of packed column aeration system involves the following relationships:

   a. $Z = (HTU)\ (NTU)$, where:

      Z = packing height (ft)
      HTU = Height of transfer unit (ft)
      NTU = Number of transfer units

b. $HTU = \frac{L}{K_L a C_o}$, where:

L = liquid flow, lb mole/hr/sq ft
C_o = molar density of water, lb mole/cu ft

c. $NTU = \frac{R}{R-1} \ln\left[\frac{(x_i/x_o)(R-1) + 1}{R}\right]$

Where: x_i/x_o = Ratio of influent to effluent liquid phase concentration
R = Dimensionless stripping factor

d. $\frac{(A)(H)}{(W)} \frac{MW_{H2O}}{MW_{Air}} \frac{Density_{Air}}{Density_{Water}}$

$= \frac{A}{W}(H)(7.512 \times 10^{-4})$

Where: A = Air Flowrate (cfm)
W = Water Flowrate (cfm)
H = Henry's Constant (atm)

2. Develop mass transfer relationships as shown on Figure 37.

3. Select the packing material with largest $K_L a$, and optimum liquid loading rate (gpm/sf).

4. Estimate optimum A/W ratio based on A/W ratio - packing height relationship, as shown on Figure 38.

5. Nomographs for preliminary design of packed columns have been developed by Speece, Niamalakhandan and Lee (Nomograph for Air Stripping of VOC from Water, Journal of Environmental Engineering, Vol. 113, No. 2, April 1987).

E. Facility Design Considerations

1. Major Process Elements

a. Column and column intervals
b. Packing medium
c. Blower
d. Booster pump
e. Instrumentation and control

2. A schematic diagram of a packed column facility is shown on Figure 39.

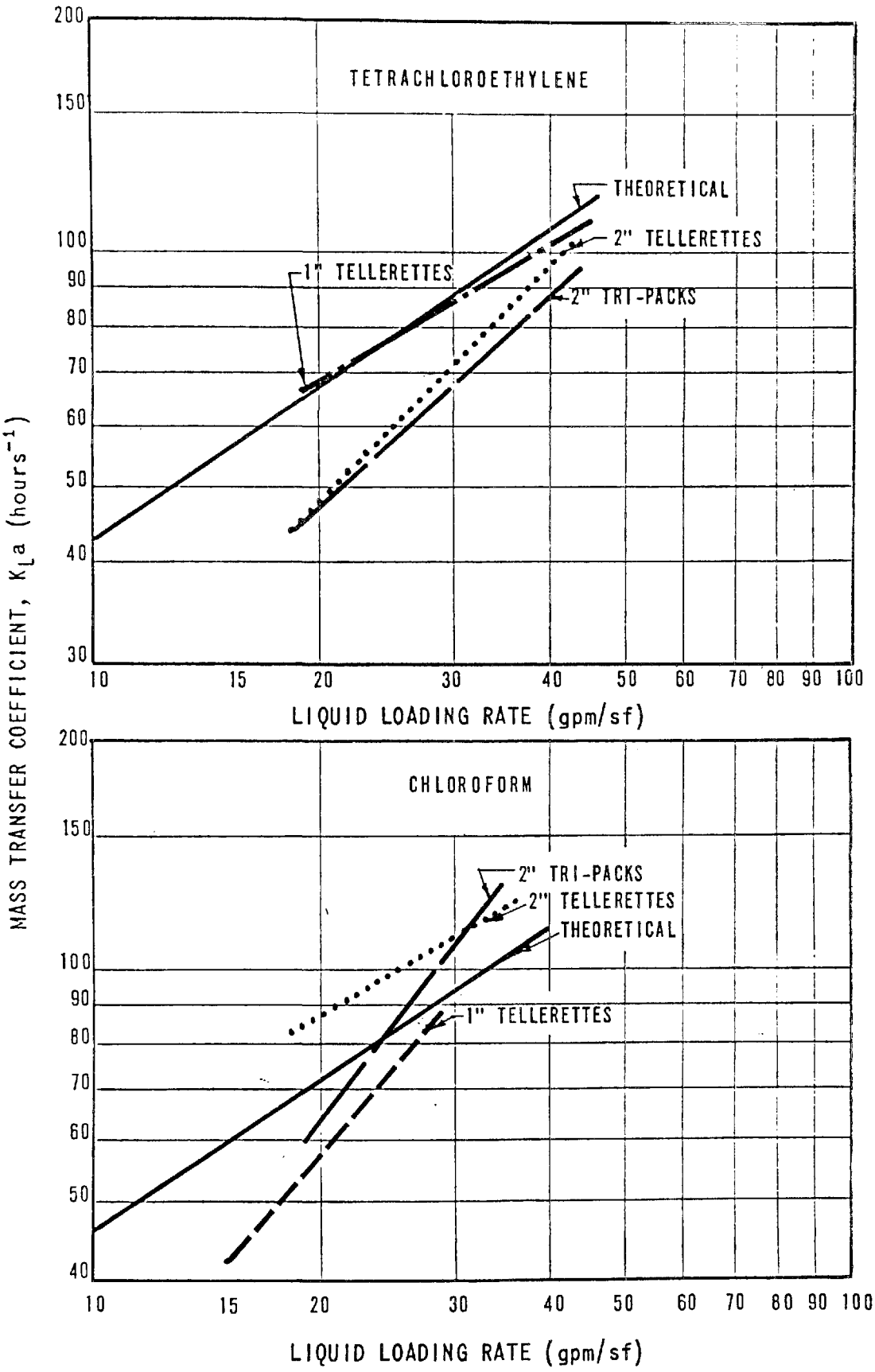
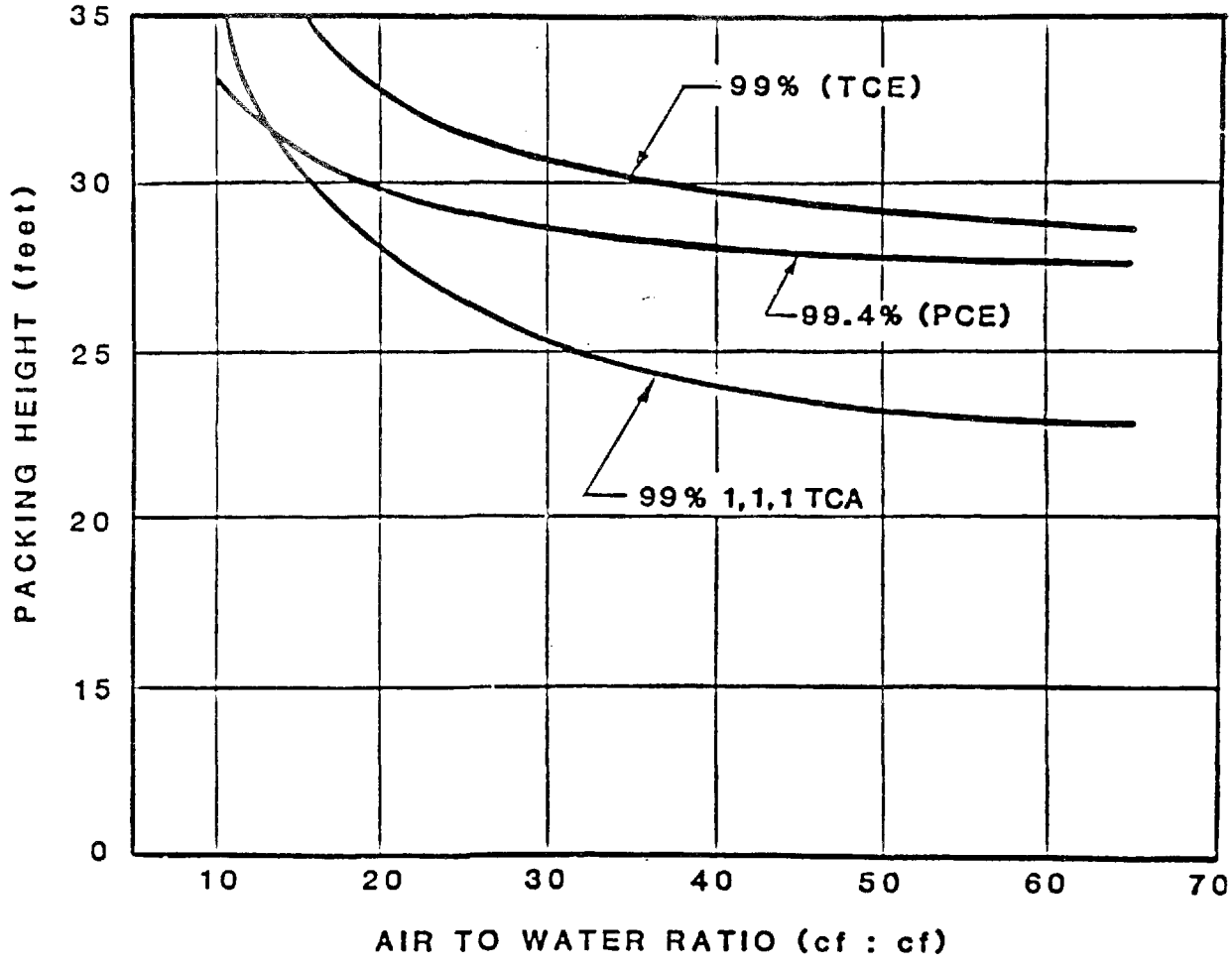


FIGURE 37- MASS TRANSFER RELATIONSHIP FOR PACKED COLUMN



LIQUID LOADING RATE = 30 GPM/SF

FIGURE 38- PACKING HEIGHT VS AIR TO WATER RATIO

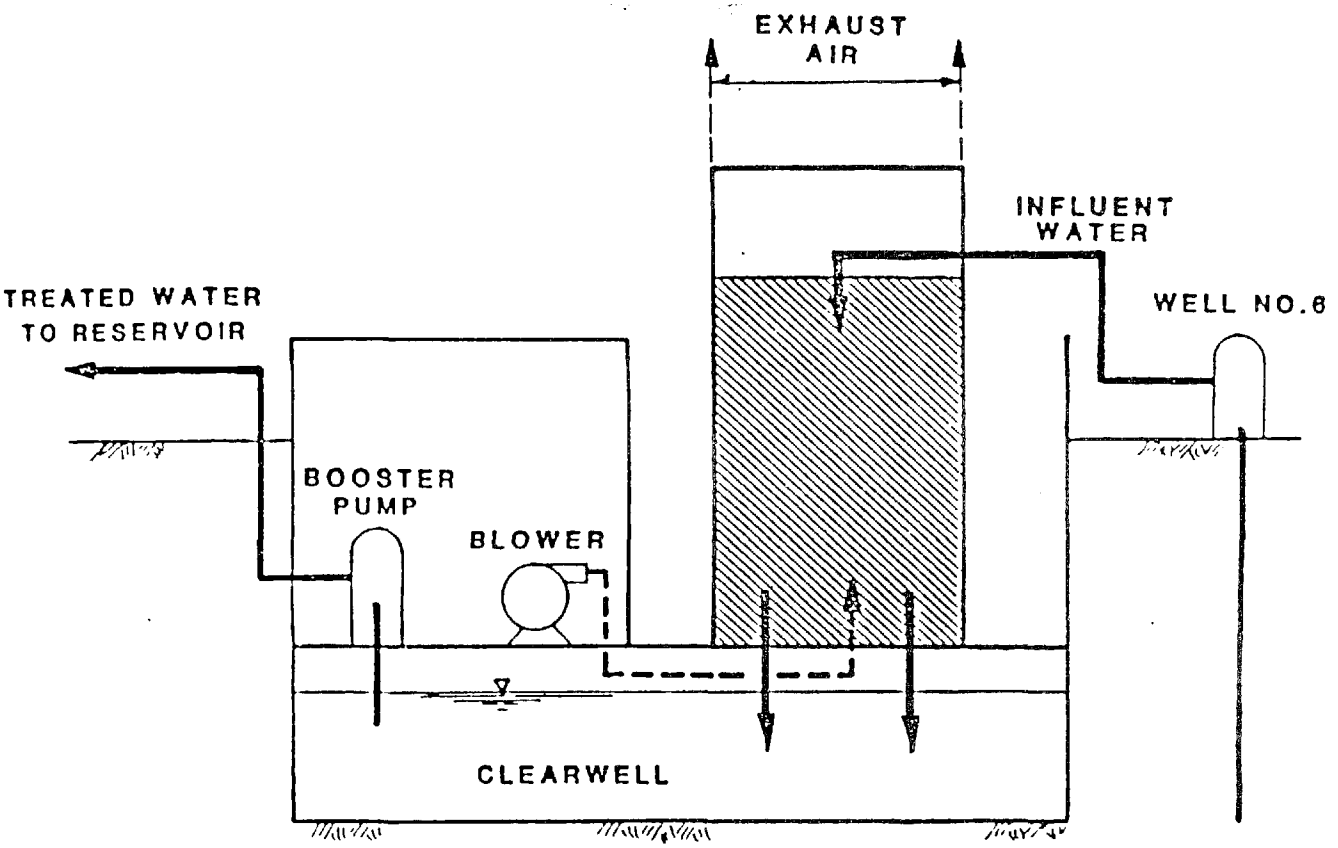


FIGURE 39- SCHEMATIC OF A TYPICAL PACKED COLUMN FACILITY

3. Location/Site Constraints

   a. Zoning requirements
   b. Height restrictions
   c. Location of air intake louvers

4. System Hydraulics

   a. Restaging well pumps
   b. Flow and system pressure
   c. Repumping to distribution system

5. Housing

   a. Freezing potential
   b. Noise
   c. Security
   d. Equipment maintenance

6. Column and Column Internals

   a. Column Construction

      - FRP (fiberglass-reinforced plastic)
      - Aluminum
      - Stainless steel
      - Concrete

   b. Mist eliminator

   c. Liquid distributor

      - orifice plate (shown on Figure 40)
      - trough-type distributor (shown on Figure 40)
      - orifice headers
      - spray nozzles

   d. Support grid

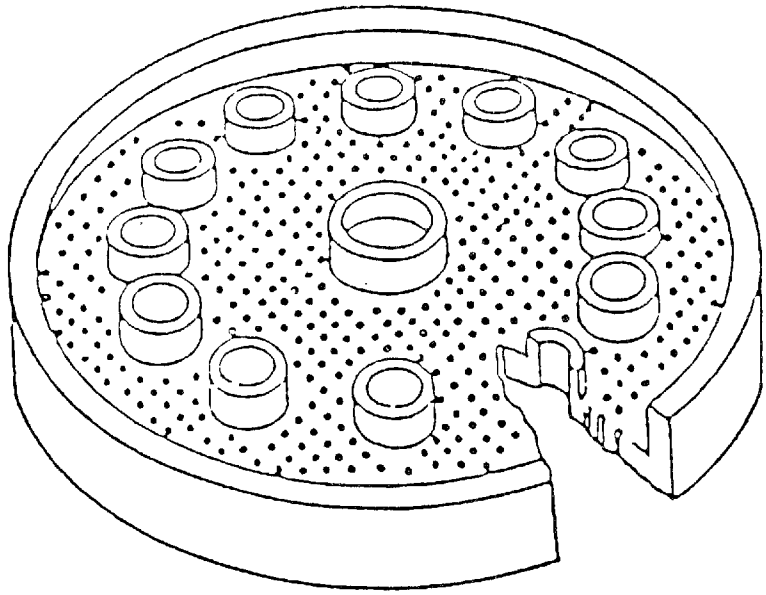
   e. Packing Media

7. Air Quality

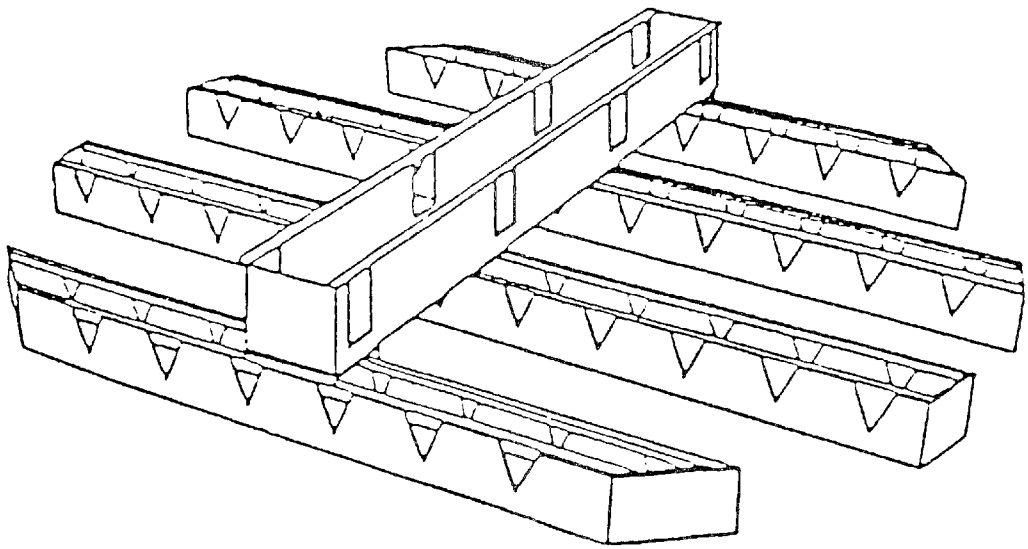
   a. Intake air - air-bourne contaminants
   b. Exist air - discharge regulations

8. VOC Emissions

   a. Emission rate in the exit air is calculated based upon:



Orifice - type distributor



Trough - type distributor

FIGURE 40- DISTRIBUTOR TYPES

$$\text{Emission rate (lbs/hr)} = (C_i - C_e) \times V \times \frac{5}{10^7}$$

Where: C_i = Influent concentration in raw water (ug/L)

C_e = Effluent concentration in treated water (ug/L)

V = Water flow rate (gpm)

b. Ambient concentrations

c. Modeling

d. Column modifications

- Height
- Air flowrate
- Exist velocity

e. Treatment Options:

- Thermal incineration of the organics - Disadvantage of high energy requirements

- Catalytic incineration of the organics (shown on Figure 41) - Lower temperature requirements than thermal incineration, but currently not effective for removing chlorinated organics at low levels.

- Ozone destruction - catalyzed by UV radiation. At present, limited application for vapor-phase treatment.

- Vapor phase carbon adsorption (shown on Figure 42) - Appears to be the most feasible method at present. Carbon replacement frequency can be estimated by:

  - Mass balance based on packed column exit air concentration and flow rate.

  - Monitoring using gas chromatography or mass spectrometry. Samples can be collected in bags and steel cannisters or using carbon and synthetic resins.

  - Using a combination of mass balance (initially) and monitoring (towards the anticipated carbon exhaustion period).

9. Clogging of Packing

a. Iron

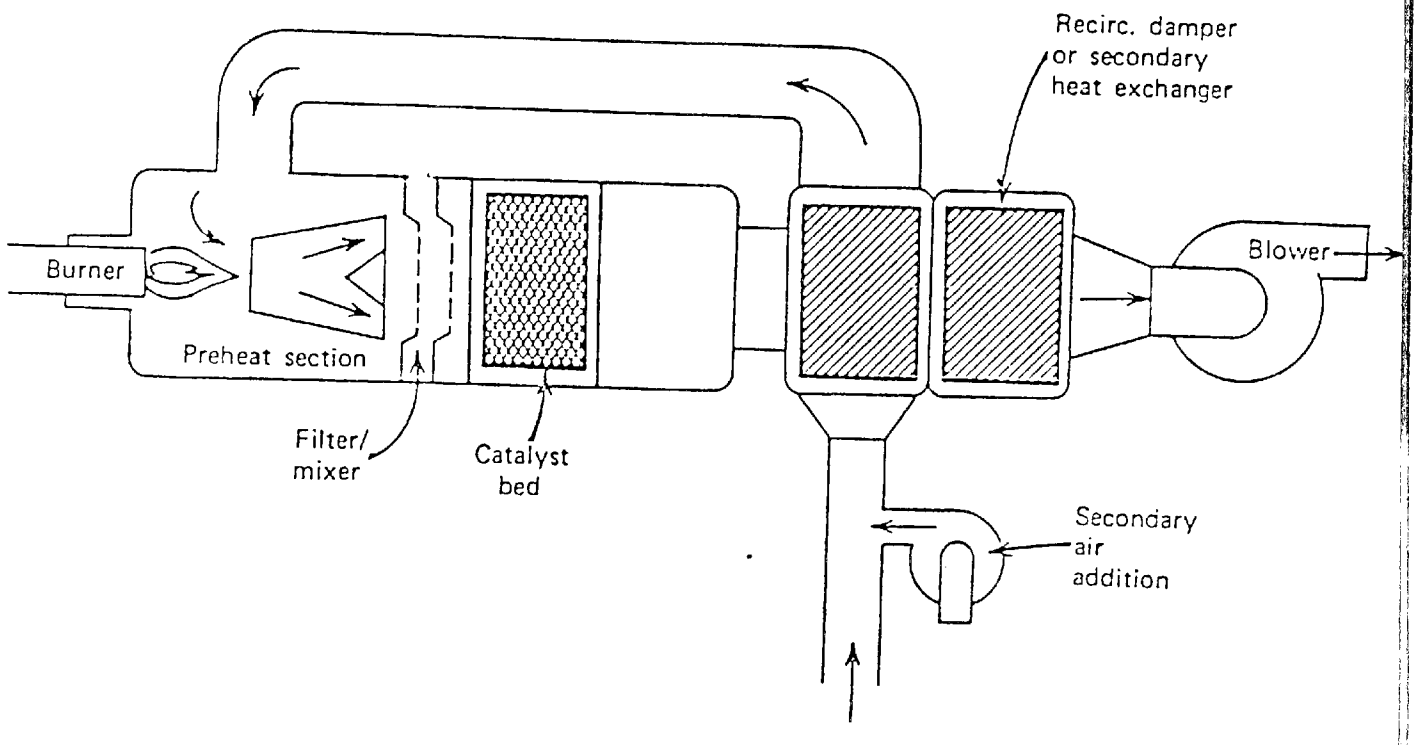


FIGURE 41 - SCHEMATIC OF CATALYTIC INCINERATION PROCESS

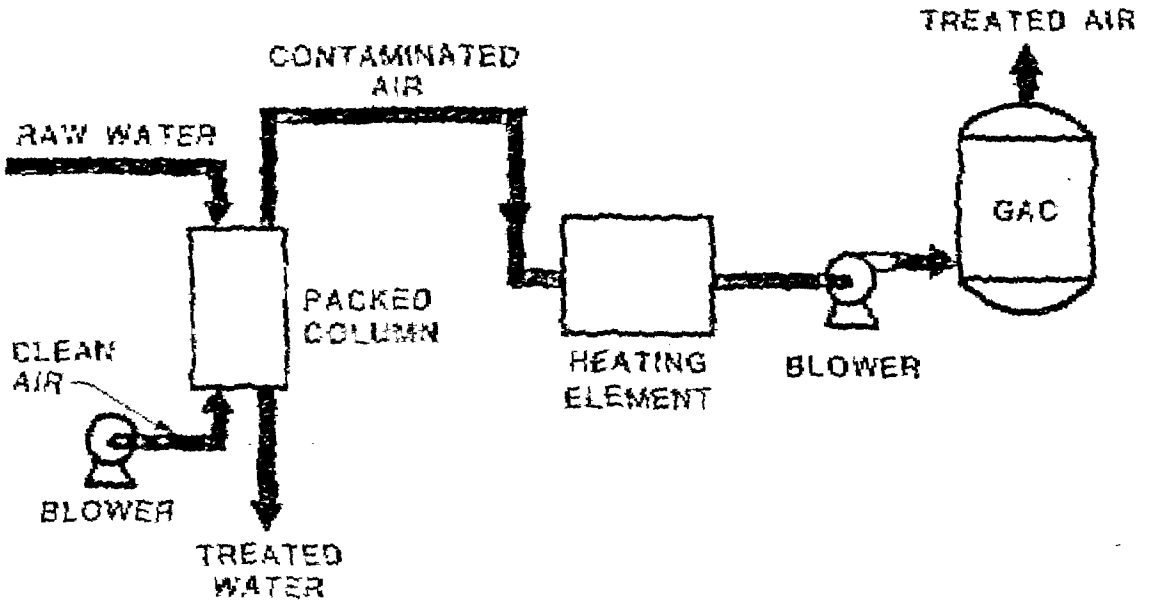


FIGURE 42- SCHEMATIC OF VAPOR PHASE GAC SYSTEM

b. Solids

c. Biological growth

d. Pretreatment requirements may have to be considered for any one of these problems

10. Corrosivity of Treated Water

a. Problem: increased DO, reduced CO_2
b. Solution: increase pH; provide post treatment

F. Applicability to Various System Sizes

1. Organics removal

a. All system sizes
b. Typically used for ground water systems

2. Radon removal

a. Small systems: home diffused aeration units preferred

b. Large systems: use may be limited by radon emission in exit air

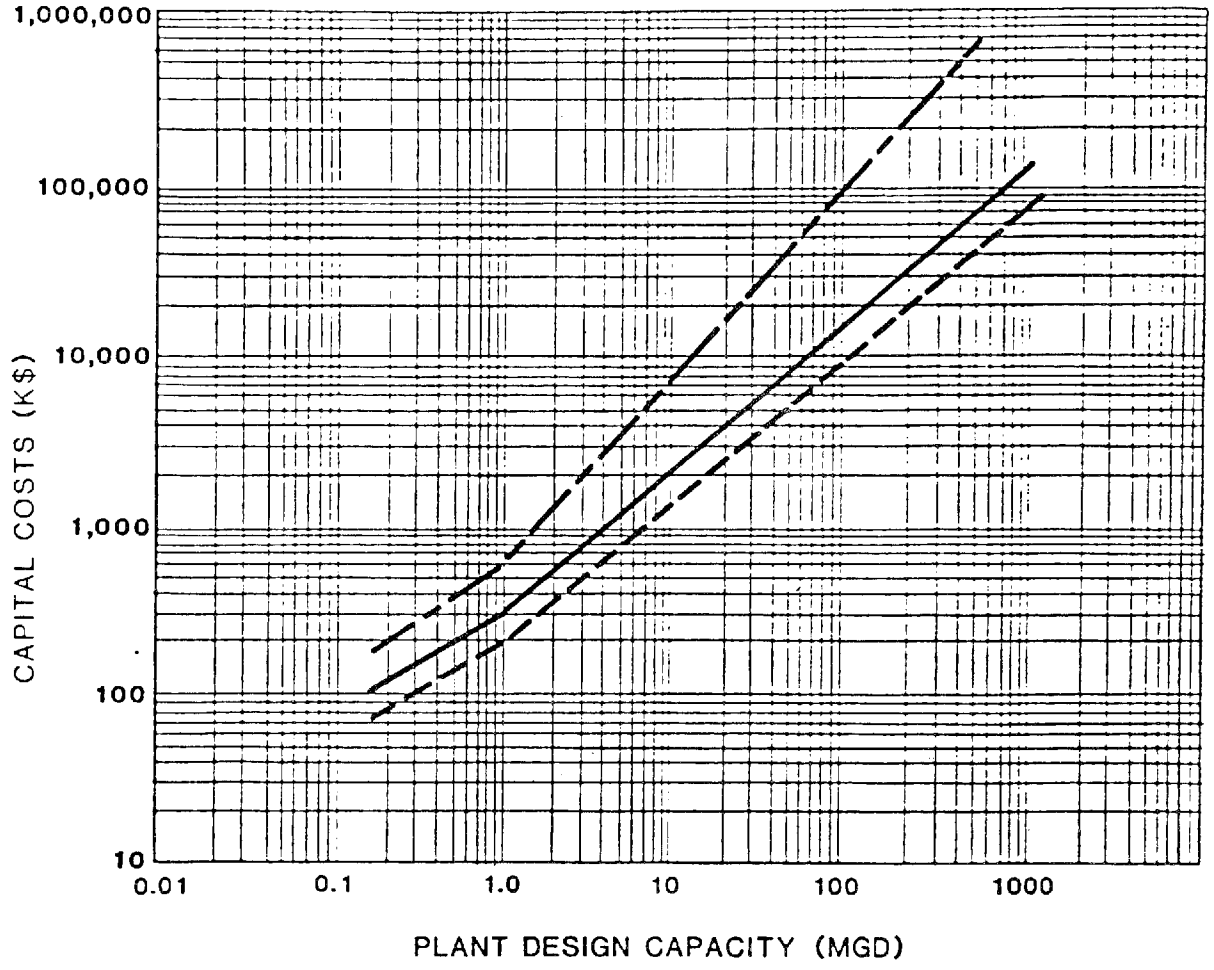
G. Treatment Economics

1. Packed column cost components.

Basic	Site Specific
Column Structure	Special Sitework
Internals	Raw water holding tank
Packing	New/restaged well pump
Blower(s)	Blower building
Clearwell	Booster pump building
Booster pump(s)	Chemical facility
Piping	Noise control installation
	Air emissions control

2. Cost curves for different contaminant groups are shown on Figure 43 (capital cost) and Figure 44 (O&M cost). In general:

Vinyl Chloride - least costly to remove
PCE
TCE
Carbon Tetrachloride
1,2-Dichloroethane
DBCP - most costly to remove



— — — VINYL CHLORIDE, RADON

——— TCE

— - — DBCP (PESTICIDE)

FIGURE 43 - CAPITAL COST CURVES FOR PACKED COLUMN AERATION FACILITIES

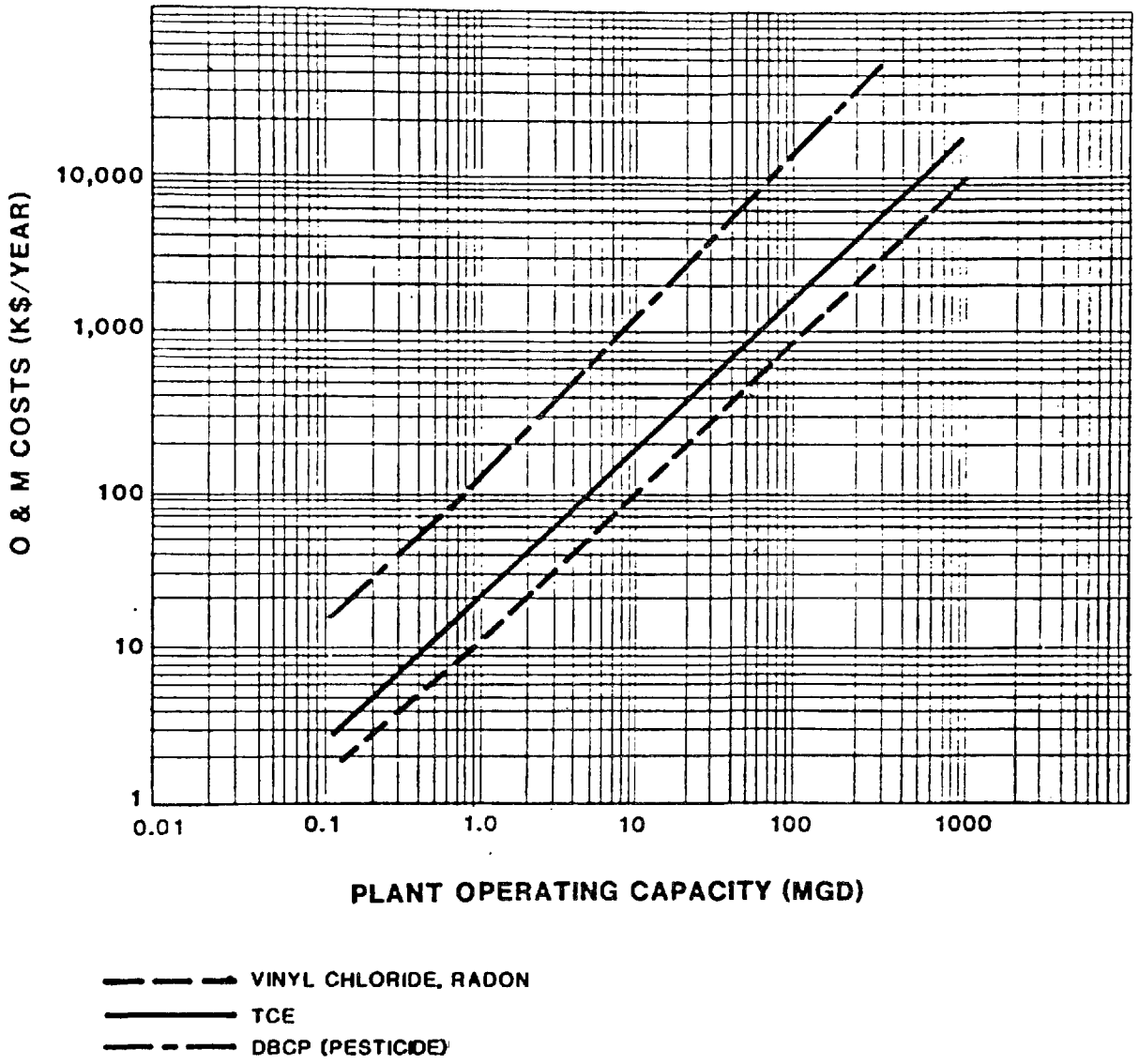


FIGURE 44 - O & M COST CURVES FOR PACKED COLUMN AERATION FACILITIES

3. Vapor Phase GAC Cost

   a. May dictate system economics and choice of the process.

   b. Typical costs for different system sizes at air to water ratio of 40:1 are:

System Size (MGD)	Capital Cost (K$)
1	40
10	200
100	1,400
1,000	9,000

   c. Cost includes carbon contactors, initial carbon charge, gas heater and installation.

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WORKSHOP ON EMERGING TECHNOLOGIES

FOR DRINKING WATER TREATMENT

TECHNICAL SESSION ON ORGANICS REMOVAL

CASE STUDY

EXAMPLE 1:

A municipal ground water supply has been contaminated with several organic chemicals. Based on the raw water quality given below, determine:

- An appropriate treatment method
- Size and process design of the treatment facility

ORGANIC CONTAMINANT LEVELS
IN LITTLETOWN WELLS
(all units in micrograms/liter)

	Well No.		
	10	11	14
Trichloroethylene	200	200	100
Tetrachloroethylene	1,000	1,000	200
1,1,1-Trichloroethane	750	600	300

Notes:

1. Total Combined Flowrate = 225 gpm

Consider:

- Treatment objective
- Treatment options
- Treatability testing required
- Cost

TREATMENT OBJECTIVES

VOC	Composite of All Wells	Design Effluent Concentration	Required Percent Removal
Trichloroethylene	160	5	97
Tetrachloroethylene	650	10	98.5
1,1,1-Trichloroethane	500	10	98

Note:

1. All concentrations given in ug/L.

Define:

- What are the treatment options?

CONTAMINANT CHARACTERISTICS

VOC	Henry's Constant (H)* (atm)	Adsorption Isotherm Constants K	1/n	Carbon Usage Rate (lbs/1,000 gal)
Trichloroethylene	155	28	0.62	0.19
Tetrachloroethylene	274	50.8	0.56	0.18
1,1,1-Trichloroethane	288	2.48	0.34	2.8

* at 20 C

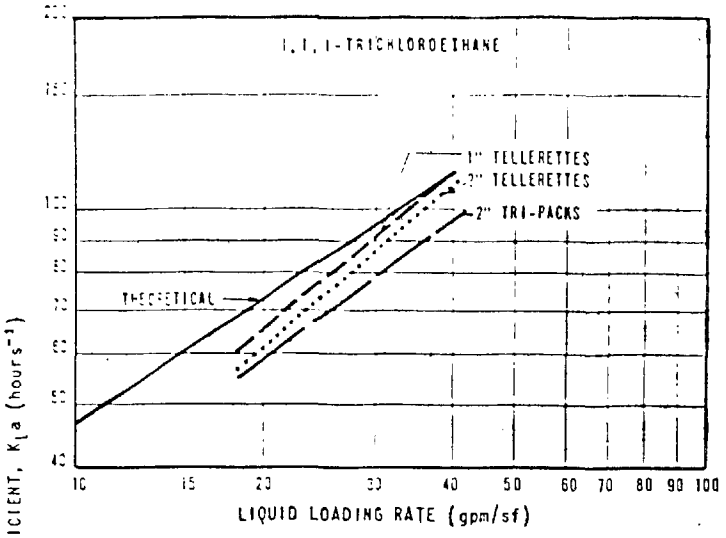
Define:

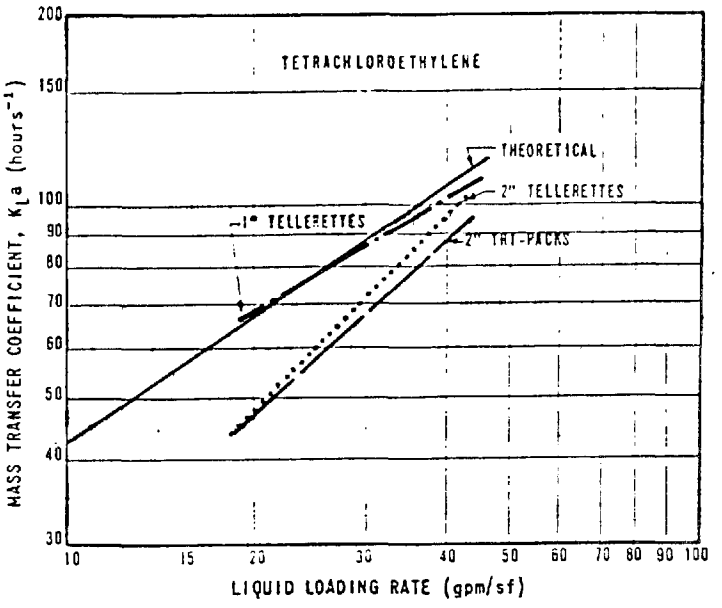
- Which treatment process will work (aeration or GAC)?

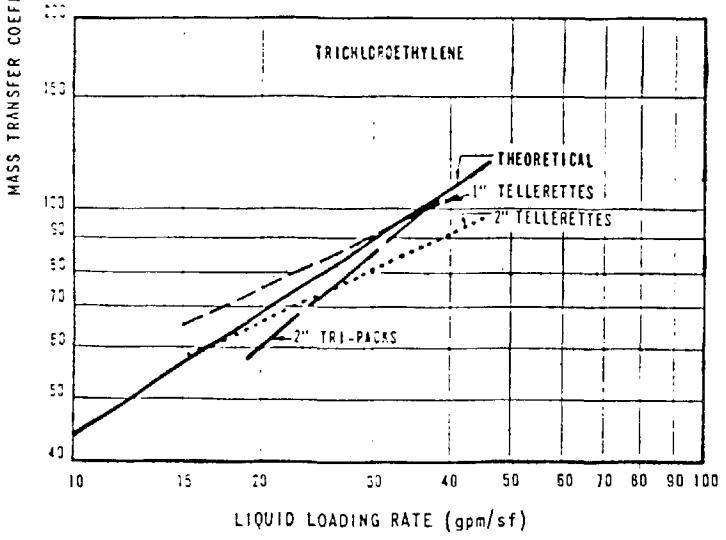
Consider:

- Volatility of the contaminants
- Carbon usage rates

PACKED COLUMN - PILOT STUDY RESULTS



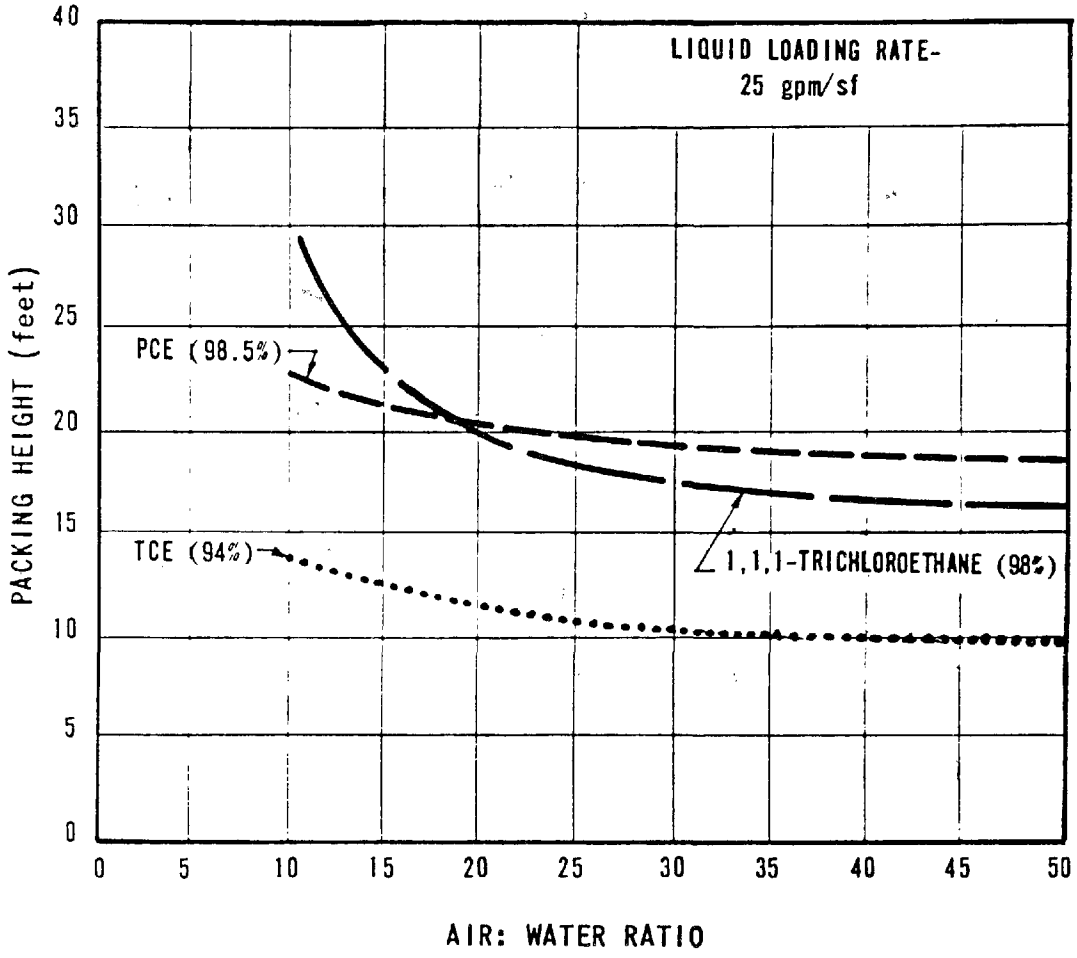




Define:

- Optimum loading rate
- Type of packing material
- K_La
- A:W Ratio
- Packing height

Air:Water Ratio Versus Packing Height



NOTE: (98.5%) DENOTES 98.5 PERCENT REMOVAL OF COMPOUND.

Define:

- Optimum A:W ratio
- Required packing height
- Preliminary process design

PACKED COLUMN PROCESS DESIGN CRITERIA

A sample calculation for developing the process design criteria is shown below:

Pilot Study Results

VOC = Tetrachloroethylene

Packing height = 10 ft

Column diameter = 1 ft

Packing material = 2-inch Tri-packs

Run No.	Water Flow Rate (gpm)	Air Flow Rate (gpm)	A/W	PCE (ug/L) Influent	PCE (ug/L) Effluent	% Removal
1	16	43	20:1	100	7	93

1. Calculation $K_L a$ (Refer to workshop notes for formulas)

a. $$R = \frac{(A)\ (H)}{(W)} \times 7.5212 \times 10^{-4}$$

$$= 20 \times 274 \times 7.5212 \times 10^{-4}$$

$$= 4.12$$

b. $$NTU = \frac{R}{R-1} \ln \left[\frac{(x_i/x_o)\ (R-1) + 1}{R} \right]$$

$$= \frac{4.12}{4.12 - 1} \left[\ln \frac{(100/7)\ (4.12 - 1) + 1}{4.12} \right]$$

$$= 3.2$$

c. $$HTU = \frac{z}{NTU} = \frac{10}{3.17} = 3.2 \text{ ft}$$

d. $$K_L a = \frac{L}{HTU} = \frac{16 \text{ gpm}}{\frac{\pi}{4} (1)^2 \text{ft}^2} \times \frac{1}{3.2 \text{ ft}} \times 60 \frac{\text{min}}{\text{hr}} \times \frac{1}{7.48} \frac{\text{ft}^3}{\text{gal}}$$

$$= 51 \text{ hr}^{-1}$$

$K_L a$ for other loading rates are calculated similarly. A plot of $K_L a$ versus loading rate is made.

2. Calculation of Packing Height

Optimum loading rate = 25 gpm/ft^2

$K_L a$ at 25 gpm/ft^2 for 2-inch Tri-paks = 58 hr^{-1} (from graph)

Assume A/W ratio = 40

% removal required (PCE) = 98.5%

a. $$R = \frac{(A)\ (H)}{(W)} \times 7.5212 \times 10^{-4}$$

$$= 40 \times 274 \times 7.5212 \times 10^{-4}$$

$$= 8.24$$

b. $$x_i/x_o = \frac{1}{1 - \frac{\%\ \text{Removal}}{100}} = \frac{1}{1 - \frac{98.5}{100}} = 66.7$$

c. $$NTU = \frac{8.24}{8.24 - 1}\ hr\ \frac{(66.7)\ (8.24 - 1) + 1}{8.24}$$

$$= 4.64$$

d. $$HTU = \frac{L\ (gpm/ft^2)}{K_L a\ (hr^{-1})} \times 60\ \frac{min}{hr} \times \frac{1}{7.48}\ \frac{ft^3}{gal}$$

$$= \frac{25}{58}\ \frac{gpm/ft^2}{hr^{-1}} \times 60\ \frac{min}{hr} \times \frac{1}{7.48}\ \frac{ft^3}{gal}$$

$$= 3.5\ ft$$

e. Required packing height = (NTU) (HTU)

$$= 4.64 \times 3.5\ ft$$

$$= 16.2\ ft$$

Packing heights for other A/W ratios are calculated similarly. A plot of packing height versus A/W ratio is made. Optimum A/W ratio can be estimated from such a plot.

VOC Emission Rate

PCE concentration in raw water (C_i) = 650 ug/L

PCE concentration in treated water (C_e) = 10 ug/L

$$\text{PCE Emission rate (lbs/hr)} = C_i - C_e \times V \times \frac{5}{10^7}$$

$$= (650 - 10) \times 225 \text{ gpm} \times \frac{5}{10^7}$$

$$= 0.072 \text{ lb/hr}$$

Since OSHA regulations require exit air treatment only at emission rates of above 0.1 lb/hr, no additional treatment is required for the exit air at this facility.

PACKED COLUMN PROCESS DESIGN CRITERIA
BASED ON PILOT STUDY

- Maximum Flowrate = 225 gpm
- Hydraulic Loading Rate = 25 gpm/ft^2
- PCE Mass Transfer Coefficient, $K_L a$ = 56 hr^{-1}
- A:W Ratio = 40:1
- Air Flow = 1,200 cfm
- Packing Height[1] = 20 feet

Note:

1. Based on 98.5% removal of PCE

VOC REMOVAL AT DESIGN CONDITIONS

VOC	Design Percent Removal	Actual Percent Removal	Design Effluent Concentrations (ug/l)	Actual Effluent Concentration (ug/l)
TCE	97	)99	5	(5
PCE*	98.5	98.5	10	10
1,1,1-Trichloroethane	98	98	10	10

*Denotes critical compound.

Define:

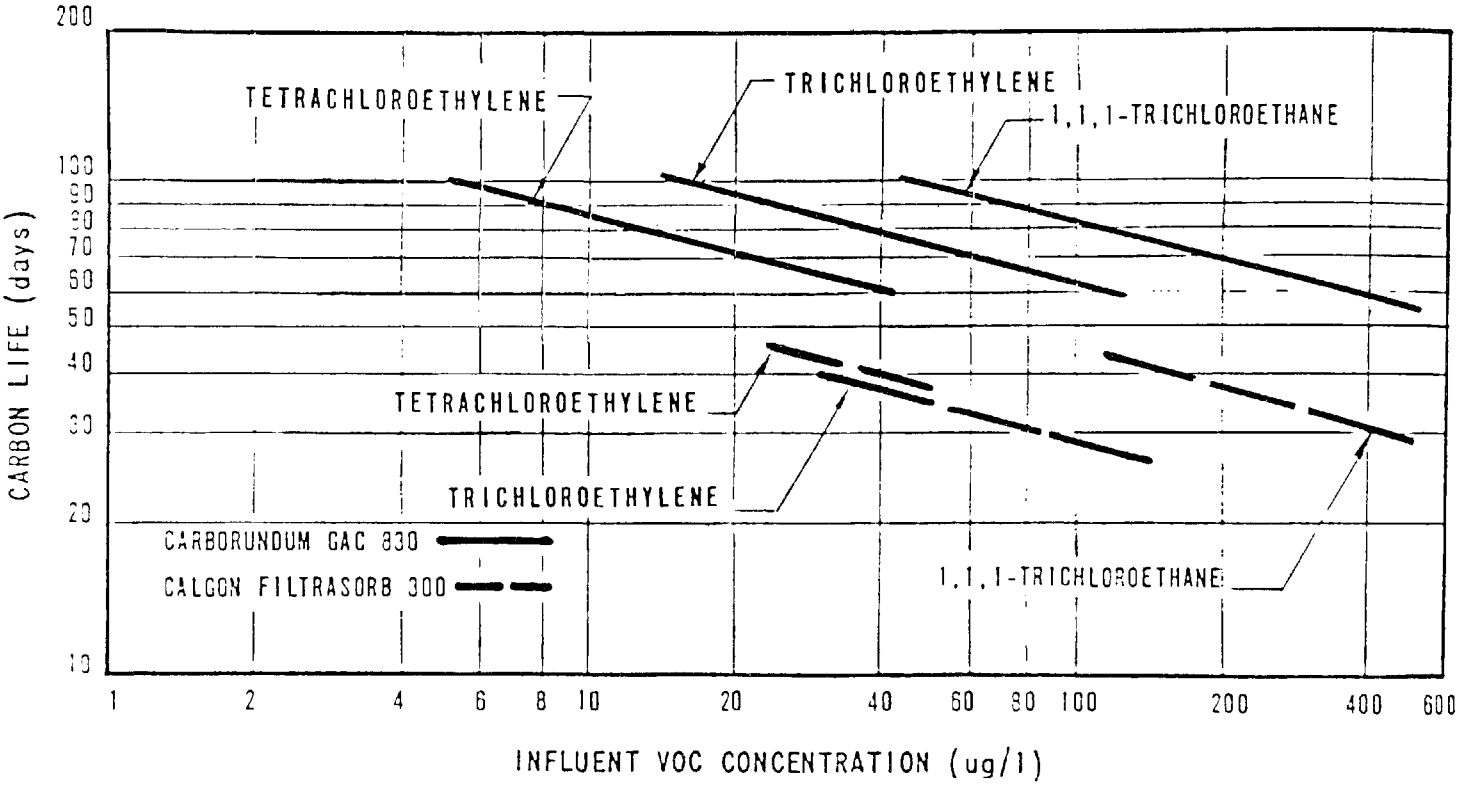
- Treatment costs

PRELIMINARY COST ESTIMATES FOR
PACKED COLUMN AERATION PROCESS

Based on cost curves presented in the workshop report:

Capital Cost (Figure 43)	=	$150,000
O&M Cost (Figure 44)	=	$ 8,000/year
Total Cost (20 year amortization period and 10% interest rate)	=	$0.22/1,000 gallons

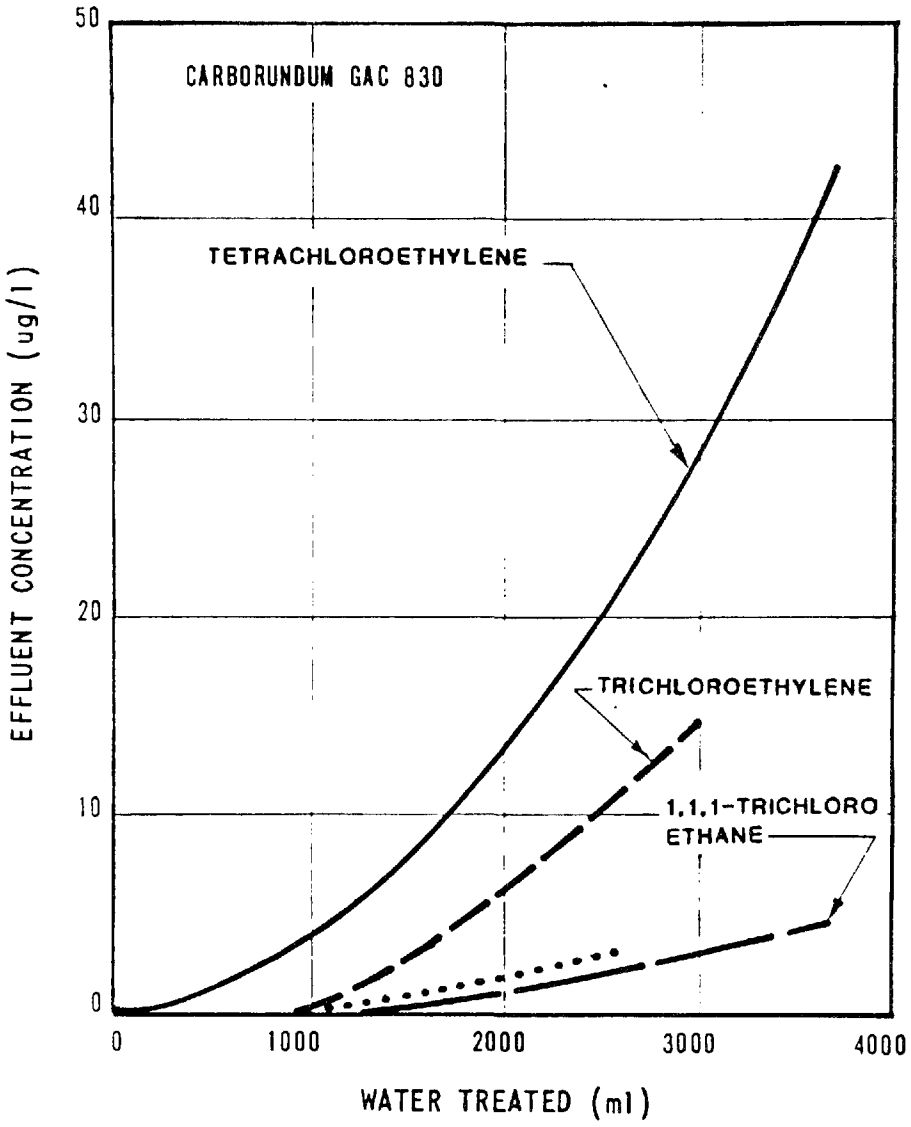
MINI-COLUMN TEST RESULTS



Define:

- Carbon Type

MINI-COLUMN TEST RESULTS



Define:

- Controlling VOC

- Carbon Usage based on:

$$\text{Carbon usage (lbs/1,000 gal)} = \frac{W}{V} \times 8461.5$$

where W = weight of carbon (0.1 gm)
V = volume treated (ml)

- Preliminary Process Design

GAC PROCESS DESIGN CRITERIA

1. Maximum Flowrate: 225 gpm

2. Carbon Usage Rate:

   - weight of carbon in the mini-column (W) = 0.1 gm
   - volume treated based on tetrachloroethylene breakthrough at 10 ug/L (V) = 1,500 ul

   $$\text{Carbon Usage (lbs/1,000 l)} = \frac{W}{V} \times 8461.5$$

   $$= \frac{0.1 \text{ gm}}{1{,}500 \text{ ml}} \times 8461.5 = 0.56$$

3. Carbon Charge:

   Assume EBCT = 10 minutes

   $$\text{Carbon volume} = 225 \frac{\text{gal}}{\text{min}} \times 10 \text{ min} \times \frac{1}{7.48} \frac{\text{ft}^3}{\text{gal}} = 300 \text{ ft}^3$$

   $$\text{Carbon weight} = 300 \text{ ft}^3 \times 29 \frac{\text{lbs}}{\text{ft}^3} = 8{,}700 \text{ lbs}$$

4. Contactor Dimensions:

   Assume hydraulic loading rate = 5 gpm/ft^2

   $$\text{Contactor diameter} = \sqrt{\frac{225 \text{ gpm}}{5 \text{ gpm/ft}^2} \times \frac{4}{\pi}} = 7.5 \text{ ft}$$

   $$\text{Carbon bed depth} = \frac{300 \text{ ft}^3}{\frac{\pi}{4} (7.5)^2 \text{ ft}^2} = 7 \text{ ft}$$

   Contactor height = 15 feet

5. Replacement Frequency:

   $$\text{Replacement frequency} = \frac{\text{carbon charge (lbs)} \times 0.7}{\text{carbon usage } \left(\frac{\text{lbs}}{1{,}000 \text{ gal}}\right) \times \text{flow (gpm)}}$$

   $$= \frac{8{,}700 \text{ lbs} \times 0.7}{0.56 \frac{\text{lbs}}{1{,}000 \text{ gal}} \times 225 \text{ gpm}} = 48 \text{ days}$$

GAC PROCESS DESIGN CRITERIA

- Maximum Flowrate = 225 gpm
- Hydraulic Loading Rate = 5 gpm/ft^2
- Carbon Usage = 0.56 lbs/1,000 gallons
- EBCT = 10 minutes
- Number of Contactors = 1
- Contactor Dimensions = 7.5 ft (diameter) x 15 ft (height)
- Depth of GAC Bed = 7 ft
- Carbon Charge = 8,700 lbs
- Type of GAC = Carborundum GAC 830
- Carbon Life = 48 days

Define:

- Treatment costs

PRELIMINARY COST ESTIMATES FOR GAC ADSORPTION PROCESS

Based on cost curves presented in the workshop report:

Capital Cost (Figure 31)	= $160,000
O&M Cost (Figure 32)	= $ 25,000/year
Total Cost (20 year amortization period and 10% interest rate)	= $.375/1,000 gallons

PROCESS SELECTION

DEFINE:

- Recommended treatment process

CONSIDER:

- Treatment efficiency
- Operational factors
- Treatment costs

COMPARISON OF ALTERNATIVES
LITTLETOWN WELLFIELD

Packed Column	GAC Adsorption
- High removals	- High removals
- Continuous operation	- Requires down time for Carbon replacement
- VOC emissions in exit air less than OSHA limit	- No air emissions
- No waste disposal	- Disposal of backwash water and spent carbon
- Costs: -	Costs:
Capital Cost = $150,000	Capital Cost = $160,000
O&M = $ 8,000/yr	O&M = $25,000/yr
Total = $0.22/1,000 gallons	Total = $0.375/1,000 gallons

Technical Session: Inorganics
J. Edward Singley, *Vice President, James M. Montgomery Consulting Engineers, Inc., Gainesville, FL*

Emerging Technologies for Control of Inorganic Contaminants

J. Edward Singley

I. Introduction

- A. Regulations
  - 1. Present
  - 2. Proposed
- B. Metals
  - 1. Lead
  - 2. Barium
  - 3. Cadmium
  - 4. Chromium
  - 5. Mercury
  - 6. Radium
  - 7. Selenium
  - 8. Silver
  - 9. Strontium
- C. Non-Metals
  - 1. Arsenic
  - 2. Fluoride
  - 3. Nitrate

II. Lead

- A. Lead leaching
- B. Workmanship
- C. Control techniques
- D. Data needs

III. Barium

IV. Cadmium

V. Chromium

VI. Mercury

VII. Radium

- A. Chemistry
- B. Control techniques
  - 1. Precipitative softening
  - 2. Ion exchange
  - 3. Demineralization
- C. Radioactivity

VIII. Selenium

IX. Silver

X. Strontium

XI. Arsenic

XII. Fluoride

- A. Activated alumina adsorption
- B. Ion exchange

XIII. Nitrate

XIV. Summary

Emerging Technologies for Control of Inorganic Contaminants

GENERAL

Of the 12 inorganic contaminants that are presently regulated by primary agencies, the one most commonly present at levels in excess of the primary MCL is lead, Pb. The others are less common but are present in site or regionally specific cases. For this reason major attention will be focused on Pb with limited attention to the others.

REGULATIONS

Present.

The present regulations on the inorganic contaminants under the National Interim Drinking Water Regulations cover 12 different substances:

	MCL (mg/L)*
Arsenic	0.05
Barium	1.0
Cadmium	0.010
Chromium (total)	0.05
Fluoride	4.0**
Lead	0.05
Mercury	0.002
Nitrate, as N	10
Selenium	0.01
Silver	0.05
Radium	5 (pCi/L)
Strontium-90	8 (pCi/L)

*as of August 1, 1987

**Secondary MCL of 2.0 mg/L

The significance of the twelve varies considerably since their presence and concentrations vary so much. For example silver is rarely, if ever, found unless a point-of-use water treatment device is used by the consumer, whereas lead is found to be almost ubiquitous in samples from the consumer's tap. Radium, strontium, cadmium, selenium, arsenic, mercury, barium, nitrate, chromium and excess fluoride are found only in

site-specific cases although their concentrations may vary widely. For some of the above the problem of elevated concentrations is indigenous to a section, or sections, of the country. Thus a treatment technique may be of limited applicability. Despite this the need is real and must be addressed because the MCLs must be met.

Proposed.

There is no doubt that additional inorganic contaminants will be regulated nor that there will be changes in the MCLs of some of those presently regulated. Some will increase and some decrease. The proposed regulations are shown in Table 1.

Since silver is not found in the raw water, added in treatment or by corrosion of the system, it will likely be dropped entirely. On the other hand, the present lead MCL of 0.050 mg/L will certainly be reduced to 0.020 mg/L or less, unless a treatment technique is specified. Other changes in the regulations, as proposed can be observed in the Table.

The presence of lead, zinc, copper and cadmiun in water entering the distribution system is rare. They occur because of reactions between the water and the conveying system in transit from the plant to the tap of the consumer. The particular contaminant(s) picked up depends upon the composition of the pipes, valves, meters, etc., with which the water comes in contact. The corrosion reactions that occur between the water and metallic substances are electrochemical in nature and result in converting the free metals, which are very insoluble in water, to their ionic forms which are usually very soluble. The ionic solubility is strongly influenced by the water quality. It may be stated safely that "all metals corrode in direct contact with water." The rate is determined primarily by the properties of the metal itself and secondarily by the properties of the water, i.e., the water quality. The most common metals used in transmission mains and plumbing systems are steel (iron), galvanized steel, copper, lead, brass and bronze. The presence of zinc and cadmium, and to a lesser extent lead, in water samples comes from the zinc used in galvanizing pipe. The lead may come from lead services, lead goosenecks, lead pipes (rare) and from lead-based solders used to join copper pipes. In most parts of the U.S. the latter is the major source of lead at the tap.

LEAD

It is of historical interest to note that lead pipes were used in Rome to distribute the water from the Aquaducts to the homes of the wealthy, which is cited by some authorities as the cause of the decline of the Roman Empire.

Lead Leaching.

Lead based solders used to connect copper plumbing for many years have been based on tin-lead combinations, the most common being 50:50 and 60:40 tin:lead. The recent ban on lead in such solders will strongly affect lead content in water obtained from the taps of homes constructed

after the states implement the ban but will have minimal effect on water samples from homes and businesses constructed prior to the ban.

There is an extensive discussion of the rate of leaching of lead from lead-based solders and fluxes in "Internal Corrosion of Water Distribution Systems" published by the American Water Works Association Research Foundation jointly with the Engler-Bunte Institute of the University of Karlsruhe, West Germany. Examples from the U.S. have been cited by Norman Murrell in testimony before Congress. The concentration of lead varies with the amount of water that has been withdrawn both in the sample itself and before the sample, as well as the time of contact of the water with the household plumbing. Thus first draw samples give the worst case examples and the smaller the sample the higher the concentration measured. One study in Scotland by Lyon and Lenihan in Glasgow in 1977, cited by Schock and Wagner in the reference above, showed that as much as 20 ug of lead per fitting per hour could be picked up for new connections in copper pipes even though they were "well made." This declined to about 1.25 ug/fitting/hr in 4-5 weeks and remained at that level for many years. Studies at the Illinois State Water Survey by Neff and Schock also showed that lead can be leached from chrome plated brass fixtures.

Workmanship.

There is no doubt that a major contribution to lead corrosion is poor workmanship in the formation of lead-based soldered joints in copper pipes. This leads to galvanic corrosion of the lead in contact with the more cathodic copper and tin. It is likely that the lead concentration in water in contact with poorly made joints is almost independent of the water quality, thus there is little that the utility can do to reduce lead levels significantly when such a mechanism predominates except to provide a protective coating, such as $CaCO_3$.

Control methods.

Early studies in 1887 in Germany by Wolfhugel, identified oxygen, carbon dioxide, water quality, age and quality of lead pipes, stagnation time, flow velocity and temperature as contributing factors. These include essentially all of the factors recognized today as important in lead pick-up. These observations resulted from a serious leach problem in Dessau and the effective solution was the addition of limestone (calcium carbonate). Later soda ash (sodium carbonate) was added. These treatments increased the pH thus reducing the free carbon dioxide and increasing the carbonate alkalinity. Today, one hundred years later, we use the same approach when treating the same water qualities that caused the problems, i.e., low hardness, low alkalinity, and low pH.

Some of the classic cases in the U.S. were discussed and studied by Karalekas, et al. starting in 1976 in Massachusetts. They showed that pH adjustment to a value above 8.0 using caustic soda (NaOH) reduced the pick-up of lead significantly. The use of zinc orthophosphate at levels as high as 12 mg/l showed little if any improvement. These effects correlated well with the effects in Glasgow ninety years earlier. Figure 1 shows the solubility of lead in water.

The use of various corrosion inhibitors has been studied extensively with the following results:

Carbonates and pH. These two are almost inseparable because of the chemical interdependence of the carbonate system and pH. Whereas many authors have concluded that a major water quality factor in a particular corrosion situation was free carbon dioxide, none have shown carbon dioxide, per se, as a participant in the corrosion reactions. Rather it is the dependence upon the historical precedence of citing carbon dioxide rather than pH because the term pH was not used or defined prior to 1909 when Sorenson simplified the discussion of the hydrogen ion concentration by defining a new term "pH". Until shortly before that time it was not possible to measure the hydrogen ion concentration in aqueous solution accurately, and even then it was a laborious procedure. On the other hand it was possible to analyze accurately for the "free carbon dioxide" in the middle 1880's.

The shift in the carbonate system from carbon dioxide to bicarbonate and then carbonate as the pH is increased conforms to the well known definition of the various forms of alkalinity. The relevant reactions and equilibrium constants are:

$$CO_2 + H_2O = H_2CO_3, pK = 1.5$$
$$H_2CO_3 = H^+ + HCO_3^-, pK_1 = 6.3$$
$$HCO_3^- = H^+ + CO_3^=, pK_2 = 10.3$$

The conversion of free carbon dioxide to bicarbonate is complete at a pH of about 8.3 and to carbonate above a pH of 10.3.

A comprehensive study of the effect of these variables on lead corrosion was conducted by Schock, et al. at the EPA Laboratories in Cincinnati. From these studies they developed chemical models of lead solubility as functions of carbonate, pH, orthophosphate, sulfate and chloride. They concluded that orthophosphate could be an effective corrosion control inhibitor under a limited range of carbonate and hydrogen ion concentrations.

Silicates. Although some authors and studies have suggested the efficacy of silicates, no studies have supported the hypothesis.

Orthophosphates. The suggestions of the use of these to reduce lead corrosion has not been borne out in many studies performed in the U.S. and Europe. These studies showed that the solubility of lead was greater than predicted by the models that had been developed. See Figure 2.

Sulfate, Chloride and Nitrate. These have been shown repeatedly to have little effect on lead solubility.

Organics. Some studies have shown that natural organics may increase lead solubility.

Chlorine. The solubility of lead from lead-based solders has been shown to be increased in the presence of chloramines as compared to free chlorine.

Polyphosphates. Recent studies have shown no advantage over the simple orthophosphates. The addition of zinc sulfate did not improve the effect.

Calcium Carbonate Films. One of the traditional methods of control of corrosion is to interpose a barrier between the metal and the water. This can be accomplished by reference to one of the indices of calcium carbonate saturation, such as the Langelier Index or others. Modifications of water quality that will initiate the precipitation of a protective coating of calcium carbonate is generally based on pH control, if adequate concentrations of alkalinity and calcium ion are present.

pH Control. It has been shown that pH values above 9.0 lead to reduced lead concentrations because of the reduced availability of electron acceptors. This has been one of the most effective methods of control of lead corrosion. When pH control is practiced in conjunction with alkalinity supplementation in low alkalinity waters, lead corrosion is reduced. Waters of high alkalinity may require softening, to reduce lead corrosion.

BARIUM.

Barium has chemical properties very similar to the other alkaline earth elements calcium, magnesium and radium, though its removal from drinking water parallels that of the other members of the family. Its sulfate is less soluble than calcium sulfate but coagulation with ferric sulfate or alum is relatively ineffective. $BaSO_4$ has a solubility of only 2.2 mg/L at 25°C, which exceeds the MCL of 1.0 mg/L. The solubility product constant is about $1x10^{-4}$. Barium carbonate has a solubility of about 18 mg/L at 25°C but is removed, almost quantitatively, by lime softening at pH values over the range of 9.5 to 10.5.

CADMIUM

This metal rarely, if ever, occurs in raw water. It is a contaminant in zinc used for galvanizing, thus occurs when zinc galvanizing corrodes. Its electrode potential is very close to that of iron (-0.402v. vs -0.441v.), thus it would corrodes only slowly if used alone to protect steel. In contrast, zinc's potential is much more anodic (-0.76v.) and thus provides the desires cathodic protection.

The removal of cadmium from drinking water is rarely needed but the prevention of its presence can be accomplished by corrosion control. Figure 3 shows the effect of pH on cadmium solubility.

CHROMIUM.

Chromium exists in water as the +3 or +6 valence state. The chromium +3 ion is relatively insoluble as the hydroxide, see Figure 4, but the +6 state is very soluble as the chromate or dichromate ion. The chromate ion varies with pH , as shown in Figure 5. The dichromate ion is converted to chromate at pH values above 7. Its high solubility prevents its removal by any technique but ion exchange (anionic) or

demineralization (reverse osmosis or electrodialysis). Chromium III is readily removed by coagulation or lime softening.

MERCURY.

Although mercury occurs only rarely in untreated waters and then even more rarely above the present MCL of 0;002 mg/L, its high toxicity justifies concern. It can occur as two mercury ions, +1 or +2. The +2 form is the more common but still contributes little to the total mercury in natural water. The predominant forms are free metallic mercury above above pH 5 and organically complexed mercury. Surprisingly the free metal has a solubility of 0.025 mg/L. The only effective methods for removal is adsorption on activated carbon.

RADIUM.

Although the radium concentration in most of the major surface supplies in the U.S. is low, as shown in Table 2, there are several areas of the country where radium is a major problem, principally Illinois, Iowa and Florida. Some examples of raw water quality in these areas are shown in Table 3. Treatment of a water containing Ra-226 plus Ra-228 at concentrations above the MCL of 5 pCi/L can be estimated from calculating the amount that must be removed. This can be expressed as f=1-(5/RWR) where f is the radium removal fraction required, and RWR is the raw water radium concentration. This is shown graphically in Figure 6.

Chemistry.

It is to be noted from Table 3 that the waters containing radium also have high total hardness (TH). The chemical properties of radium are similar to those of calcium and magnesium; thus it is not unexpected that those processes which remove hardness (primarily calcium and magnesium salts) will also remove radium.

"The hardness of almost all water supplies is caused by the presence in solution of calcium and magnesium ions. Other divalent ions such as strontium, ferrous iron and manganese may contribute to the hardness to a much lesser degree. The lime-soda process is a precipitative softening process which uses the addition of lime (CaO-quicklime, or $Ca(OH)_2$-slaked or hydrated lime) to convert the soluble bicarbonates of calcium and magnesium into insoluble calcium carbonate and magnesium hydroxide. This is the removal of "carbonate hardness", or the calcium and magnesium ions associated in solution with the bicarbonate ion. Calcium and magnesium associated with the sulfate, chloride or other ions, ("non-carbonate hardness"), are removed by the addition of both lime and soda ash (Na_2CO_3) which provides the carbonate ion necessary for formation of calcium carbonate. Since magnesium removal occurs only above a pH of about 11 at normal water temperatures, excess lime sufficient to raise the pH to 11 must be added prior to removal of magnesium as magnesium hydroxide.

The precipitated compounds are flocculated, settled, and removed as sludge while the clarified effluent is usually filtered in order to polish the effluent by removing residual floc particles.

The chemistry of water softening is probably best explained or illustrated by showing the chemical reactions that take place when lime and soda ash are added to water containing calcium and magnesium salts. The reactions in the lime-soda process, then are:

$$CO_2 + Ca(OH)_2 = CaCO_3 + H_2O \quad (1)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O \quad (2)$$

$$Mg(HCO_3)_2 + Ca(OH)_2 = CaCO_3 + MgCO_3 + 2H_2O \quad (3)$$

$$MgCO_3 + Ca(OH)_2 = CaCO_3 + Mg(OH)_2 \quad (4)$$

$$2NaHCO_3 + Ca(OH)_2 = CaCO_3 + Na_2CO_3 + 2H_2O \quad (5)$$

$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO \quad (6)$$

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4 \quad (7)$$

These equations show all of the reactions taking place in softening a water containing both carbonate and noncarbonate hardness by the lime-soda process. It should be noted that, in Equation 1, the carbon dioxide is not hardness as such, but in proportion to its content in the water will consume lime and must therefore be considered in calculating the amount of lime required. Similarly, in Equation 5, the sodium bicarbonate or sodium alkalinity, if present, is not part of the hardness but, since it is included in the total alkalinity, it will consume lime. Equations 2 and 4 show the removal of carbonate hardness by lime. Whereas only one molecule of lime is required for one molecule of calcium bicarbonate, Equation 2, two molecules of lime are required for the removal of one molecule of magnesium bicarbonate hardness, Equations 3 and 4. Equation 6 shows the removal of magnesium noncarbonate hardness, shown as magnesium sulfate, by lime. No softening is effected by this reaction because, for each molecule of magnesium noncarbonate hardness removed, an equivalent amount of calcium noncarbonate hardness is formed. Equation 7 shows the removal of calcium noncarbonate hardness, shown as calcium sulfate, whether originally in the water or formed as shown in Equation 6.

From these reactions it is apparent that the amounts of lime and soda ash required to soften a water may be calculated from the concentrations of free carbon dioxide, bicarbonate (usually the total alkalinity), magnesium hardness, and noncarbonate hardness." (Singley, et al. 1977).

Control Techniques.

Soluble radium, a divalent alkaline earth metal ion similar to calcium and magnesium is also removed in the lime-soda softening process. Table 4 shows the radium and total removal hardness efficiencies of seven lime-soda softening plants in the United States. The data from Iowa and Illinois are the most reliable, in that radium and hardness analyses were performed on water samples taken at the same time. The hardness data from Florida, on the other hand, were

reconstructed from plant operating records on the same day that the radium samples were taken by another agency. This means that the two samples may have been taken as much as eight hours apart. It can be seen from Table 4 that radium removal varied from plant to plant and ranged from 59-96 percent removal, averaging 80 percent. Figure 7 shows a plot of total hardness removal versus radium removal based on the data presented in Table 4. If the two points from Florida plants are discounted, the line $y = x^{2.86}$ fits the data reasonably well and serves as the basis for a radium removal model in lime-soda plants." (Singley, et al., 1977) Despite the fact the the data show some scatter, a model based on the data in Table 4 for the fraction of hardness removal as

$$\text{Total Hardness Removed Fraction} = THR = f^{2.86}$$

where f is the radium removal fraction, as before. The total hardness removal fraction for achievement of a final radium concentration of 5 pCi/L can be estimated by combining the equations and getting

$$THR = 1 - (5/RWR)^{2.86}$$

This is plotted in Figure 8 for radium concentrations in the raw water from 16 to 50 pCi/L. The lower limit for radium of 16 was chosen since a lime-soda softening plant would rarely if ever reduce the total hardness by less than 35%, i.e., from 150 to 100 mg/L, as $CaCO_3$. This would compare to a radium removal fraction of about 70%, or from a RWR of 16 pCi/L down to 5 pCi/L. A correlation of radium concentrations with other raw water quality parameters is shown in Table 3.

A major problem with any process for removal of radium is the disposal of the waste stream(s). In the case of lime-soda softening there are two streams, filter backwash and precipitated sludge.

Another process for the removal of ionic species, including hardness, ion exchange, is also applicable to the removal of radium. In this process the divalent radium ion is exchanged for sodium or hydrogen ions. Simultaneously other divalent ions such as calcium and magnesium are also exchanged for sodium ions to accomplish softening. Fortunately, the ion exchange materials have a greater affinity for radium than either calcium or magnesium since the concentration of radium is always much lower than either calcium or magnesium. This also provides an additional measure of protection since the hardness breakthrough precedes the radium breakthrough. A study, sponsored by EPA, evaluated a radium selective complexer (Dow Chemical Company, RSC) for removal of radium from brines. The resin was shown to have a very high capacity for radium in water having a TDS of 450 mg/L (51,000 pCi/g dry resin); Both weak and strong acid exchange resins were shown to remove radium at over 96% efficiency (Clark, 1987). Conventional cation exchange resins have exchange capacities of 18,000 to 30,000 grains of hardness per cubic foot. A diagram of a typical ion exchange unit is shown in Figure 9.

Since ion exchange for radium removal is almost 100% effective, the flow fraction to be treated can be obtained from Figure 1. The actual efficiencies for ion exchange in operating plants are shown in Table 5. They are seen to average over 95% for those plants where no operational

problems affected the results, thus the flow fraction can be modified to accommodate the difference. Figure 10 shows the relationship between radium and total hardness removal for the plants shown in Table 4. It illustrates the greater affinity of the resins for radium than for hardness ions.

Since the resins are greater than 95% effective for removal of both hardness and radium, it is usually necessary to treat a fraction of the water and blend with a by-passed untreated fraction. Assuming 95% efficiency, the fraction to be treated can be calculated from: fraction treated = Ft = 1.053(1-5/RWR).

As with lime-soda softening a major problem is disposal of the waste stream, in this case the unused regenerate brine containing the radium that was removed, diluted with the wash water.

Another method for removing radium is reverse osmosis. This method is effective for ionic species as well as any molecular species which has a size greater than the pores in the semipermeable membrane used. The pressure required to produce a water of acceptable quality depends upon overcoming the osmotic pressure of the raw water, the percent recovery required, the properties of the membrane and the quality of the finished water desired. Studies supported by EPA (Clark, 1987) showed that from 82-96% removal of radium could be accomplished.

Radioactivity. The control of radioactivity in drinking water is summarized in Figure 11, from Aieta et al, (1987).

The only element presently regulated is radium, thus emphasis was placed on it. Table 6 provides more detail as to the efficiency of the various treatment technologies.

SELENIUM.

Selenium is chemically similar to arsenic and is generally present in two valence states in water Se IV, selenite, and Se VI, selenate, both as the oxides SeO_3^{-2} and SeO_4^{-2}. It is obvious that anionic exchange resins will effectively remove both species. Coagulation with ferric sulfate results in about 80% removal of Se IV but less than 10% Se VI. Lime softening at high pH, i.e. $>$ 11.5, was only about 50% effective for Se IV and less than 10% for Se VI.

SILVER.

The occurence of silver in untreated water is so rare that EPA has proposed that it be eliminated from the regulated inorganics.

STRONTIUM.

Since strontium is an alkaline earth metal in the same chemical family as calcium, barium and magnesium, its chemical properties are similar. The technology for removal of strontium is the same as discussed above for barium and radium.

ARSENIC

Arsenic occurs in water primarily in the tri- and pentavalent form, usually as anionic oxides, AsO_3^{-3} and AsO_4^{-3} see Figure 12 for effect of pH on arsenic species. The treatment techniques for arsenic V removal using conventional coagulation with alum or ferric salts show good removal below pH 8 by ferric sulfate (95+%) and about 90% by alum at pH below 7. Arsenic III is only about removed 50% by ferric sulfate and less than 15% by alum at the same pH values. Lime softening removes arsenic V at pH values above 10.5 at about 99% efficiency but arsenic III at only about 80% above pH 10.5.

Although data are limited there is little doubt that reverse osmosis and anion exchange will remove both forms effectively, if the arsenic is present complexed by organics it would be removed effectively by activated carbon. Figures 13 and 14 show the effects of ferric sulfate coagulation and lime softening (Sorg and Logsdon, 1978b).

FLUORIDE.

The presence of fluoride in drinking water is regulated under both the primary and secondary contaminant limits due to its health and cosmetic effects. The anomalous addition of fluoride by many water purveyors to reduce dental caries presents a conundrum. Excessive fluoride must be removed but lower concentrations may require supplementalion.

The most cost-effective control treatment method has been shown to be the adsorption on activated alumina (Rubel, 1984). Several full-scale plants have been operated in the U.S. using this process, which was patented by Churchill in 1936. Studies at these plants and in the laboratory have shown that capacities greater than 2,000 grains/cu. ft. can be obtained by optimizing the pH at about 5.5 units. The major sources of activated alumina is Alcoa but other sources are available. It is possible to reduce the fluoride ion concentration concurrently with TDS reduction by reverse osmosis. Rejections up to 90% have been achieved. Lime softening can remove fluoride when high pH is used to precipitate magnesium. Alum coagulation will reduce fluoride because of the formation of insoluble aluminum fluoride. High concentrations of alum are required, which minimizes the selection of this process unless such alum concentrations are required for other purposes.

The design of an activated alumina plant is covered in detail by Rubel (1984) in a manual written for the U.S. EPA.

NITRATE.

Nitrate occurs at levels above the MCL of 10 mg/L (expressed as N) in many groundwater supplies in the U.S. Until recently there was little alternative to use of high nitrate water. Now there are two techniques for removal, ion exchange and reverse osmosis, R.O. Both remove nitrate so effectively that some untreated water usually can be by-passed and blended. Nitrate removals of 75-95% have been experienced in R.O. plants. (Clark, 1987).

SUMMARY

Although many inorganic species occur in natural waters, there are a limited number of applicable treatment processes for their removal. The twelve that are presently regulated appear in the regulations because of their toxicity and high incidence of occurence in raw waters used as sources for drinking water. A brief summary of the best treatment process(es) for each of the twelve is shown in Table 7. Although this is not a comprehensive compilation of relative effectiveness, it does give an overview.

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TABLE 1. PROPOSED MCLG[1] FOR INORGANIC CONTAMINANTS

CONTAMINANT	MCLG, mg/L
As	0.050
Asbestos	7.1 MFL[2]
Ba	1.5
Cd	0.005
Cr	0.12
Cu	1.3
Pb	0.020
Hg	0.003
NO_3	10.0
NO_2	1.0
Sw	0.045

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(1) MCL goal - as changed from RMCL by SDWA Amendments, 1986.

(2) MFL = million fiber/liter.

TABLE 2. Ra CONTENT OF SELECTED RIVERS IN THE UNITED STATES

City Supply	Source	Ra Concentration pCi/liter H_2O
		Raw Water
Atlanta, Ga.	Chattahoochee R.	0.017
Baltimore, Md.	Gunpowder R.	0.020
Birmingham, Ala.	Cahaba R. and L. Purdy	0.024
Bismarck, ND	Missouri R.	0.243
Boston, Mass.	Nashua R.	0.014
Charleston, S.C.	Edisto R.	0.181
Charleston, W. Va.	Elk R.	0.041
Cincinnati, Ohio	Ohio R.	0.061
Denver, Colo.	South Platte R.	0.077
Detroit, Mich.	Detroit R.	0.026
Indianapolis, Ind.	Fall Cr. and White R.	0.137
LaVerne, Calif.	Colorado R.	0.100
Louisville, Ky.	Ohio R.	0.084
Oklahoma City, Okla.	N. Canadian R.	0.106
Omaha, Neb.	Missouri R.	1.770
Philadelphia, Pa.	Delaware R.	0.048
Phoenix, Ariz.	Along Verde R.	0.027
Pittsburg, Pa.	Allegheny R.	3.700
Portland, Ore.	Bull Run R.	0.014
Raleigh, N.C.	Walnut Cr.	0.022
Richmond, Va.	James R.	0.033
Sacramento, Calif.	Sacramento R.	0.018
Salt Lake City, Utah	Cottonwood Cr.	0.034
San Francisco, Calif.	Calaveras Res.	0.018
St. Louis, Mo.	Mississippi R.	1.080
Tacoma, Wash.	Green R.	0.002
Washington, D.C.	Potomac R.	0.033

* Hursh (1953)

TABLE 3. CORRELATION OF RAW WATER QUALITY PARAMETERS WITH RADIUM
(Singley, et al. 1977)

	Ra^{226}[a]	TH[b]	Ca[b]	Mg[b]	Fe[c]	TDS[c]	ALK[b]	Ba[c]	Bo[c]
DCI, IL	3.26	286	153	133	0.44	1220	286	0.13	1.1
Peru, IL	5.82	298	188	110	0.44	890	318	0.13	0.63
Herscher, IL	14.3	404	226	178	0.12	1426	259	0.10	1.4
Elgin, IL	5.55	246	142	104	0.04	360	303	8.7	0.23
Lynwood, IL	14.7	849	620	229	0.60	1766	215	0.09	1.2
Greenfield, IA	14.0	630	400	230	1.6	2160	190	<0.10	----
Adair, IA	6.30	710	450	260	0.58	1905	158	<0.10	----
Stuart, IA	16.0	640	375	265	0.94	1770	182	<0.10	----
Eldon, IA	50.0	400	246	154	1.9	1228	252	<0.10	----
Estherville, IA	5.2	915	600	315	1.6	1350	367	<0.10	----
Grinnel, IA	6.2	368	205	163	1.1	784	298	<0.10	----
Holstein, IA	14.0	920	600	320	1.8	1510	288	<0.10	----
Webster City, IA	7.1	530	275	255	0.69	1010	294	<0.10	----
West Des Moines, IA	9.6	376	210	166	0.36	1200	260	<0.10	----
Sarasota, FL	4.30	460	---	---	----	----	----	----	----
Venice, FL	8.73	570	---	---	----	----	----	----	----
Englewood, FL	1.69	360	---	---	----	----	----	----	----
Mean	11.0	527	335	206	0.87	1327	262	1.80	0.91
r*	----	0.057	0.036	0.048	0.518	0.176	0.252	0.335	0.628
$r_\alpha = 0.05$**	----	0.606	0.532	0.532	0.532	0.532	0.532	0.878	0.878

*Correlation coefficient for bivariate linear regression of ^{226}Ra with associated chemical parameter
**Correlation coefficient for significance at $\alpha = 0.05$ level
[a] pCi/l
[b] mg/l $CaCO_3$
[c] mg/l

TABLE 4. RADIUM^{226} AND TOTAL HARDNESS REMOVAL EFFICIENCIES LIME-SODA SOFTENING
(Singley, et al. 1977)

LOCATION	CLARIFIERS							FILTERS						OVERALL	
	Ra in pCi/l	Ra out pCi/l	% RA Removal	TH In mg/l $CaCO_3$	TH Out mg/l $CaCO_3$	% TH REM	pH Treatment	RA In pCi/l	RA Out pCi/l	% Ra Removal	TH In mg/l $CaCO_3$	TH Out mg/l $CaCO_3$	% TH REM	% Ra REM	% TH REM
W. Des Moines, IA 8/1/74	9.3	2.6	72	376	215	43	10.4	2.6	2.35	10	215	190	12	75	49
Webster City, IA. Clarifier #1 8/13/74	6.1	1.9	69	507	333	34	10.05	1.9	0.9	53	333	262	21	85	48
Webster City, IA Clarifier #2 8/13/74	6.1	2.6	57	507	282	44	10.1	2.6	0.9	65	282	262	7	85	48
Webster City, IA Clarifier #1 2/20/75	7.8	0.9	88	482	150	69	10.95	0.9	0.3	67	150	106	29	96	78
Webster City, IA Clarifier #1 2/20/75	7.8	0.3	96	482	150	69	10.95	0.3	0.3	0	150	106	29	96	78
Peru, IL 2/20/75	6.49			329			8.4		0.51			174		92	47
Peru, IL 2/25/75	5.49			278			8.4		1.62			180		70	35
Peru, IL 3/4/75	5.48			236			8.4		1.33			122		76	57
Mean	5.82			289					1.15			147		79	49
Elgin, IL 3/7/75	7.45			246			10.2		.75			99		90	60
Elgin, IL 3/14/75	5.7			243			10.2		.80			112		86	54
Elgin, IL 3/21/75	3.51			242			10.2		.71			95		80	61
Mean	5.55			244					.75			102		85	59
Venice, FL 8/7/75	8.73			570			9.7		2.19			100		75	82
Englewood, FL 8/7/75	1.69			360			8.5		.69			166		59	54

Table5. RADIUM REMOVAL IN ION EXCHANGE PLANTS

Plant	Ra in pCi/L	Ra out pCi/L	% Ra Rem. ■	TH in mg/L/$CaCO_3$	TH out mg/L/$CaCO_3$	% TH Rem. ■
Eldon, Ia	49	1.9	96	375	10	97
Estherville, Ia	5.7	0.3	95	915	46	95
Grinnell, Ia	6.7	0.2	97	385	11	97
Holstein, Ia	12	0.5	96	920	18	98
Dwight Corr. Inst., Il	3.26	0.36	89	286	43	85*
Herscher, Il	14.31	1.31	91	406	60	85*
Lynwood, Il	14.69	0.41	97	848	78	91
Sarasota, Fl	4.3	0.70±	84	460	159±	65**

■ Removed

± Adjusted to take account of raw water blending.

* %Hardness and %Ra removals are somewhat low due to breakthrough occurring prior to all samples being collected.

**%Hardness and % Ra removals are somewhat low due to incomplete regeneration of media as 1/2 brine pumping capacity was down for repair.

TABLE 6. TREATMENT TECHNOLOGIES FOR REMOVING RADIONUCLIDES (Aieta, et al. 1977)

Treatment Technology	Radionuclide	Approximate Process Efficiency *percent*	Comments
Coagulation-filtration	Ra	<25	High pH and Mg required
	U	95+	High pH (10+) and high dosages of ferric chloride or alum
		18-98	Only accomplished in lab studies with diatomaceous earth filtration
	Rn		N/A*
Lime-soda softening	Ra	80-95	Best choice for large plants
		75-96	
		85	
		43-92	Plant-scale results
		80	Plant-scale results
	U	85-90	pH 10.6-11.5
		99	High pH, high Mg
	Rn		N/A
Ion exchange	Ra	95+	Best choice for small plants; cation exchangers
		99	Brine disposal problem
	U	99	Anion exchangers; largely experimental
	Rn		N/A
Adsorption	Ra	90+	Experimental
		85-90	Sand adsorption; experimental
	U		N/A
	Rn	62-99	GAC adsorption
Aeration	Ra	18	Adsorption on $Fe(OH)_3$
		20-25	$Fe(OH)_3$ and sand
	U		N/A
	Rn	20-96	Depends on process
		93+	Depends on process
Reverse osmosis	Ra	87-96	Plant-scale data
		87-98	Based on eight plants
		95+	High-volume brine solution for disposal
	U	95+	High-volume brine solution for disposal
	Rn		N/A

*N/A = not applicable

TABLE 7. SUMMARY OF BEST TREATMENT PROCESSES FOR REMOVAL OF INORGANIC CONTAMINANT

Contaminant	Coagulation	Lime Softening	Ion[d] Exchange +	Ion[d] Exchange -	Activated Alumina	GAC	R.O.[a]
As V[b]	+[c]			+		Bone char +	+
Ba		+pH 9.5-10.5	+				+
Cd	+pH>8	+	+				+
Cr III	+	+pH >10.5	+				+
F					+	Bone char +	+
Pb	+	+					+
Hg (Organic)						+	
Hg (Inorganic)						+	
NO_3				+			
Se				+	+ (Se IV)		+
Ag			+				+
Ra		E pH 9.5-10.8	+				+

a. Ro = reverse osmosis, also electrodialysis assumed to be equivalent.

b. As III can be oxidized to As V with Cl_2.

c. + means 90-100% removal.

d. + means cation exchange; - means anion exchange.

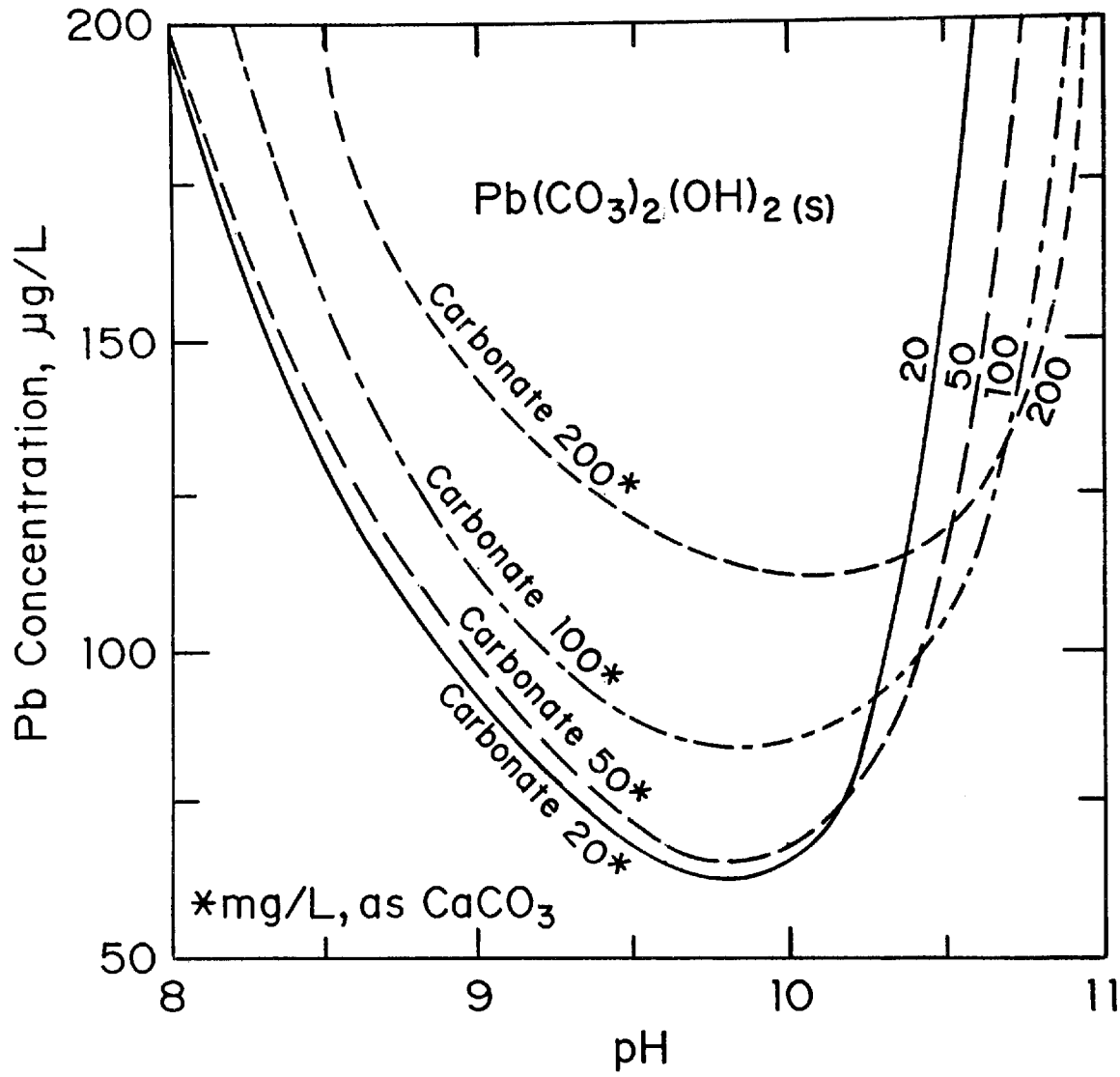


Figure 1. Solubility of Lead as a Function of pH and Carbonate. (Adapted from AWWARF/EBI, 1985)

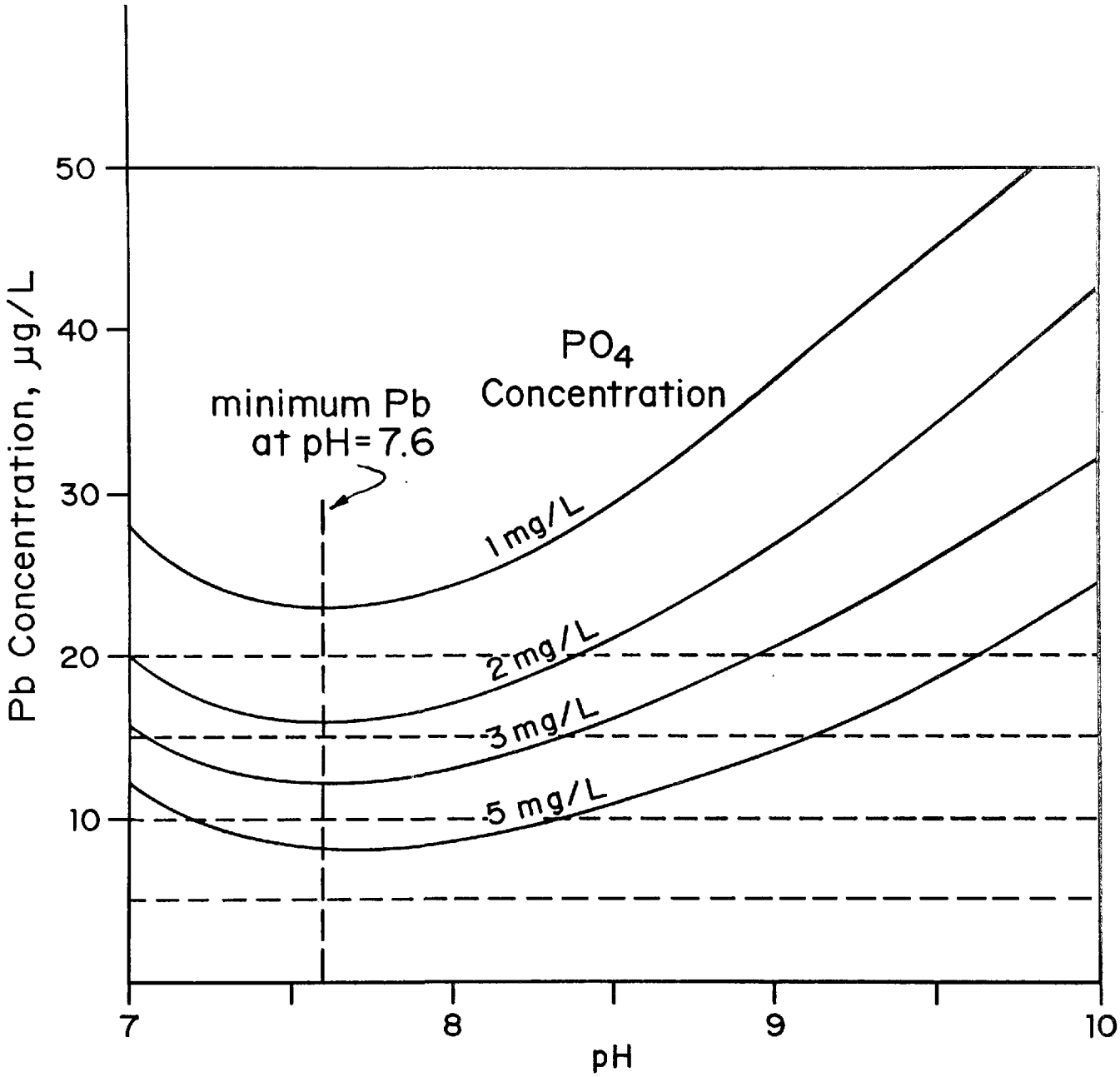


Figure 2. Lead Concentration as Function of pH and Phosphate Concentration at a Total Alkalinity of 50 mg/L (Adapted from Schock)

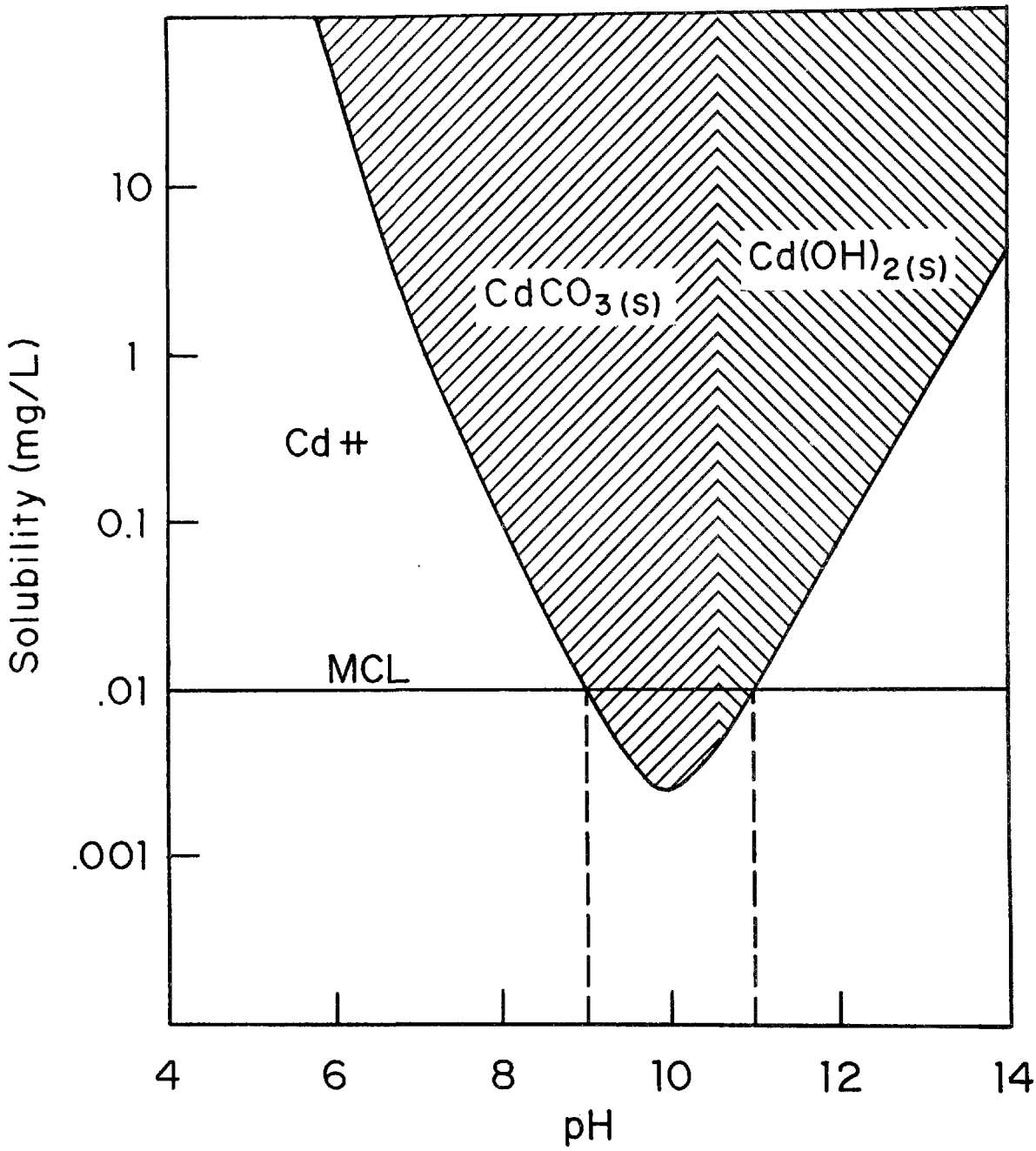


Figure 3. CADMIUM SOLUBILITY AS A FUNCTION OF pH.

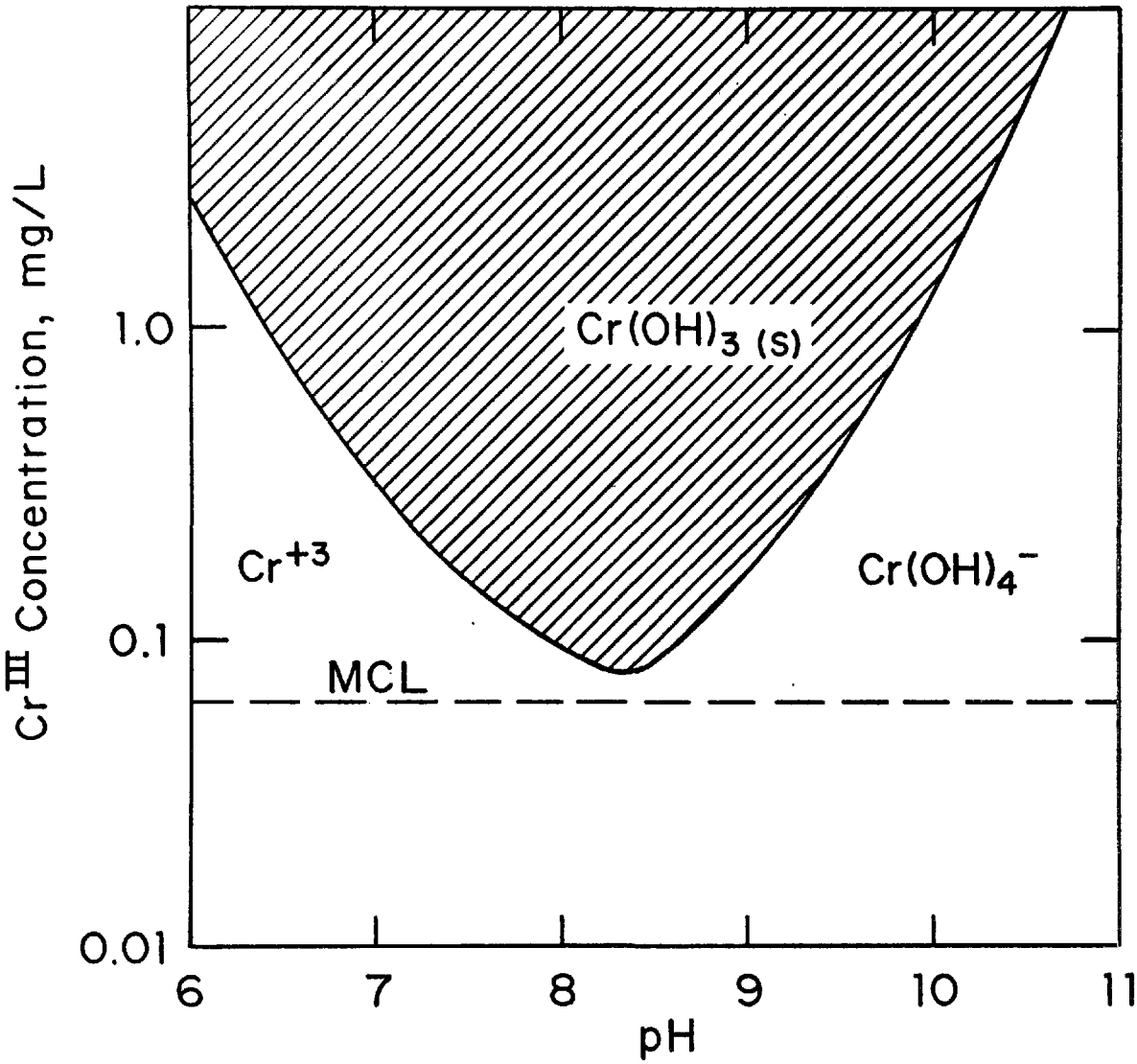


Figure 4. Solubility of Cr^{III} as a Function of pH

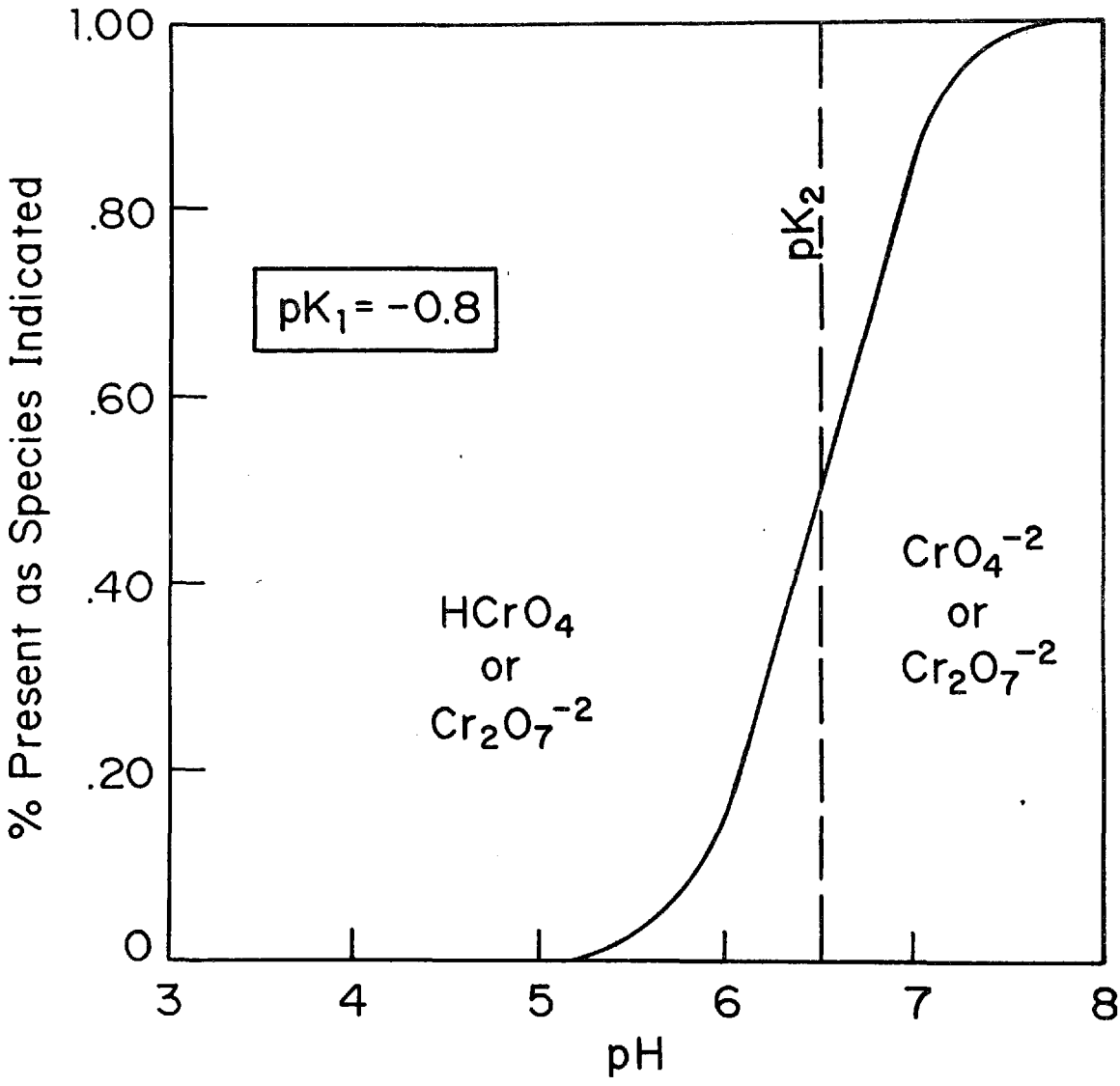


Figure5. Effect of pH on Speciation of Chromium VI

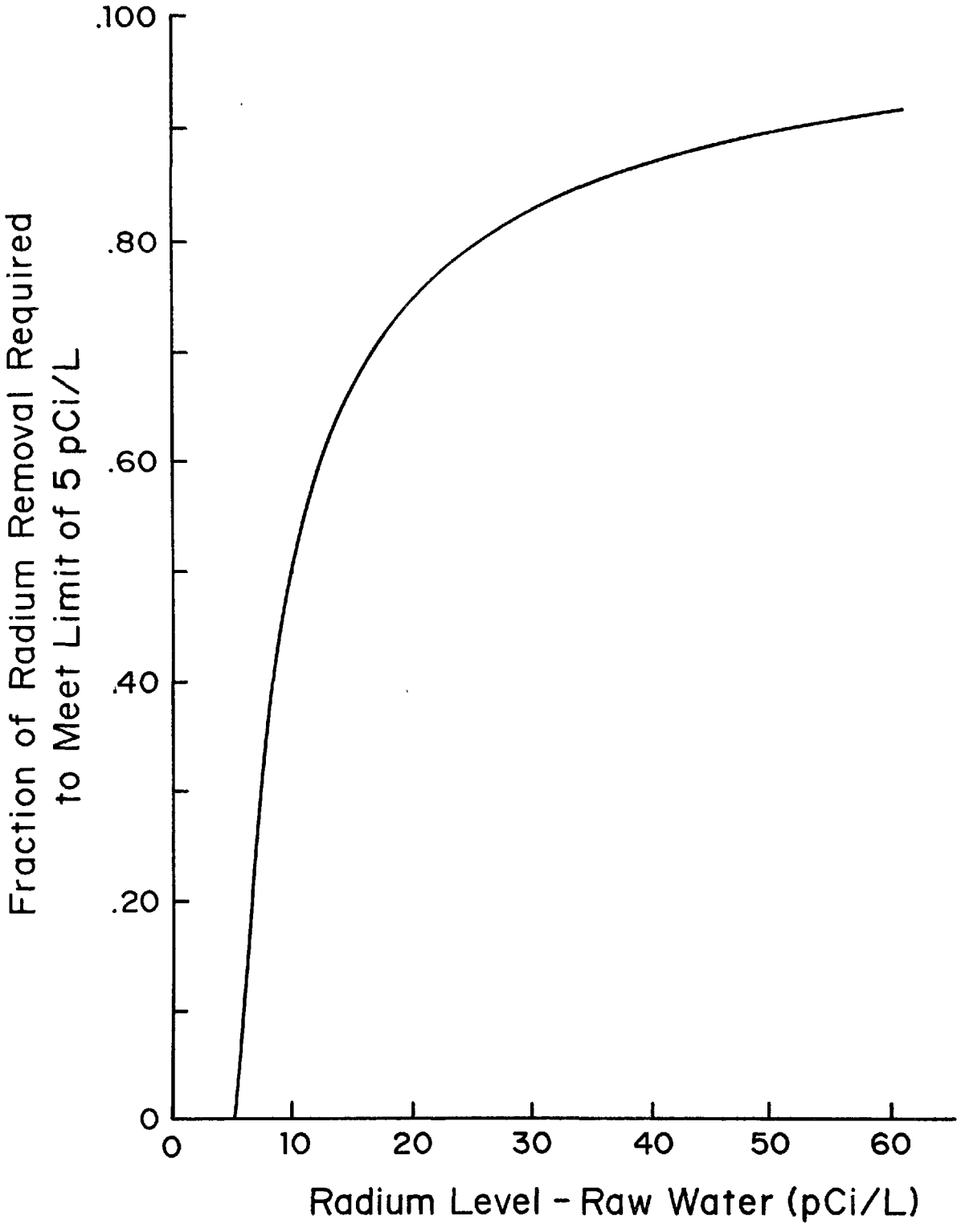


Figure 6. REQUIRED REMOVAL FRACTION FOR RADIUM

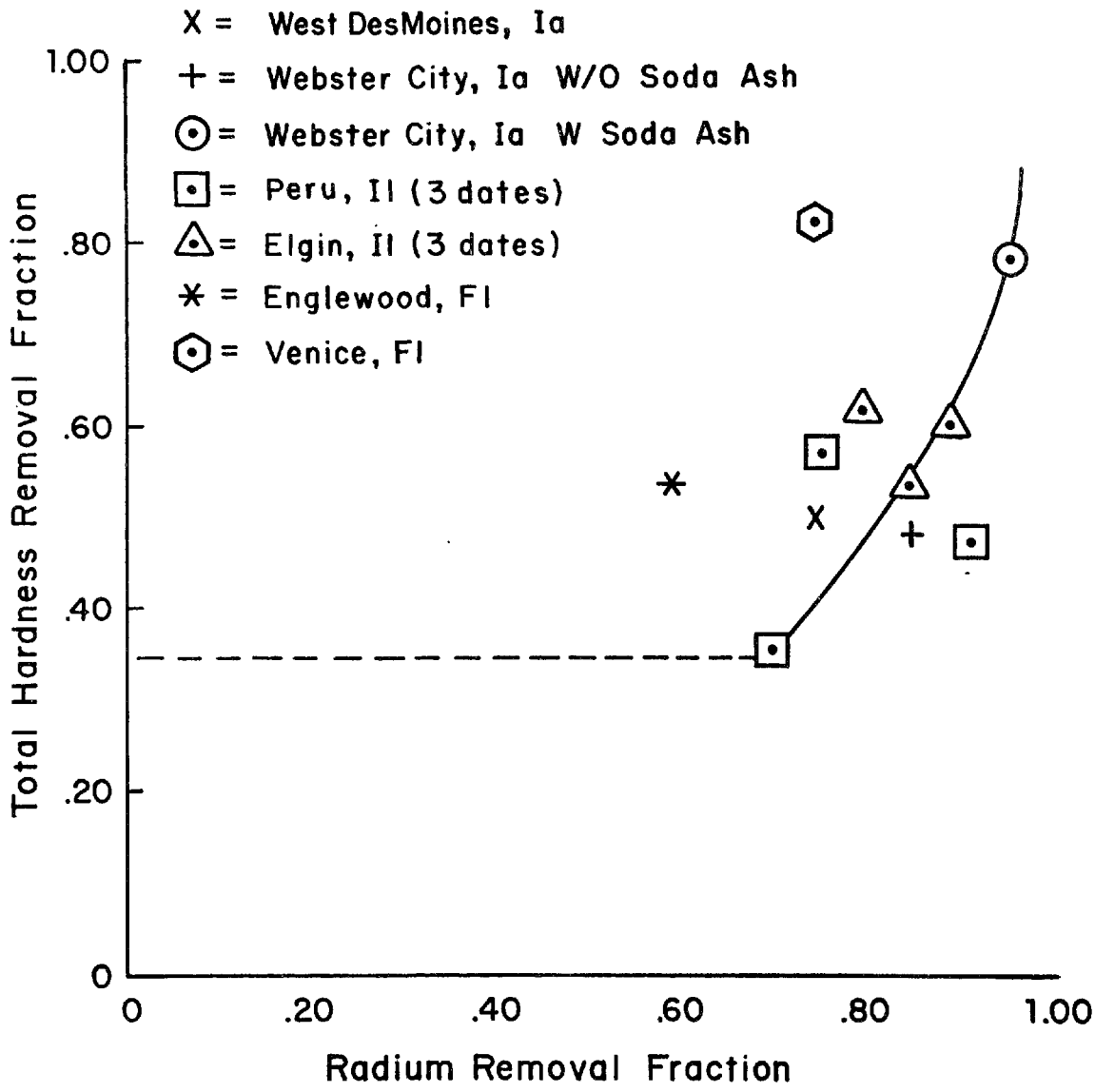


FIGURE 7. LIME SODA PROCESS, TOTAL HARDNESS REMOVAL FRACTION VS RADIUM REMOVAL FRACTION.

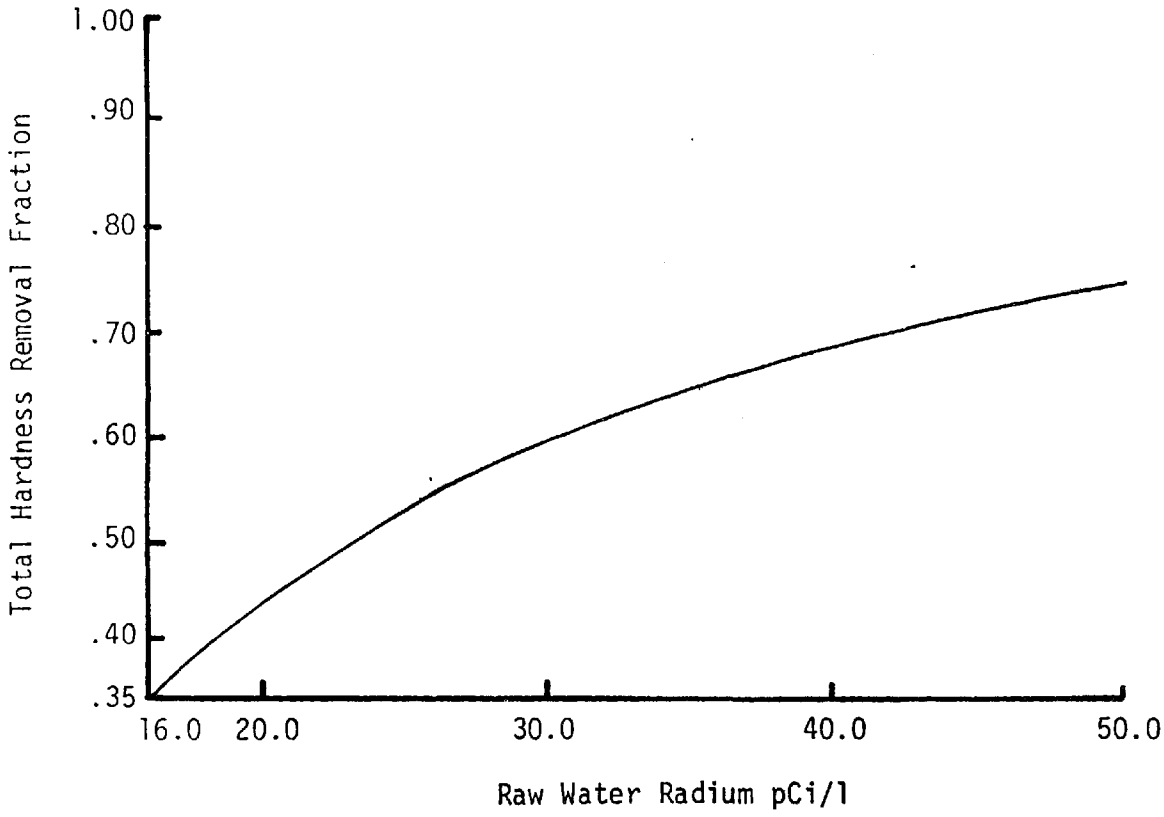


Figure 8. Total hardness removal fraction as a function of raw water radium content required to meet limit of 5.0 pCi/L finished water. (Singley, et al. 1977)

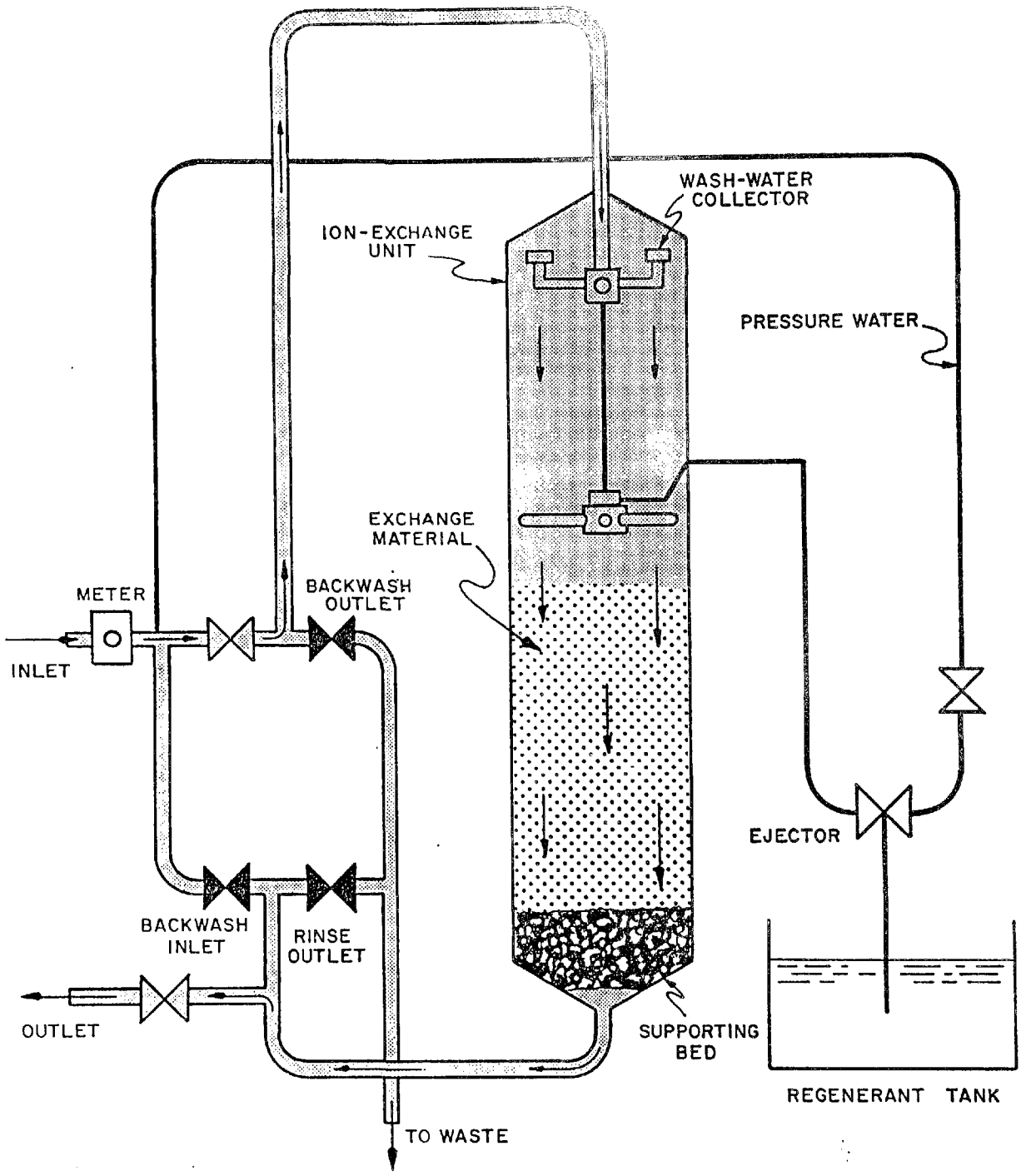


Figure 9. DIAGRAM OF TYPICAL ION EXCHANGE UNIT (3)

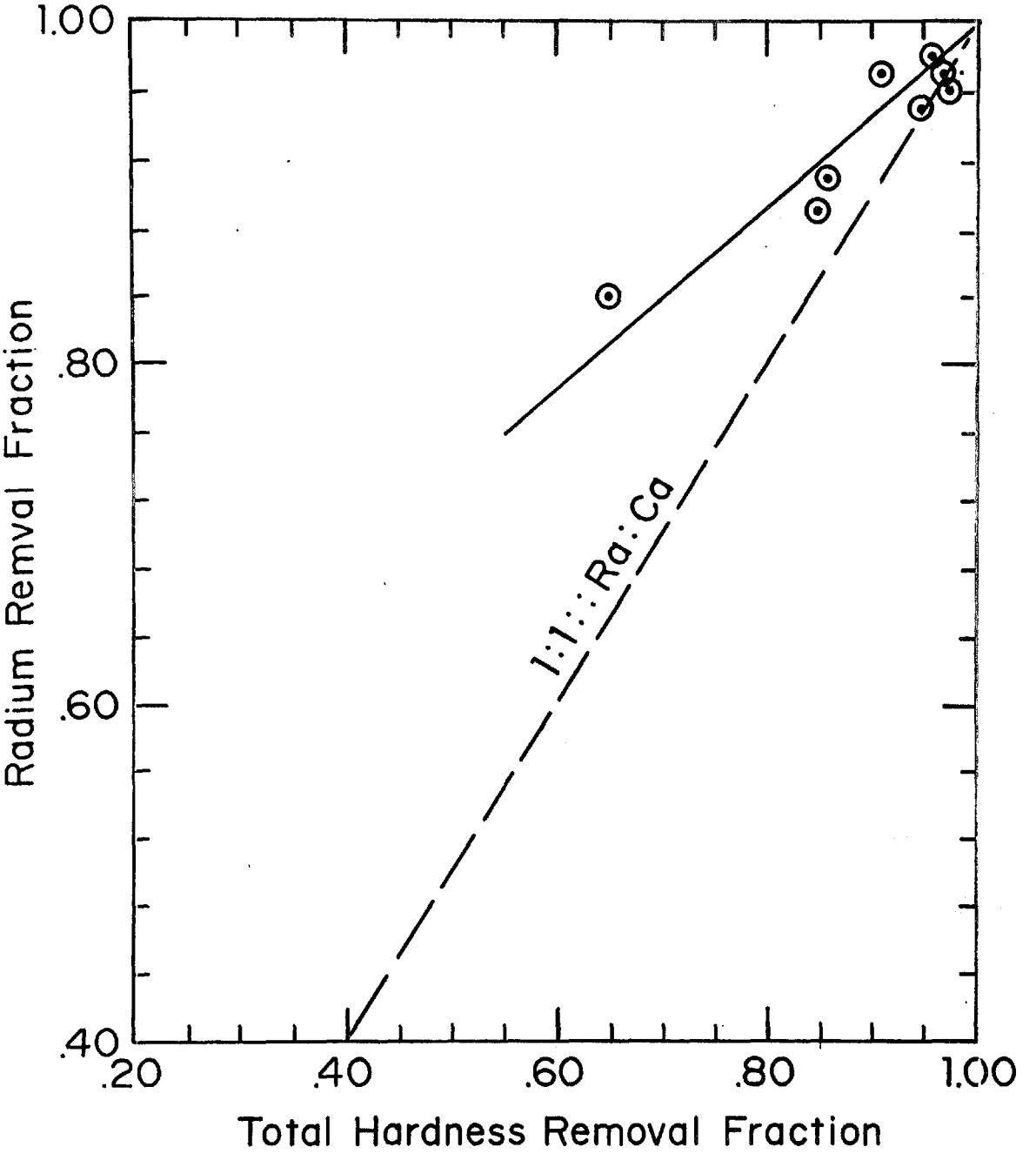


FIGURE 10. RADIUM REMOVAL FRACTION VS. TOTAL HARDNESS REMOVAL FRACTION IN ION EXCHANGE PLANTS (BEFORE BLENDING)

(Adapted from Singley, et al, 1977)

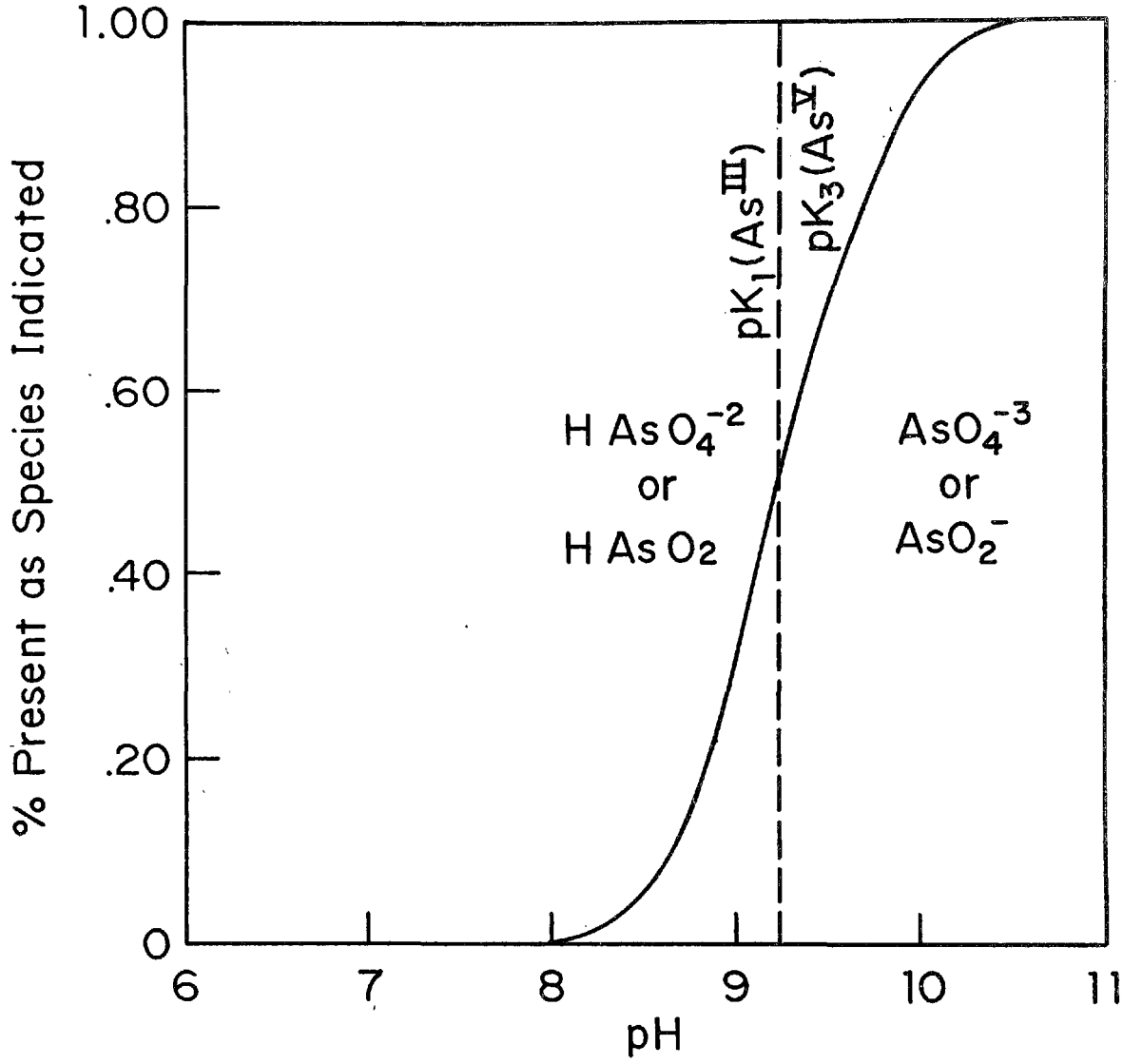


Figure 12. Effect of pH on Speciation of As

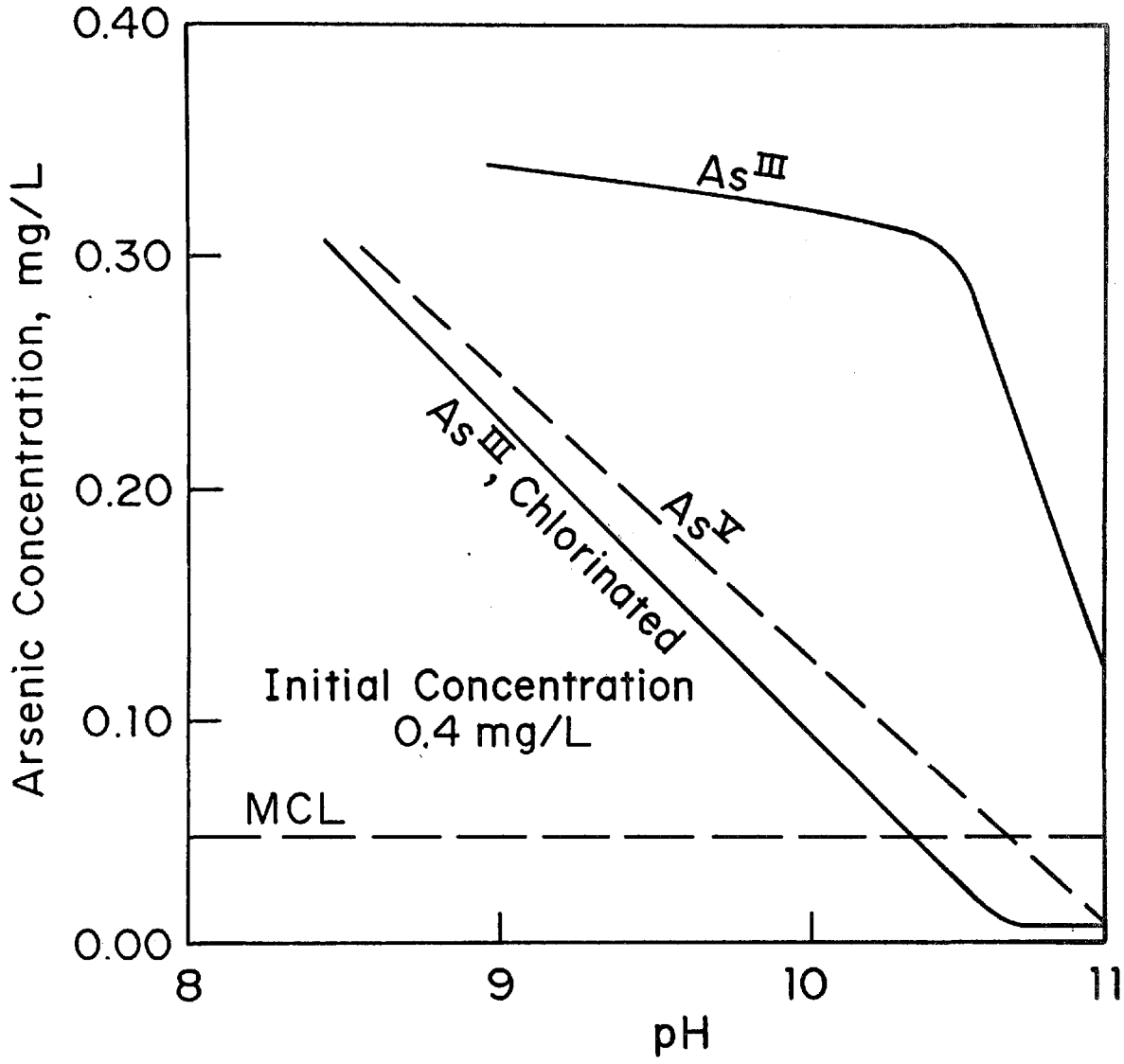


Figure 13. Effects of pH on Arsenic Removal by Lime Softening (Adapted from Sorg & Logsdon 1978)

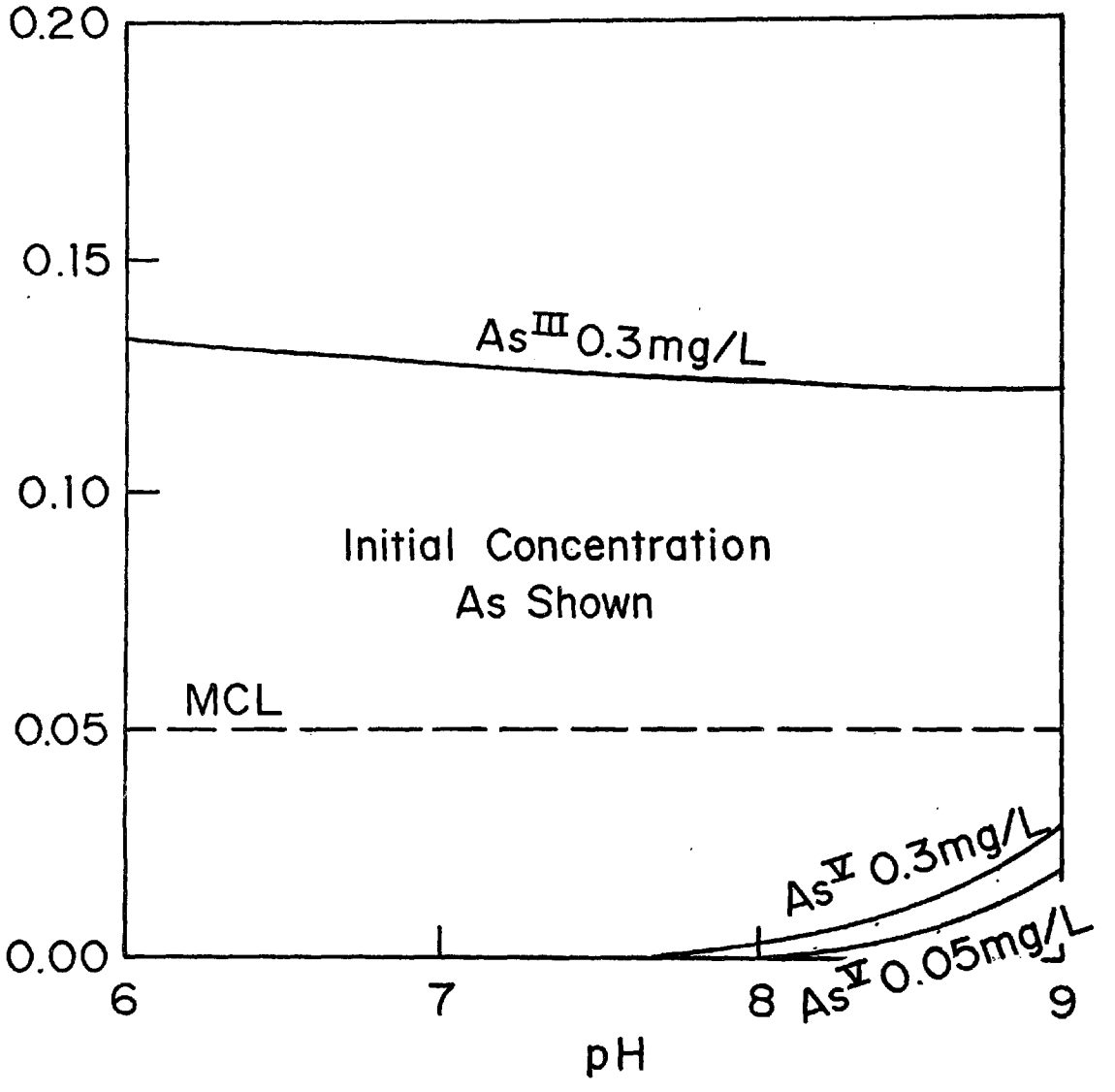


Figure 14. Effects of pH on Arsenic Removal by Ferric Sulfate Coagulation (30mg/L) (Sorg & Logsdom 1978)

WORKSHOP ON EMERGING TECHNOLOGIES FOR DRINKING WATER TREATMENT INORGANIC CONTAMINANTS PROCESS, PLANNING OVERVIEW

The planning of appropriate treatment processes for the twelve regulated inorganic contaminants is complex and thus difficult to adapt to a rigid check-list format, although there are many elements in common. It is important to keep in mind that there are many alternatives in each case, not only process-wise, but compatibility with existing process streams and equipment. In many cases the decision-making process may be considerably simplified by application of common sense---which cannot be programmed. Figure 1 shows many of the elements that can be used sequentially - most of which are obvious.

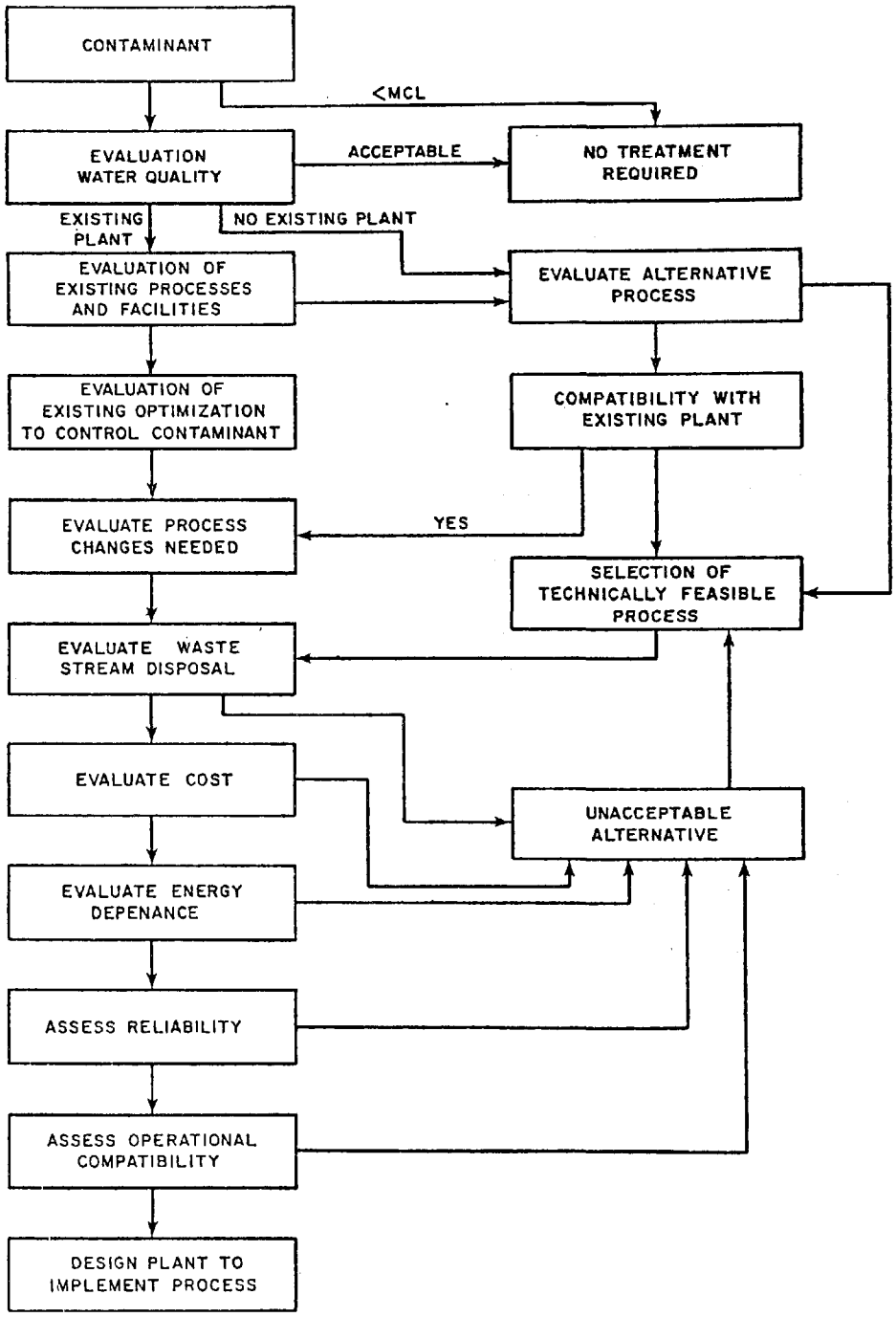


FIGURE 1. Process Planning Decision Tree

Inorganic Contaminants

Process Design Check List

I Contaminant Identification

- A. Historical Records
- B. Current Analyses

II MCL Compliance Evaluation

- A. Present MCL
- B. Proposed MCL
- C. Treatment Required

III Plant and Process Evaluation

- A. Physical Evaluation
  1. Treatment Units
  2. Appurtenances
  3. On-site Space
- B. Process Evaluation
  1. Operating Parameters
  2. Flexibility

IV Evaluation of Alternate Processes

- A. Coagulation
  1. Alum
  2. Iron Salts
- B. Lime-soda Softening
- C. Ion Exchange
  1. Cation
  2. Anion
- D. Reverse Osmosis
- E. Activated Carbon
  1. PAC
  2. GAC
- F. Activated Alumina

V Optimization of Existing Processes

A. Feasibility

VI Evaluate Compatibility With Plant

A. Physical
B. Chemical

1. Control Contaminant(s)
2. Maintain Quality

VII Evaluate Process Charges in Existing Plant

VIII Evaluate Technical Alternatives

A. Waste Stream Disposal

1. Solids

a. Hazardous
b. Non-hazardous

2. Liquids

a. Hazardous
b. Non-hazardous

B. Cost

1. Capital
2. O&M

C. Energy Dependence
D. Reliability
E. Operational Compatibility

IX Final Selection

A. Process
B. Plant

1. Modifications to Existing Plant
2. New Plant

PROCESS CHECK LIST

Evaluation of Alternative Processes

A. Contaminant(s) Present
   1. Identification of those exceeding MCL _____
   2. Historical record of contaminant(s) _____
   3.

B. Candidate Process(es) Considered
   1. Non-treatment
      a. Blending _____
      b. New source(s) _____
      c. Purchase
         1) Raw _____
         2) Treated _____
      d. Bottled water _____
      e. Point-of-use treatment _____

   2. Treatment
      a. Coagulation
         1) Alum _____
         2) Iron salts _____
      b. Softening, lime-soda
      c. Ion exchange
         1) cationic _____
         2) anionic _____
         3) pre-treatment _____
      d. Reverse osmosis (electrodialysis)
         1) high pressure _____
         2) low pressure _____
         3) pre-treatment required _____
      e. Activated Alumina _____
      f. Activated Carbon
         1) PAC _____
         2) GAC _____

C. Compatibility With Present Process
   1. Process reoptimization _____
   2. Facilities _____
   3. Retrofitting _____

D. Waste Disposal
   1. Solids
      a. hazardous _____
      b. non-hazardous _____
   2. Liquids
      a. hazardous
         1) concentrate _____
         2) neat _____
      b. non-hazardous
         1) dry (concentrate solids) _____
         2) recycle portion _____
         3) sewer _____
         4) return to source _____

E. Cost Evaluation

1. Processing
   a. Capital _____
   b. O & M _____

2. Disposal
   a. Capital _____
   b. O & M _____

3. Environmental Permits _____

Sample Ra Control Process
(Applicable to Any Other Contaminants)

I. Lime-Soda

Parameter	Raw Mg/L	Raw Meq/L	Raw pCi/L	Finished Mg/L	Finished Meq/L	Finished PCi/L
TH, as $CaCO_3$	300	-				
Ca, "	250	12.50				
Mg, "	50	4.17				
Alk, "	200	4.00				
TDS	400					
CO_2	15	3.40				
Ra			22			<5.0

A. Estimate the finished Total Hardness (TH)
B. Estimate the finished .a concentration
C. Approximate the pH of treatment
D. If the population of the service area was 15,000, what would be
   a. the approximate volume of filter backwash, in gal/day?
   b. the approximate dry weight of the sludge?
   c. the radium content of the sludge (70% dry)?
   d. the radium content of the backwash water?

II. Ion Exchange

Same water, same population

Assume 1) operating capacity of resin = 20 kgr hardness as $CaCO_3$/ft^3
2) regeneration with 10% brine
3) salt for regeneration = 0.30 pounds salt/kgr. hardness removed (as $CaCO_3$) or 6 pounds/ft.^{3}.
4) 95% TH removal
5) 95% Ra removal

A. Calculate the fraction of the flow to be treated.
B. Estimate the amount of regenerant salt, per million gallons of finished water.
D. Estimate the total volume of brine to be disposed (backwash + rinse water) per MG.
E. Estimate the Ra concentration in the waste brine (bw + rinse).

III. Reverse Osmosis

Same water, same population.
Assume 1) 95% removal of all ions
2) 95% removal of Ra
3) blending to 5 pCi/L Ra

A. Calculate the TH of the blended, finished water.
B. Calculate the fraction of water to be treated.
C. Calculate the reject brine Ra concentration.

IV. What would be the most compatible choice of treatment process for the following utilities? What factors should be most relevant?

A. Utility has only wells with chlorination.
B. Utility has lime-soda softening plant, reducing Calcium hardness from 190 to 70 mg/L, as $CaCO_3$. Its source is a river with average turbidity of 8 ntu.
C. Utility has an ion exchange plant for softening a well supply from 200 to 100 mg/L as $CaCO_3$.

SAMPLE CALCULATIONS

Lime-Soda Process

High Solids Raw Water

TH - 750 mg/l @ $CaCO_3$
Ca^{++} - 500 mg/l @ $CaCO_3$
Mg^{++} - 250 mg/l @ $CaCO_3$
ALK - 300 mg/l @ $CaCO_3$
TDS - 2000 mg/l
CO_2 - 11.4 mg/l @ $CaCO_3$

1 - Desired finished water for Ra_0 = 7.5 pCi/l
Ra removal required - 33 percent or .33
TH removal required - $Ra_{rem}^{2.86}$
$= .33^{2.86} = .042$
Minimum TH considered practical in lime-soda process is 35 percent

TH removal required = .35 (750) = 262 mg/l @ $CaCO_3$, or 5.25 meq/l
TH of finished water= 488 mg/l @ $CaCO_3$ or 9.75 meq/l

2 - Chemical requirements

Parameter	Raw		Finished	Δ	Required CaO	Required CaO
	mg/l	meq/l	meq/l	meq/l	meq/l	meq/l
CO_2	5	0.23	0	0.23	0.23	-
Ca^{++}	200	10.00	4.75	5.23	5.25	-
Mg^{++}	60	5.00	5.00	0	-	-
HCO_3	366	6.00	0	6.00	0.75	-
TOTALS					6.23	

Lime Required = $\frac{(6.23)(28)}{.90}$ = 194 mg/l

Soda Ash Required = None

I/E Exchange

1 - Mass Balance Calculation

To determine fraction of raw water influent blended, and fraction treated, assuming 95 percent removal in I/E or R/O column.

For mass balance of Ra:

$$.05\ Ra_o x + Ra_o\ (1-x) = (1)(5)$$

$$.05\ Ra_o x + Ra_o - Ra_o x = 5$$

$$x\ Ra_o\ (.05 - 1) + Ra_o = 5$$

$$-.95\ x\ Ra_o = 5 - Ra_o$$

$$x = \frac{5 - Ra_o}{-.95\ Ra_o}$$

$$x = \frac{Ra_o - 5}{.95\ Ra_o}$$

Blending allowed to attain minimum level of 5 pCi/l Ra assuming 95 percent Ra removal in I/E and R/O

Ra Level	Fraction Blended	Fraction Treated ~~Blended~~
50	.053	.947
20	.211	.789
7.5	.649	.351

2 - Regenerant Chemicals Calculations

Assume: 1) operating capacity of resin = 20 kgr hardness as $CaCO_3$/CF
2) regeneration is with a 10 percent brine concentration
3) salt required for regeneration is 0.30 lb salt/kgr hardness as $CaCo_3$ removed (6 lb salt/CF)
4) 95 percent TH removal in unit (5 percent leakage)

Solids Levels:

High - $TH_{raw} = 750$, $TH_F = .05\ (750) = 37.5$

$$TH_{rem} = 712.5 \text{ mg/l}$$

Kilograins hardness removed

$$\frac{712.5 \text{ mg/l} \times 1 \text{ grain/gal} \times 1 \text{ kgr}}{17.1 \text{ mg/l} * 1000 \text{ gr}} = .0417 \text{ kgr/gal}$$

Salt regeneration requirement/MG

$$\frac{.0417 \times 10^6 \text{ kgr}}{\text{mg}} \times \frac{.30 \text{ lb salt}}{\text{kgr}} = 12{,}510 \text{ lb}$$

Volume of rinse water/MG, assume 30 gal/CF resin

$$\frac{41{,}700 \text{ kgr THr}}{\text{mg}} \cdot \frac{\text{CF}}{20 \text{ kgr}} \cdot \frac{30 \text{ gal}}{\text{CF}} = 62{,}550 \text{ gal}$$

Volume of regeneration brine solution/MG

$$\frac{12{,}510}{.10} - 12{,}510 = 112{,}590 \text{ lb } H_2O$$

$$13{,}500 \text{ gal } H_2O$$

Total volume of backwash + rinse water/MG

High Solids - 13,500 + 62,550 = 76,050 gal or 7.6 percent of total flow

Reverse Osmosis Calculations

1 - Assumptions

High Solids - Initial TDS_i = 2000 mg/l

Product TDS_i = .05 (2000) = 100 mg/l

Calcium initial, Ca_i = 200 mg/l

2 - Brine to Product Ratio (BPR) =

$$BPR = \frac{1 - (TDS_p/TDS_i)}{(900/Ca_i) - 1}$$

$$BPR = \frac{1 - (100/2000)}{(900/200) - 1} = \frac{.95}{3.5} = .271$$

3 - Brine Volume (V_b)

$V_b = V_p \times BPR = .271\ V_p$ V_p = Product Volume

4 - Feed Volume (V_i)

$V_i = V_p + .271\ V_p = 1.271\ V_p$

REMOVAL MECHANISMS

PRECIPTATION

CO-PRECIPTATION

ADSORPTION

COAGULATION

OXIDATION

COMPLEXATION

ION EXCHANGE

SPECIATION

ANIONS:

- As (AsO_2^{-1}, AsO_4^{-3})
- Cr (CrO_4^{-2}, CrO_7^{-2})
- F^-
- N (NO_3^-, NO_2^-)
- Se (SeO_3^{-2}; SeO_4^{-2})

CATIONS:

- Ba^{+2}
- Cd^{+2}
- Pb^{+2}
- Hg^{+2}
- Ag^{+1}

COMPLEXES:

- Hg (ORGANIC)
- $HgOH^+$
- $HgCL^+$
- $CdOH^+$
- MCO_3^0
- MSO_4^0

SPECIATION PARAMETERS

pH

SPECIES CONCENTRATION

COMPLEXANT CONCENTRATION

PARTICULATE CONCENTRATION

REDOX POTENTIAL

IONIC STRENGTH

TEMPERATURE

EFFECT OF pH

IONIC SOLUBILITY:

HYDROXIDES EXCEEDS "REGS" ONLY BELOW:

Cd pH <11.0

Pb pH < 6.2

Hg pH < 7.0

ACIDIC SPECIES:

$AsO_3^- — HAsO_3$

$AsO_4^{-3} — HAsO_4^{-2} — H_2AsO_4^{-1} — H_3AsO_4$

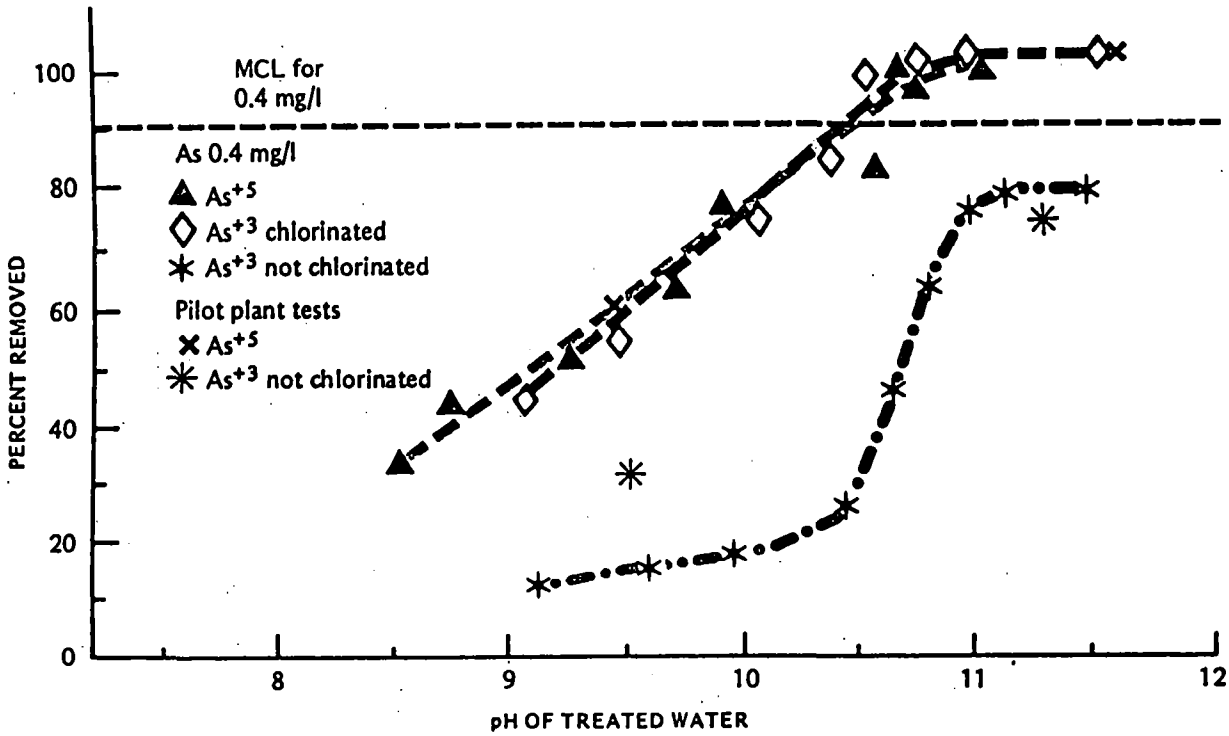
$CrO_4^{-2} — HCrO_4^- — H_2CrO_4$

$Cr_2O_7^{-2} — HCr_2O_7^- — H_2Cr_2O_7$

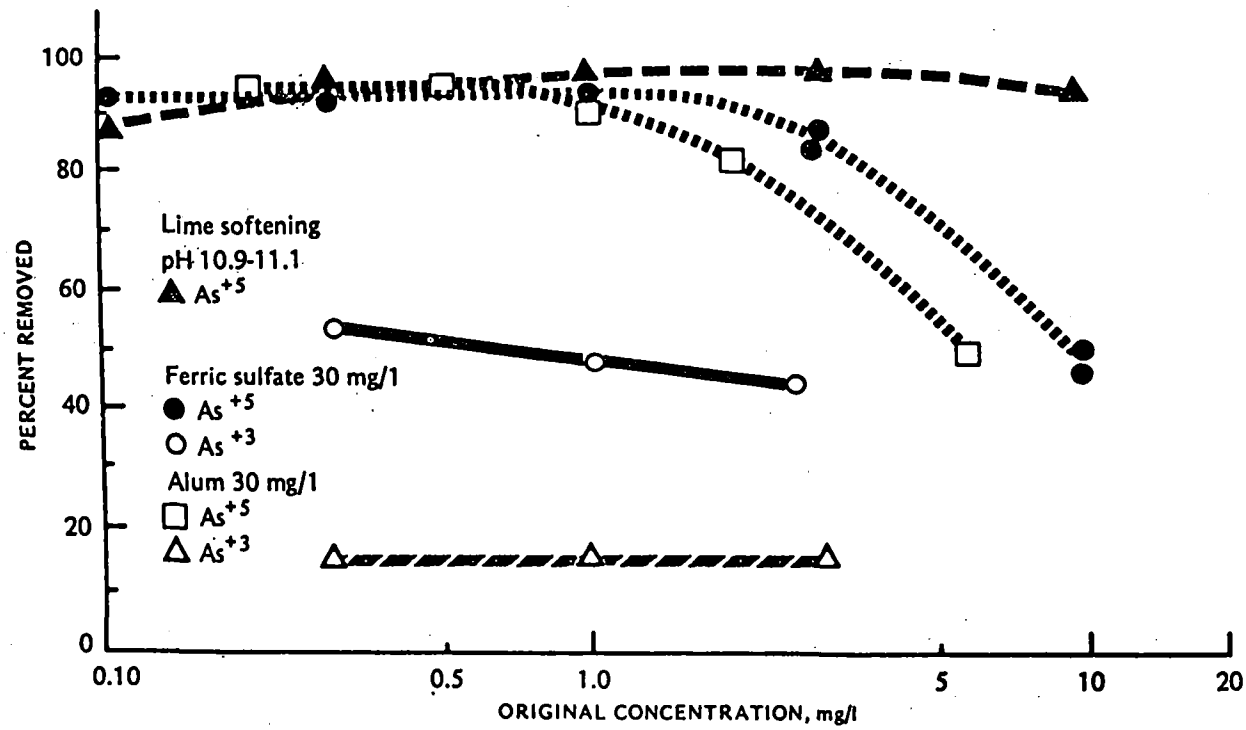
$SeO_3^{-2} — HSeO_3^- — H_2SeO_3$

$SeO_4^{-2} — HSeO_4^- — H_2SeO_4$

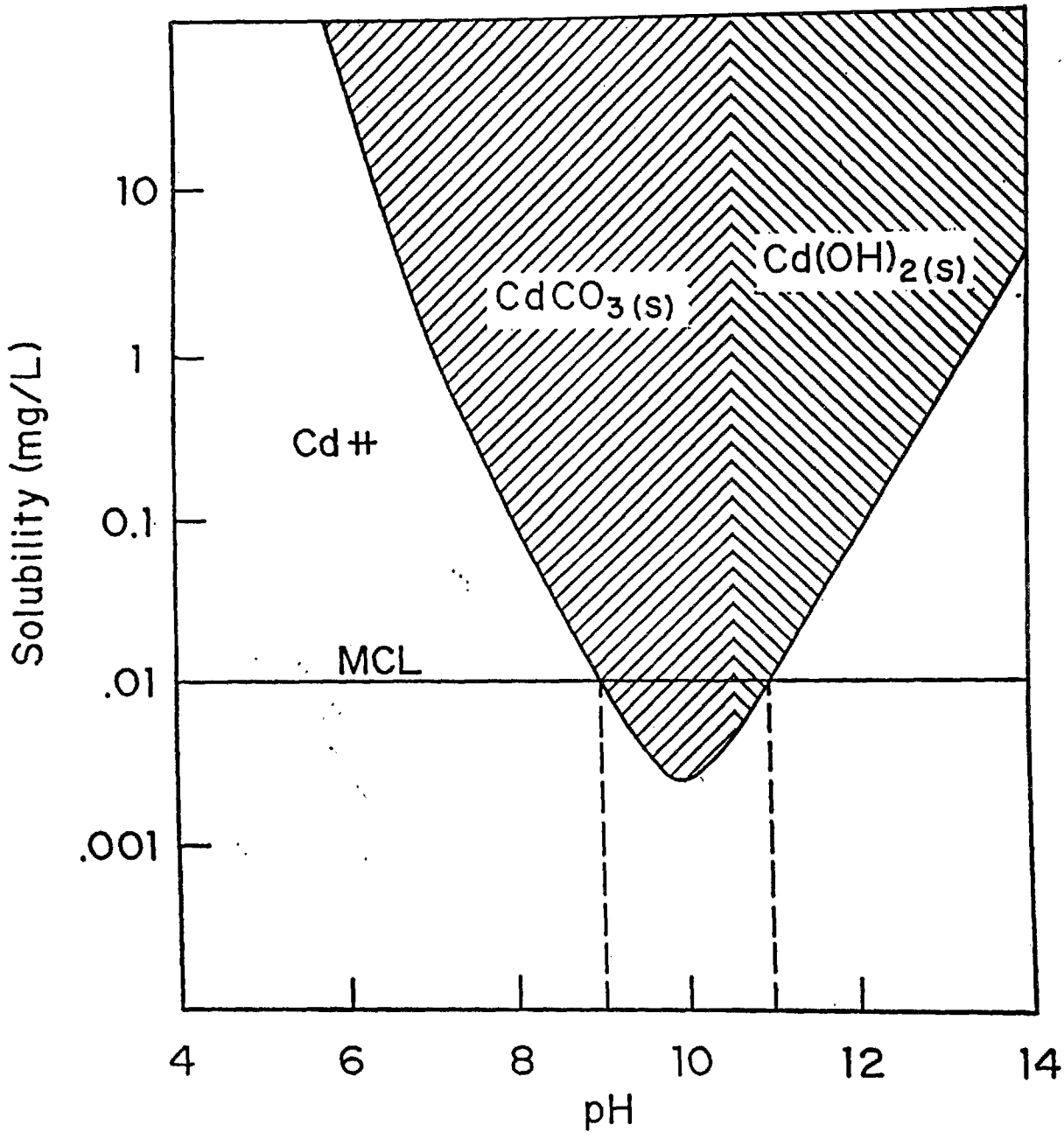
$F^- — HF$



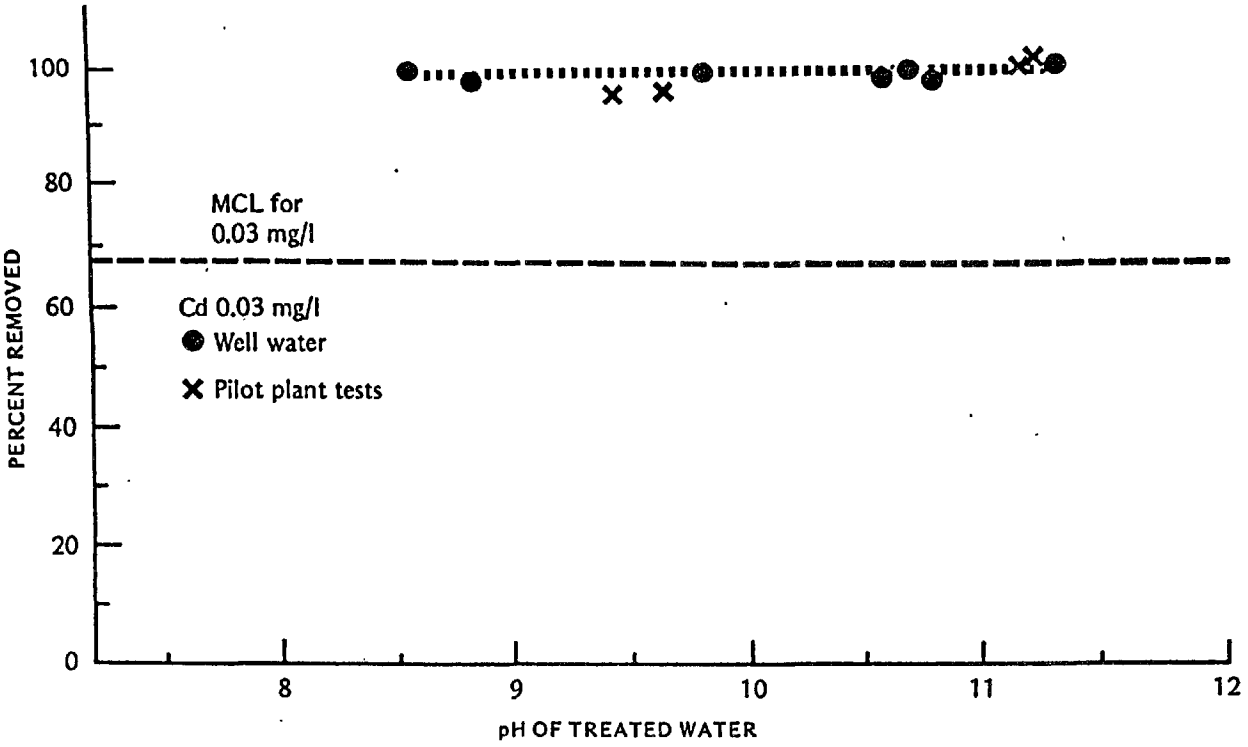
ARSENIC REMOVAL BY LIME SOFTENING



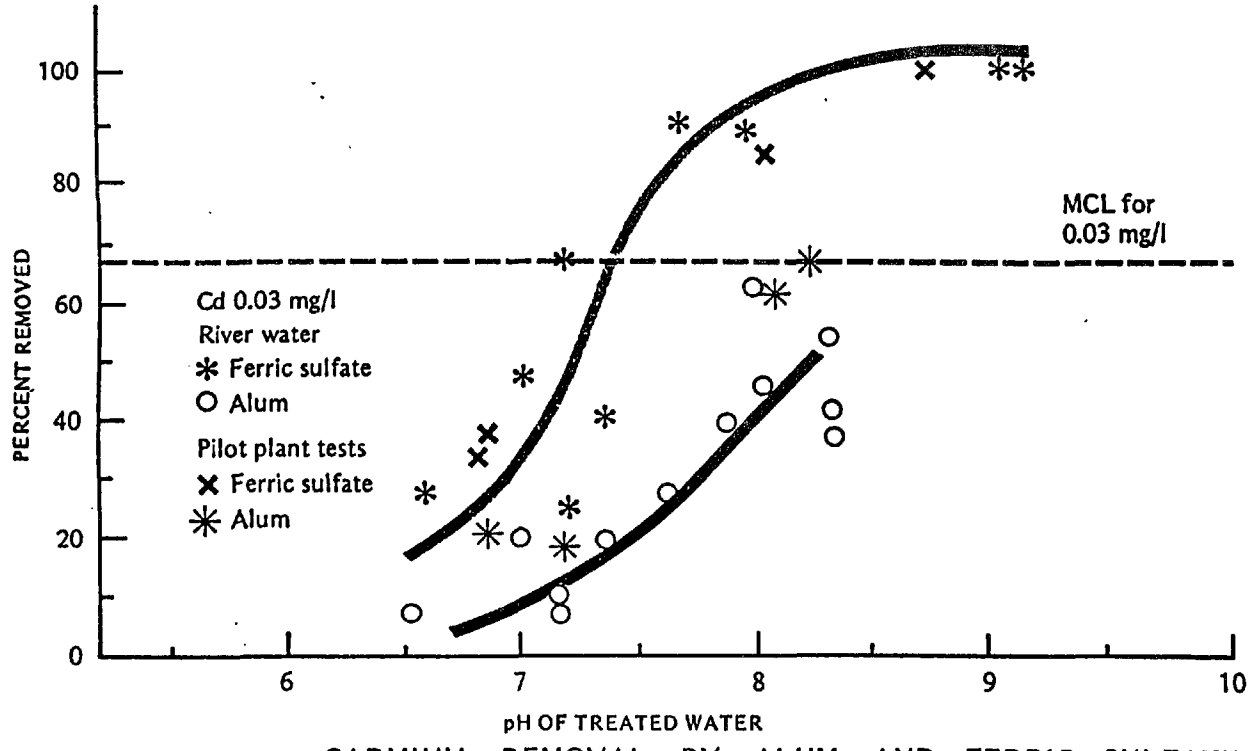
ARSENIC REMOVAL BY COAGULATION AND LIME SOFTENING



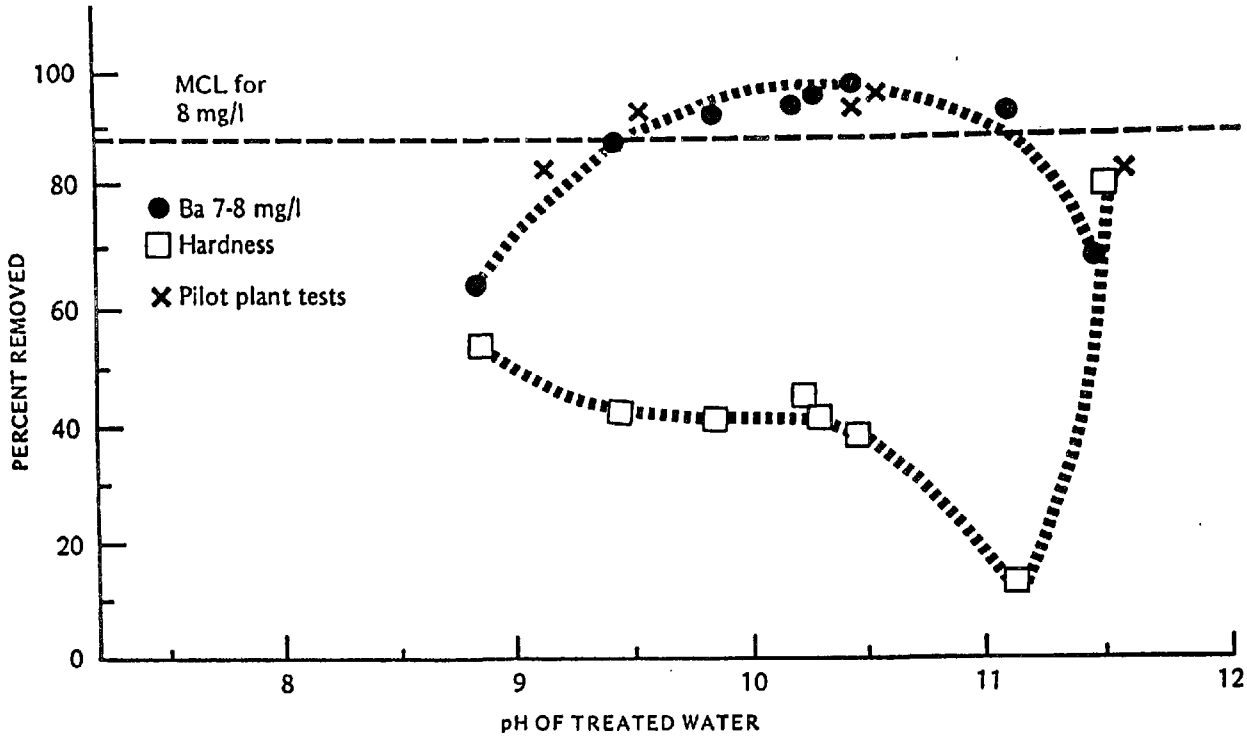
CADMIUM SOLUBILITY AS A FUNCTION OF pH.



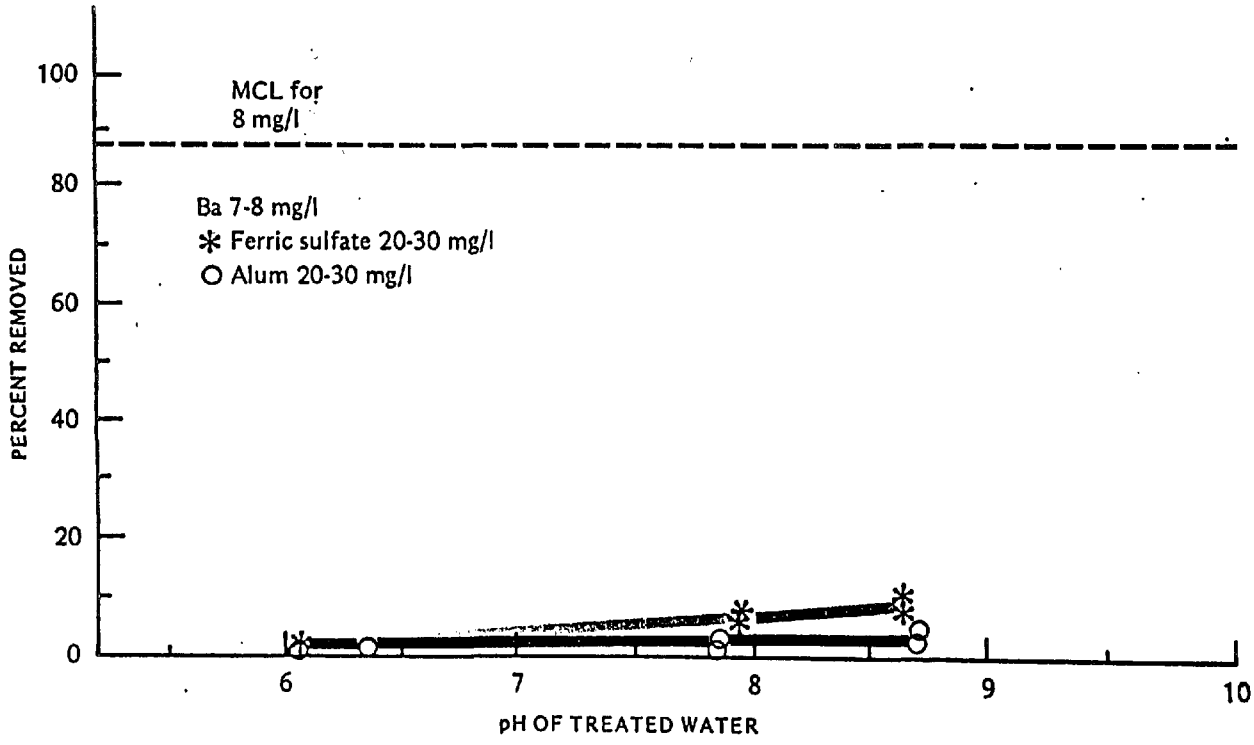
CADMIUM REMOVAL BY LIME SOFTENING



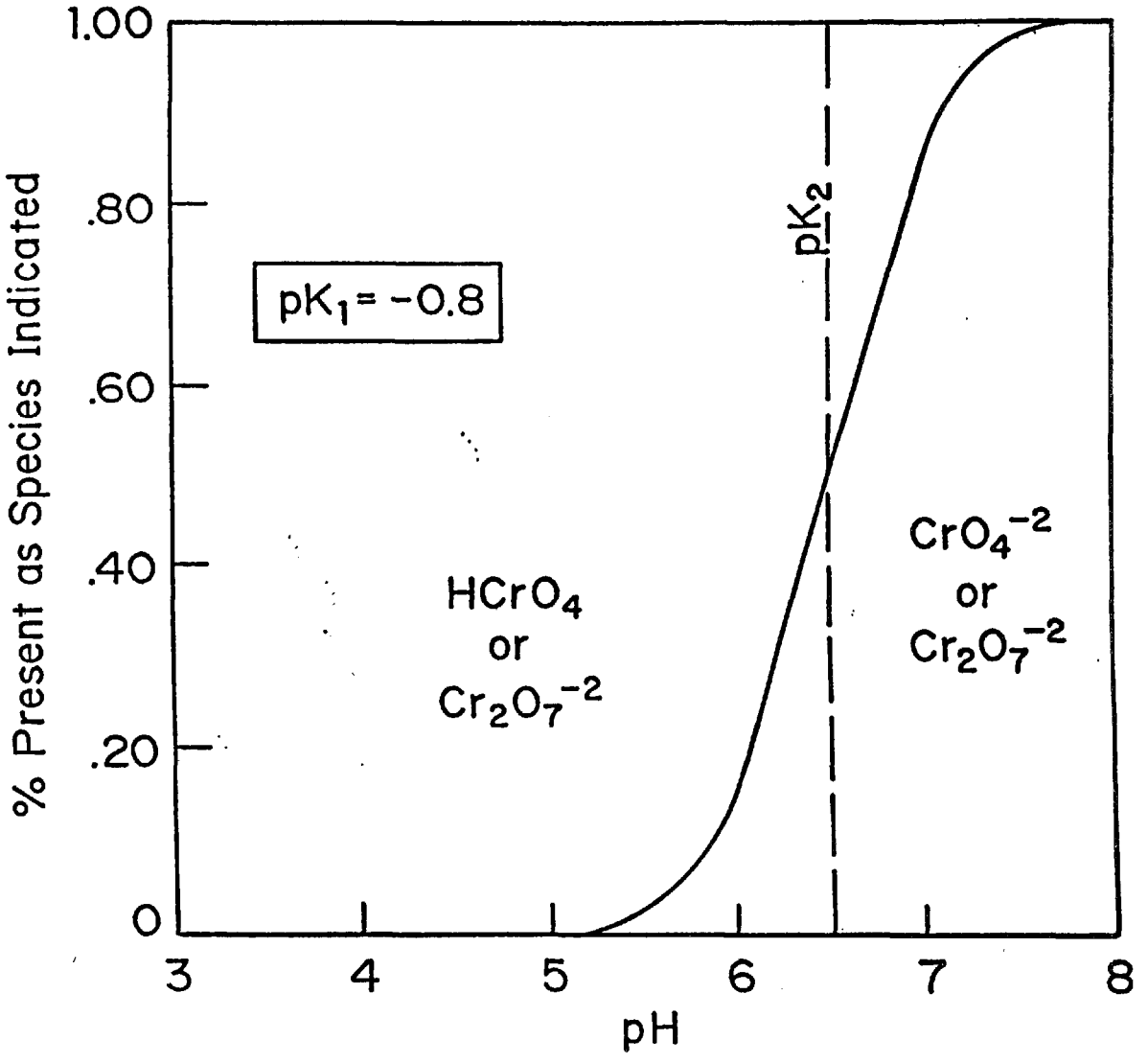
CADMIUM REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION



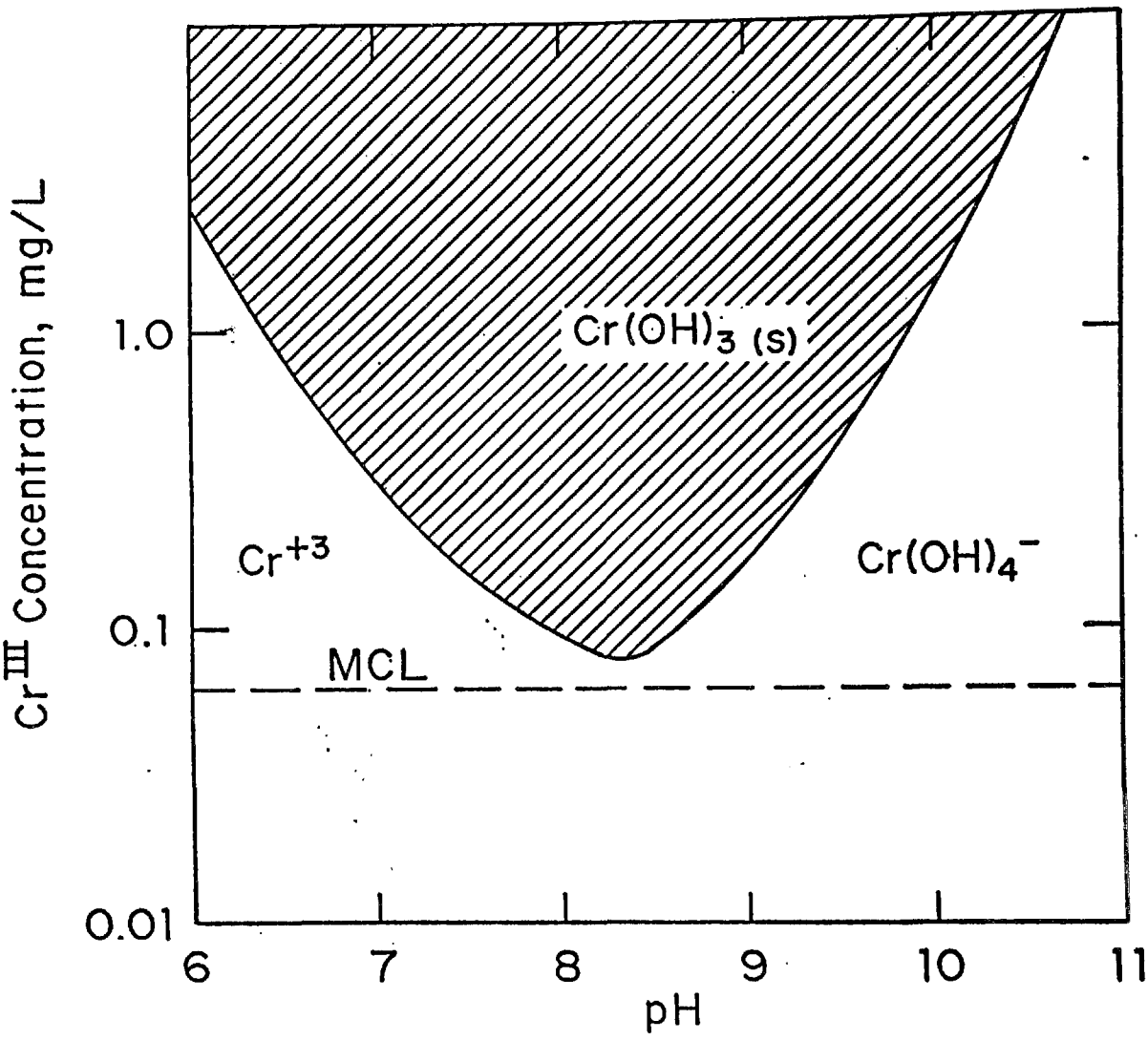
BARIUM REMOVAL BY LIME SOFTENING



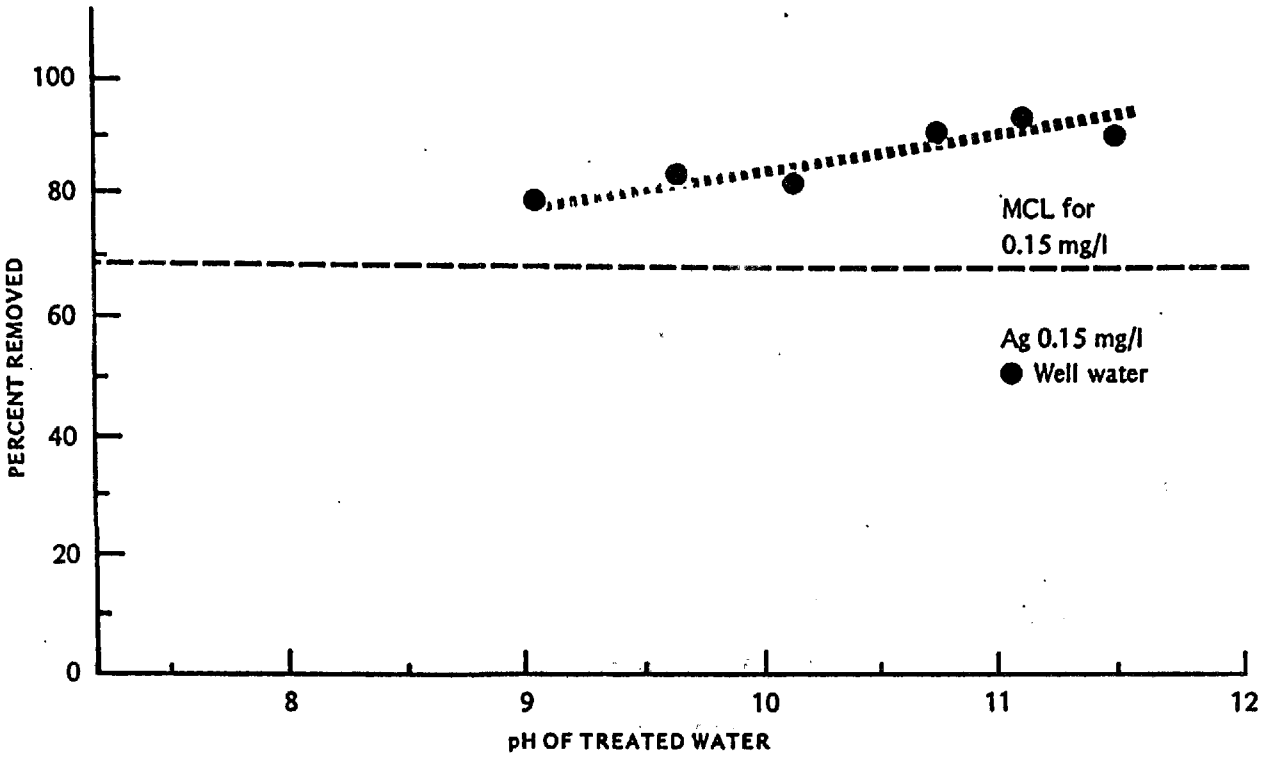
BARIUM REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION



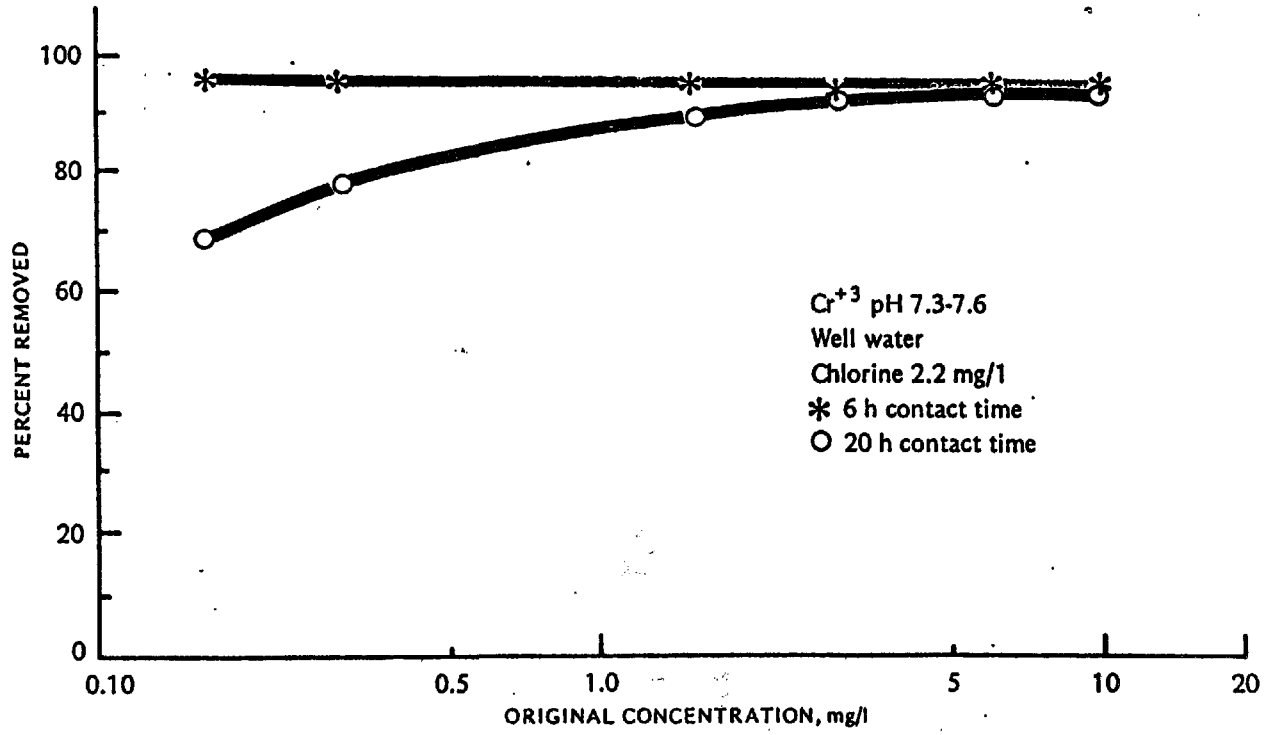
Effect of pH on Speciation of Chromium VI



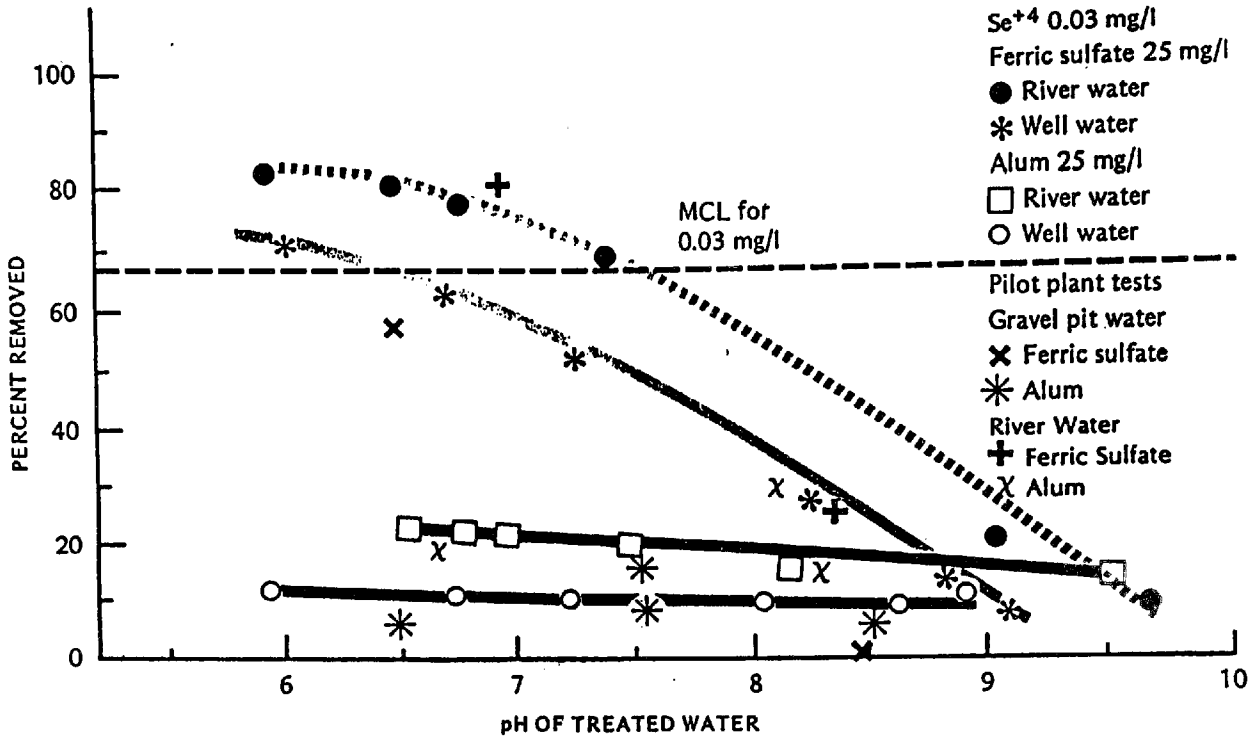
Solubility of Cr^{III} as a Function of pH



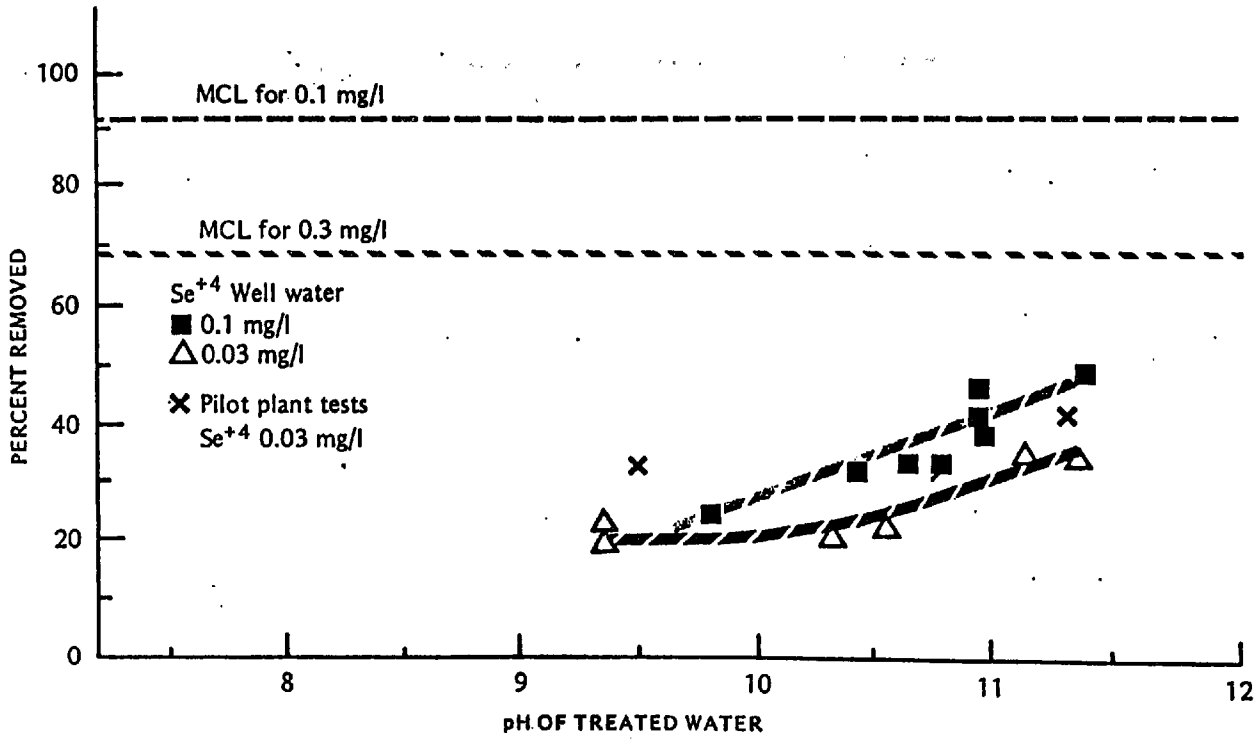
SILVER REMOVAL BY LIME SOFTENING



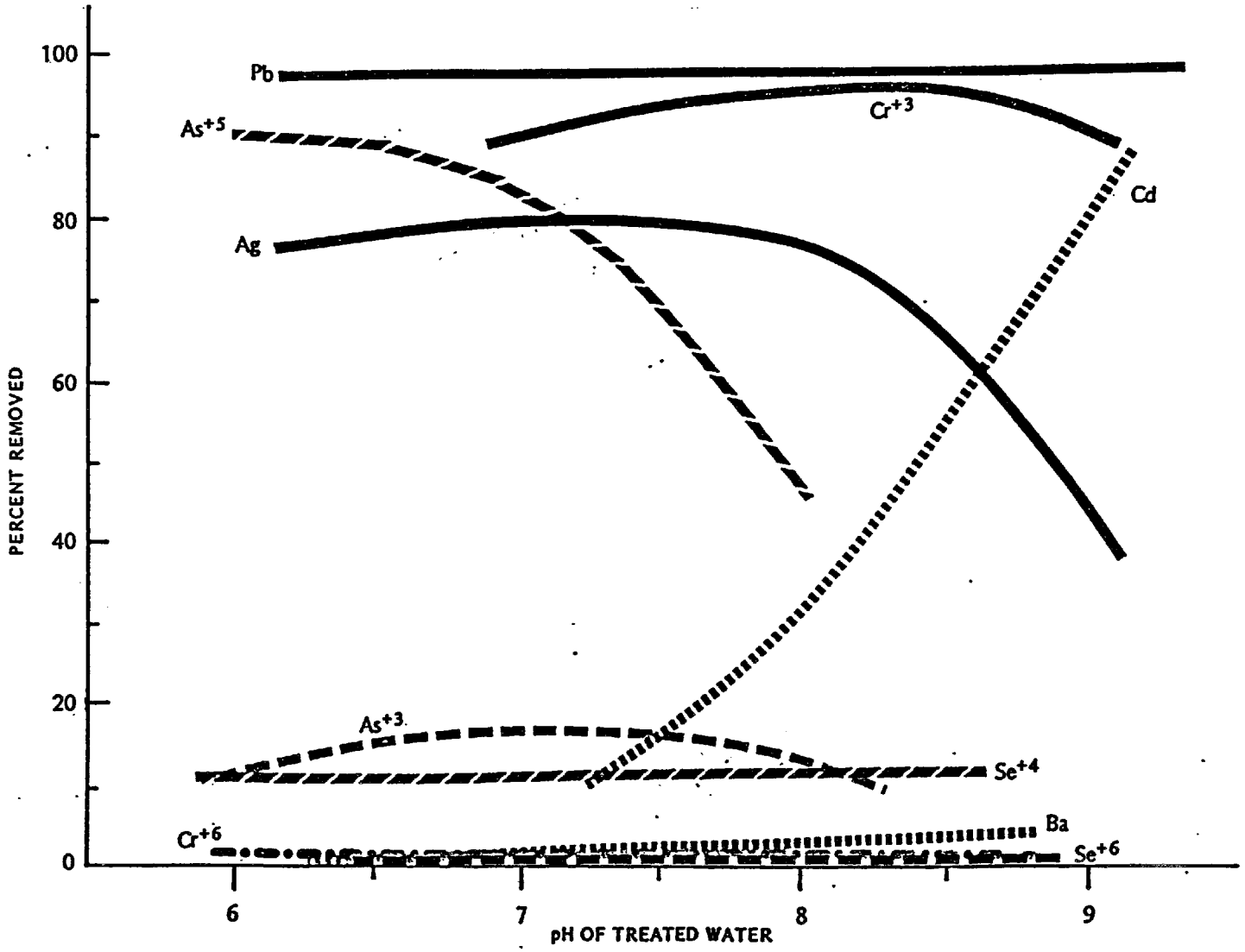
EFFECT OF PRECHLORINATION ON Cr^{+3} REMOVAL BY ALUM COAGULATION



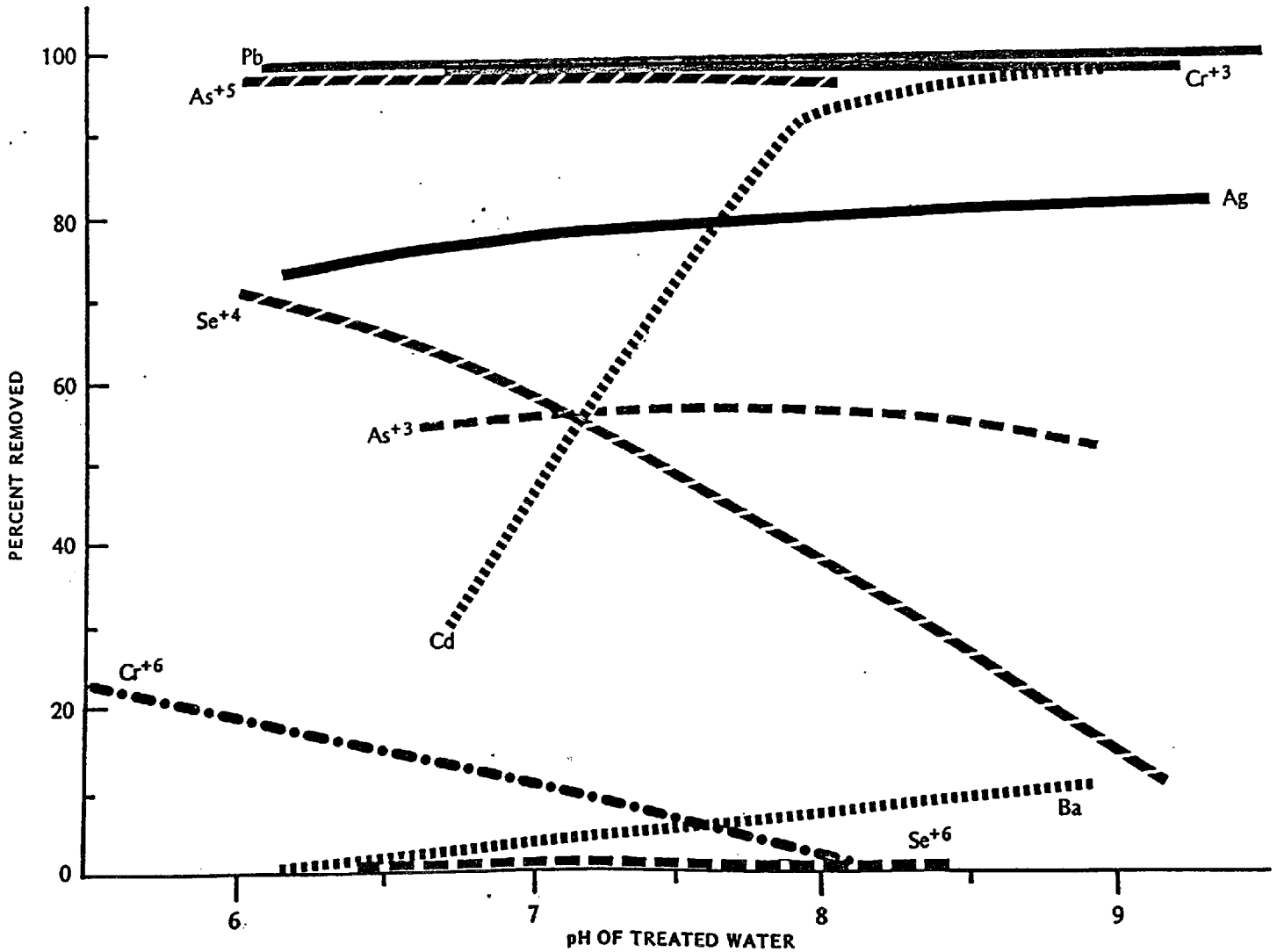
Se+4 REMOVAL BY ALUM AND IRON COAGULATION



Se+4 REMOVAL BY LIME SOFTENING



REMOVAL OF INORGANIC CONTAMINANTS BY ALUM COAGULATION



REMOVAL OF INORGANIC CONTAMINANTS BY IRON COAGULATION

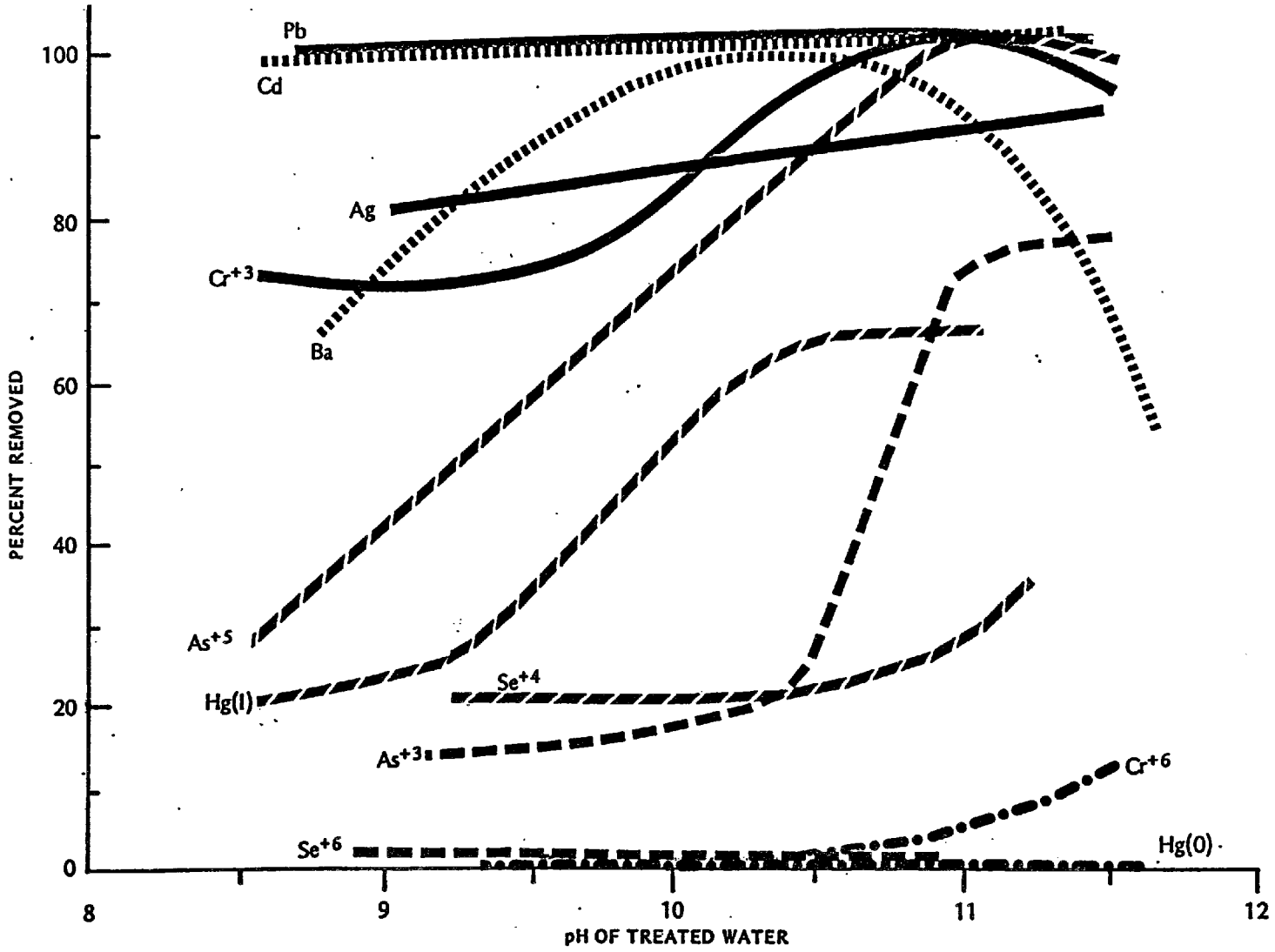


FIGURE 3 REMOVAL OF INORGANIC CONTAMINANTS BY LIME SOFTENING

TREATMENT PROCESS	CONVENTION COAGULATION	
PRINCIPAL APPLICATION FOR WATER TREATMENT	CLARIFICATION OF SURFACE WATERS	
INORGANIC CONTAMINANT TREATMENT CAPABILITY EFFECTIVENESS*	HIGH	Cd, Cr III, Cr VI, As V, Ag, Pb
	MODERATE	As III, Se IV, Hg(O), Hg(I)
	LOW	Ba, F, NO_3, Ra, Se VI
MOST PROBABLE APPLICATION FOR INORGANIC REMOVAL	REMOVAL OF Cd, Cr, As, Ag, OR Pb FROM SURFACE WATERS	

* HIGH - GREATER THAN 80 PERCENT MODERATE - 20 TO 80 PERCENT LOW - LESS THAN 20 PERCENT

TREATMENT PROCESS	LIME SOFTENING	
PRINCIPAL APPLICATION FOR WATER TREATMENT	REMOVAL OF HARDNESS FROM GROUND AND SURFACE WATER	
INORGANIC CONTAMINANT TREATMENT CAPABILITY EFFECTIVENESS*	HIGH	Ba, Ra, Cd, Cr III, As V, Pb
	MODERATE	Se IV, As III, Hg(I), F
	LOW	Cr VI, NO_3, Se VI, Hg(O)
MOST PROBABLE APPLICATION FOR INORGANIC REMOVAL	REMOVAL OF Ba OR Ra FROM GROUNDWATERS; REMOVAL OF Cd, Cr III, F, As V, OR Pb FROM HARD SURFACE WATERS REQUIRING SOFTENING	

* HIGH - GREATER THAN 80 PERCENT MODERATE - 20 TO 80 PERCENT LOW - LESS THAN 20 PERCENT

TREATMENT PROCESS	CATION EXCHANGE		ANION EXCHANGE
PRINCIPAL APPLICATION FOR WATER TREATMENT	REMOVAL OF HARDNESS FROM GROUNDWATERS		REMOVAL OF NITRATE FROM GROUNDWATERS
INORGANIC CONTAMINANT TREATMENT CAPABILITY EFFECTIVENESS*	HIGH	Ba, Ra, Cd, Pb, Cr III	NO_3, Cr VI, Se
	MODERATE		Ba, Ra, Cd, Pb, Cr III
	LOW	As, Se, NO_3, F, Cr VI	
MOST PROBABLE APPLICATION FOR INORGANIC REMOVAL	REMOVAL OF Ba OR Ra FROM GROUNDWATERS		REMOVAL OF NO_3 FROM GROUNDWATERS

* HIGH - GREATER THAN 80 PERCENT MODERATE - 20 TO 80 PERCENT LOW - LESS THAN 20 PERCENT

TREATMENT PROCESS	REVERSE OSMOSIS AND ELECTRODIALYSIS	
PRINCIPAL APPLICATION FOR WATER TREATMENT	DESALTING OF SEA WATER OR BRACKISH GROUNDWATER	
INORGANIC CONTAMINANT TREATMENT CAPABILITY EFFECTIVENESS*	HIGH	As V, Ba, Cr, Pb, Cd, Se, Ag, F, Ra, Hg
	MODERATE	NO_3, As III
	LOW	
MOST PROBABLE APPLICATION FOR INORGANIC REMOVAL	REMOVAL OF ALL INORGANICS FROM GROUNDWATERS	

* HIGH - GREATER THAN 80 PERCENT MODERATE - 20 TO 80 PERCENT LOW - LESS THAN 20 PERCENT

TREATMENT PROCESS	POWDERED ACTIVATED CARBON		GRANULAR ACTIVATED CARBON
PRINCIPAL APPLICATION FOR WATER TREATMENT	REMOVAL OF TASTE AND ODORS FROM SURFACE WATERS		REMOVAL OF TASTE, ODORS, AND ORGANICS
INORGANIC CONTAMINANT TREATMENT CAPABILITY EFFECTIVENESS*	HIGH		Hg(I), Hg(O),
	MODERATE	Hg(I), Hg(O), Cd	Cd
	LOW	Ba, Ra, Cr III, F, NO_3, Ag	Ba, Ra, Cr III, F, NO_3
MOST PROBABLE APPLICATION FOR INORGANIC REMOVAL	REMOVAL OF Hg FROM SURFACE WATERS DURING EMERGENCY SPILLS		REMOVAL OF Hg FROM SURFACE OR GROUND-WATERS

* HIGH - GREATER THAN 80 PERCENT MODERATE - 20 TO 80 PERCENT LOW - LESS THAN 20 PERCENT

TREATMENT PROCESS	ACTIVATED ALUMINA	
PRINCIPAL APPLICATION FOR WATER TREATMENT	REMOVAL OF FLOURIDE FROM GROUNDWATERS	
INORGANIC CONTAMINANT TREATMENT CAPABILITY EFFECTIVENESS*	HIGH	F, As, Se
	MODERATE	
	LOW	Ba, Ra, Cd
MOST PROBABLE APPLICATION FOR INORGANIC REMOVAL	REMOVAL OF F, As, OR Se FROM GROUNDWATERS	

* HIGH - GREATER THAN 80 PERCENT MODERATE - 20 TO 80 PERCENT LOW - LESS THAN 20 PERCENT

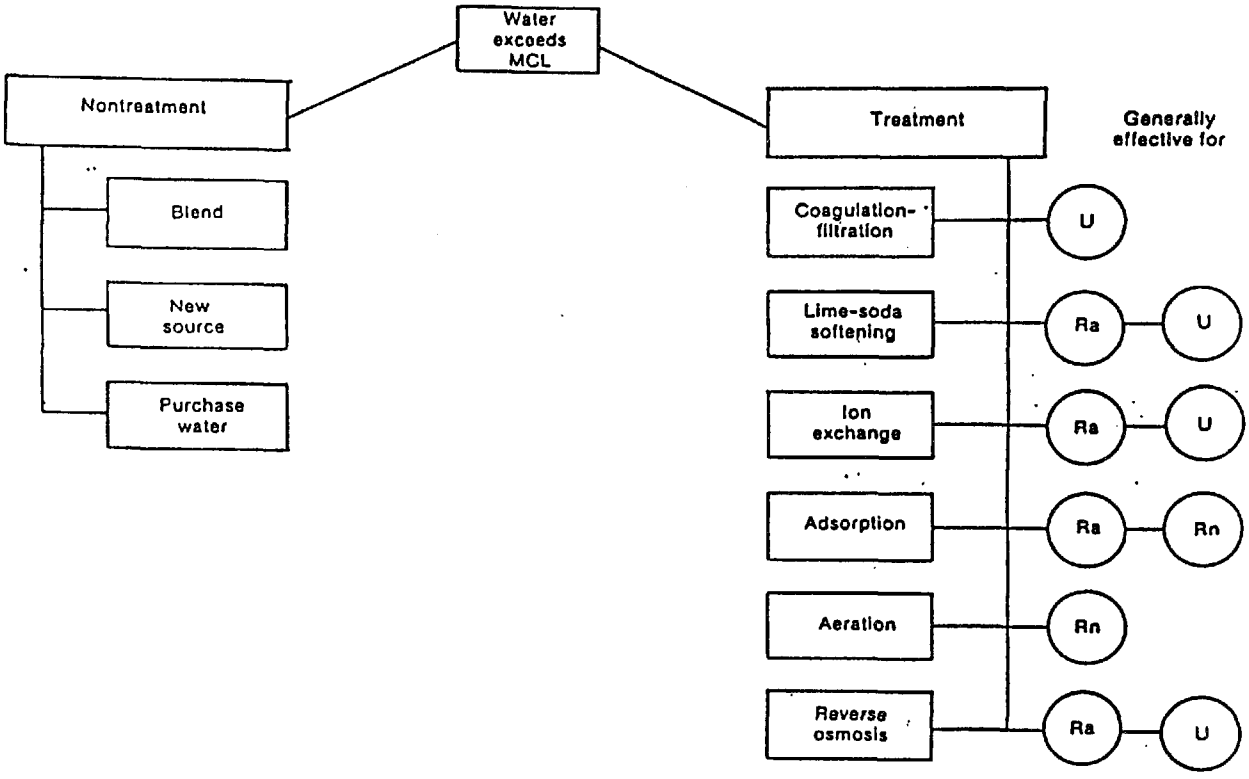
PERFORMANCE SUMMARY FOR INORGANIC TECHNOLOGIES EXAMINED

Inorganic Compound	Reverse Osmosis	Removal Efficiency		
		Ion Exchange	Aeration	Carbon Adsorption
Nitrate	++	++		
Radium	++	++		
Uranium	++	++		
Radon			*	*

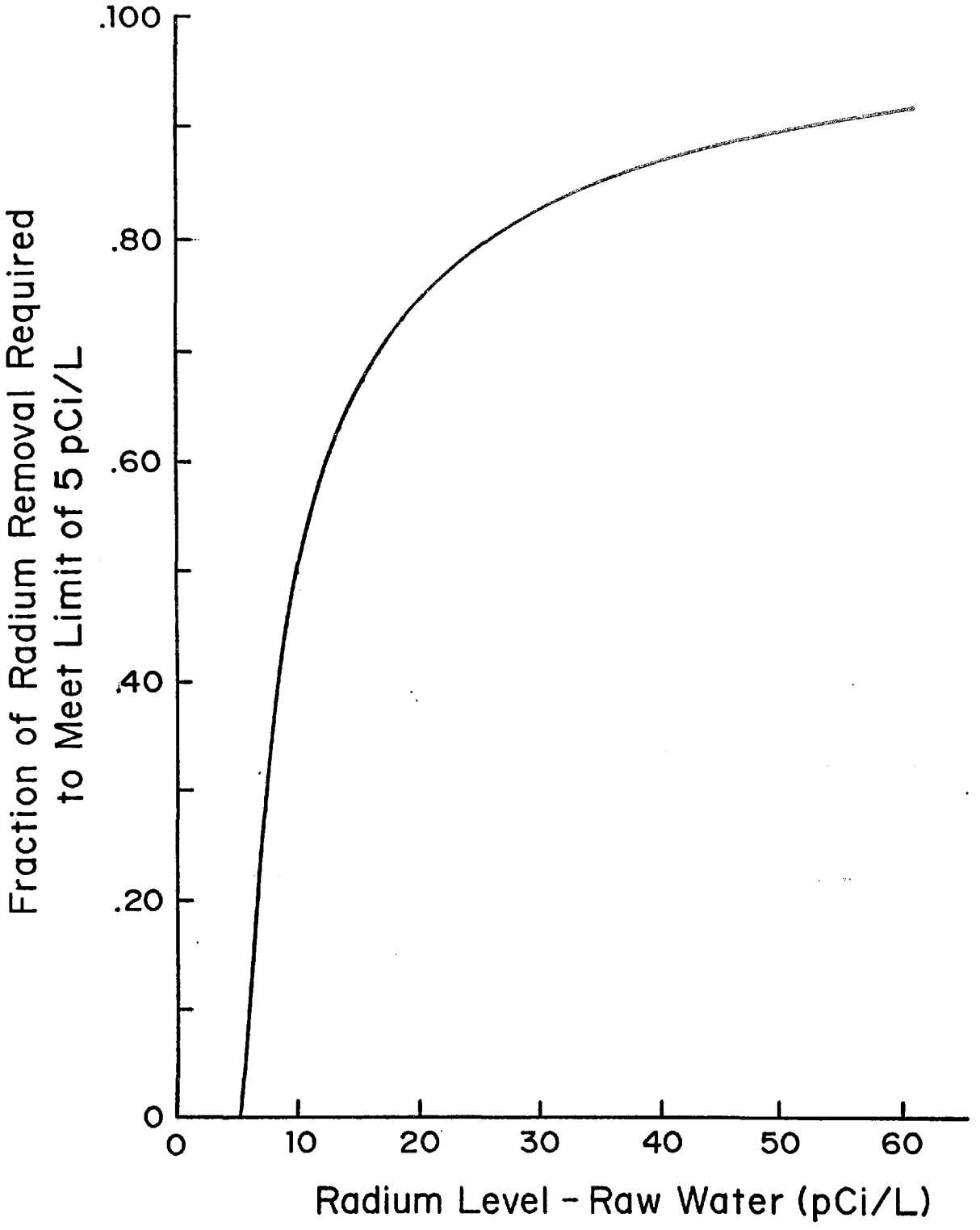
++ = Excellent 70%-100%

* = Research Being Conducted By DWRD

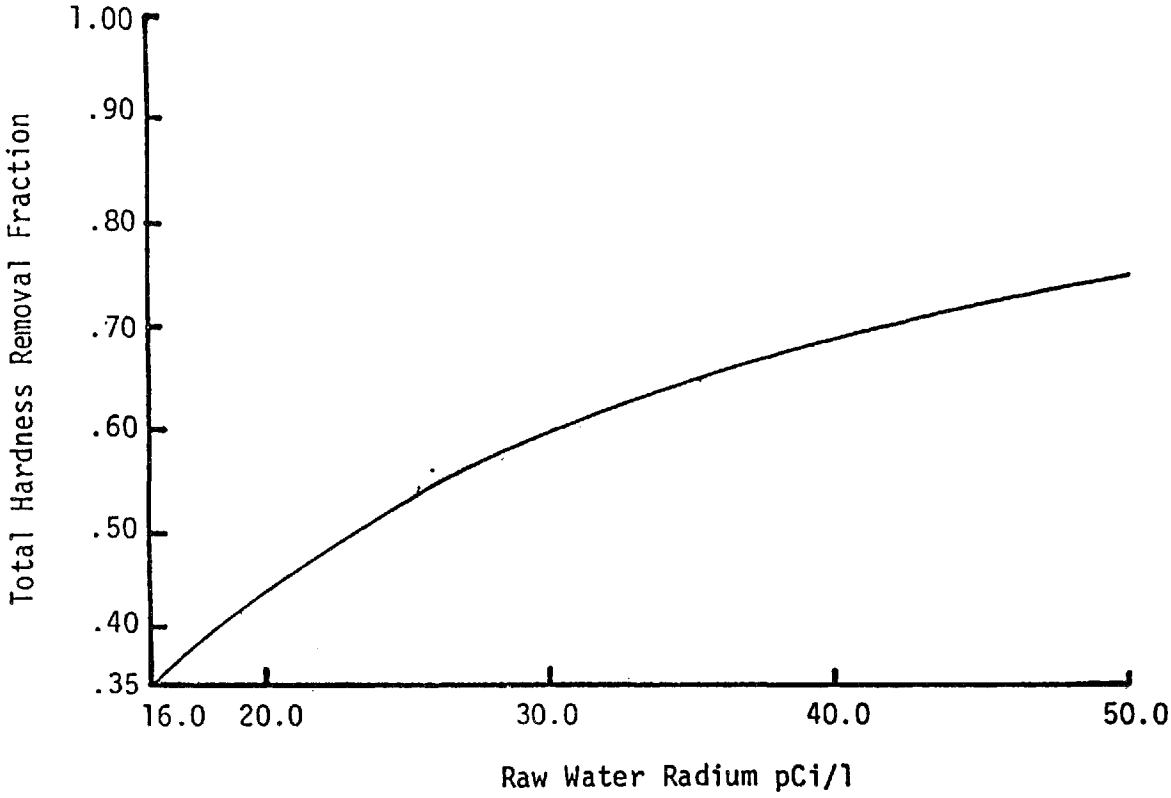
MOST PROBABLE APPLICATIONS OF WATER TREATMENT PROCESSES FOR INORGANIC CONTAMINANT REMOVAL



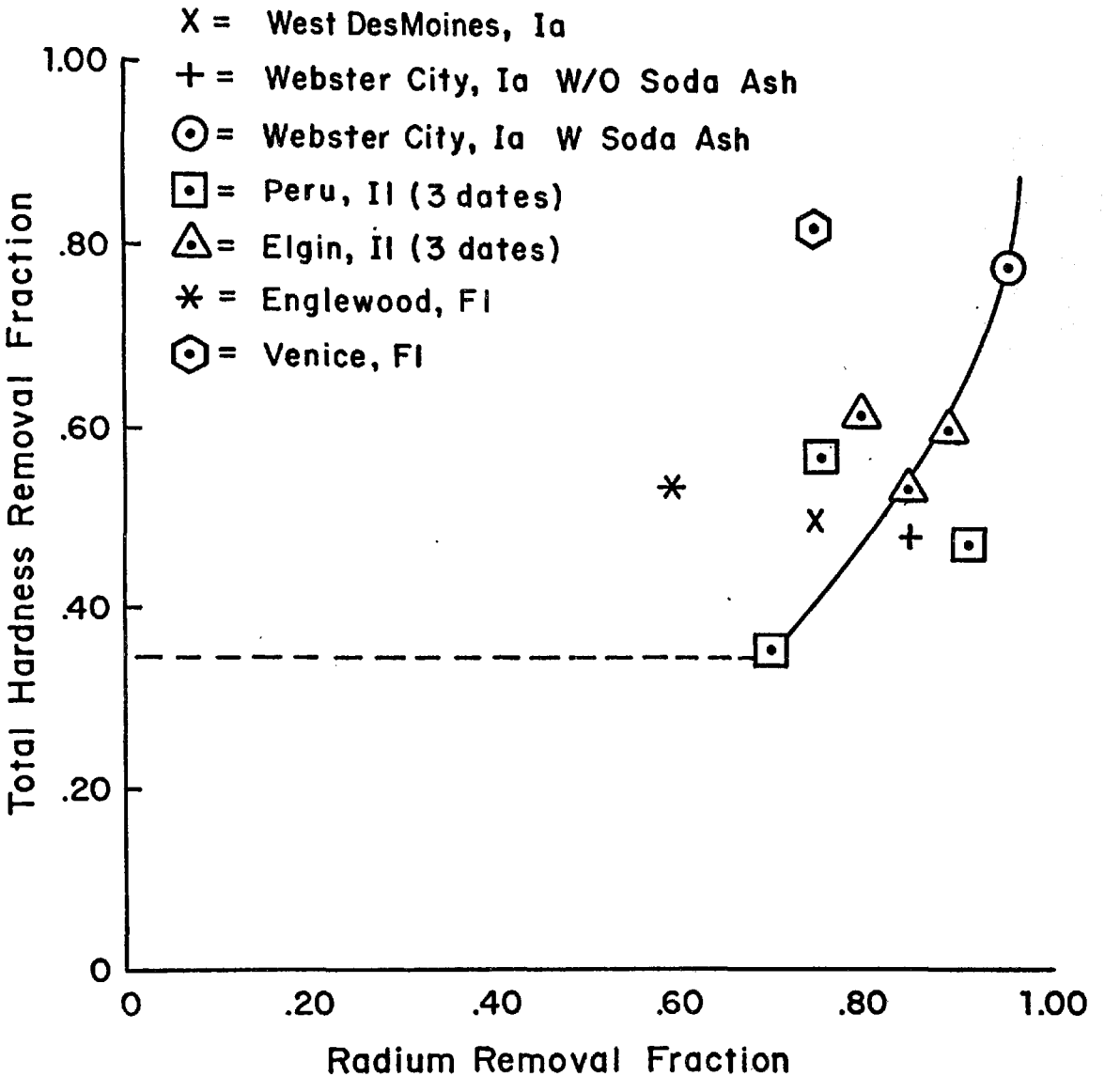
Alternatives for reducing radionuclide concentrations in drinking water (all alternatives can include blending) (Aieta, et al. 1987)



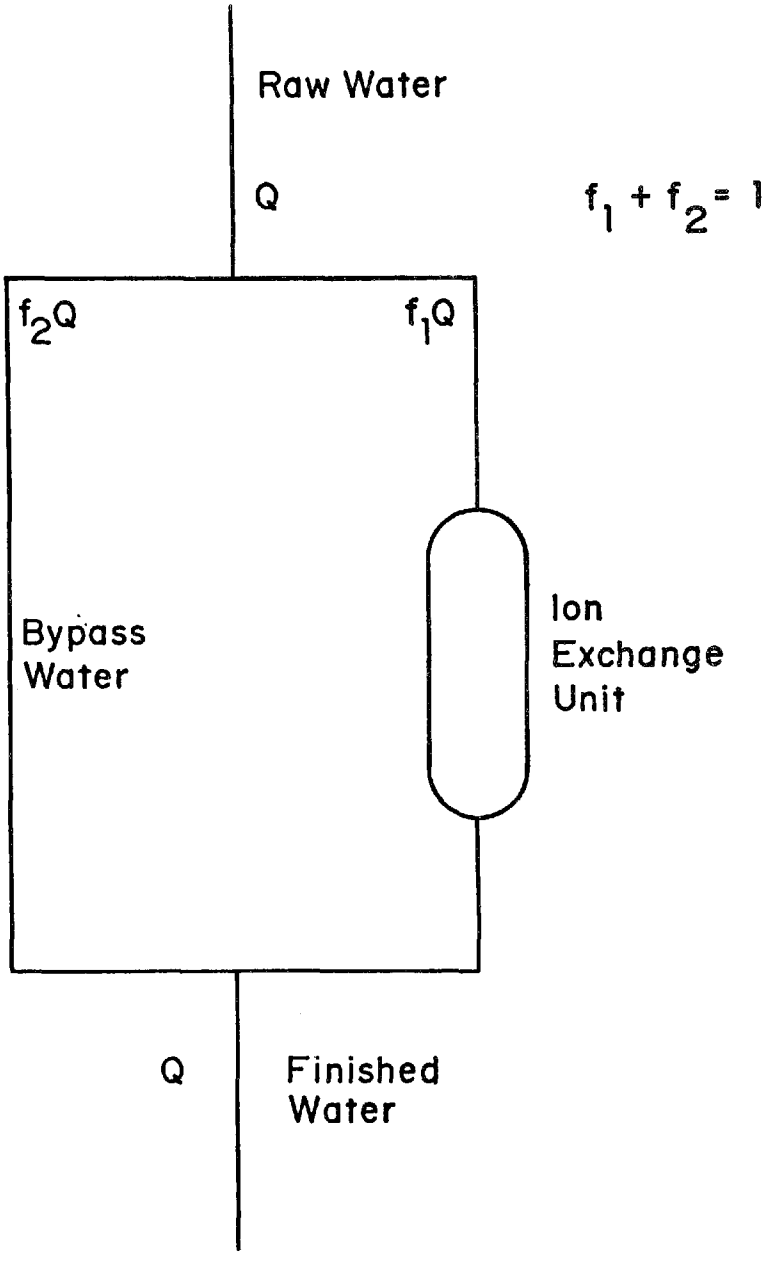
REQUIRED REMOVAL FRACTION FOR RADIUM



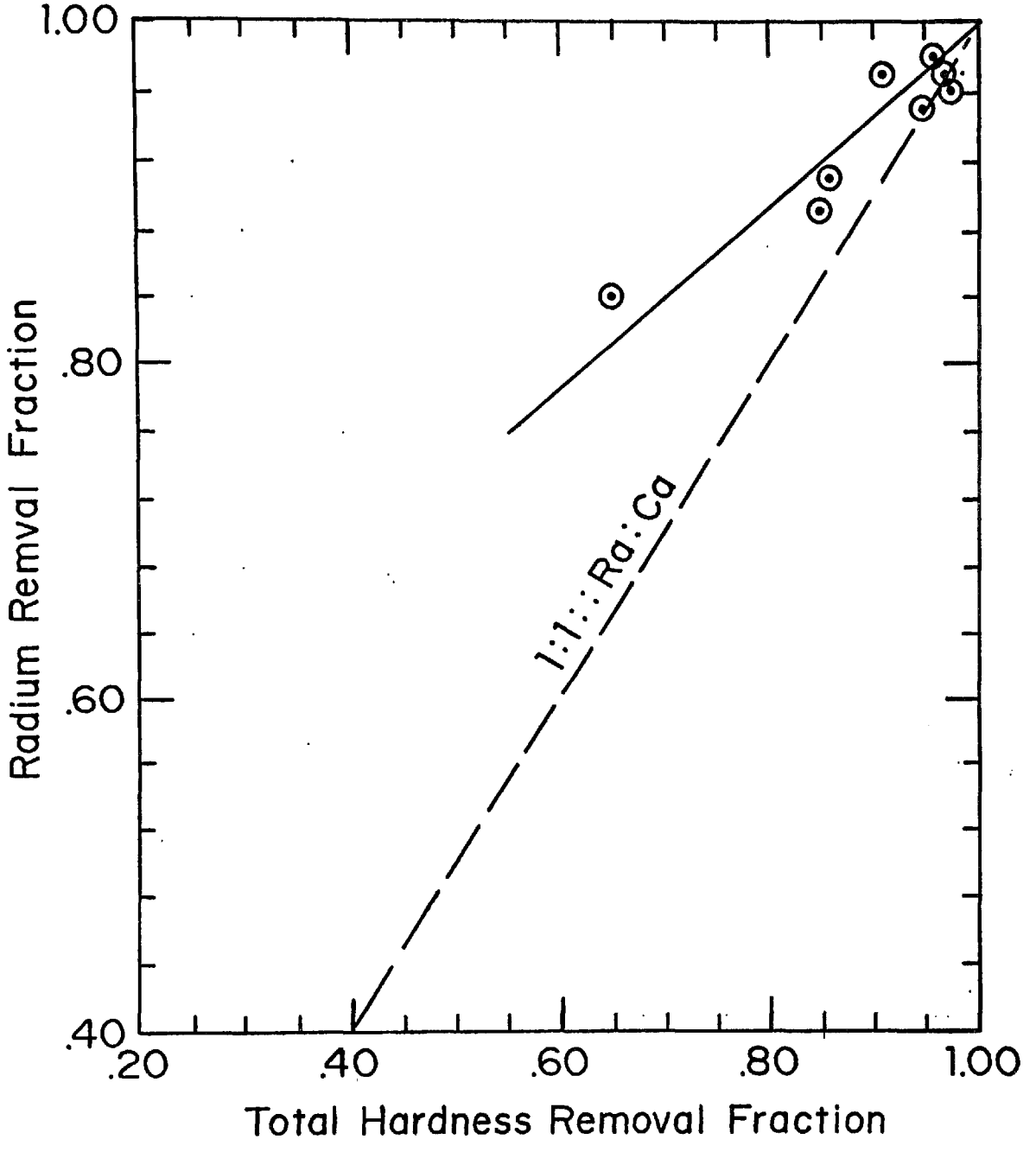
Total hardness removal fraction as a function of raw water radium content required to meet limit of 5.0 pCi/L finished water. (Singley, et al. 1977)



LIME SODA PROCESS, TOTAL HARDNESS REMOVAL FRACTION VS RADIUM REMOVAL FRACTION.



MASS BALANCE FOR DETERMINING FRACTION OF RAW WATER TO BE TREATED



RADIUM REMOVAL FRACTION VS. TOTAL HARDNESS REMOVAL FRACTION IN ION EXCHANGE PLANTS (BEFORE BLENDING)

(Adapted from Singley, et al, 1977)

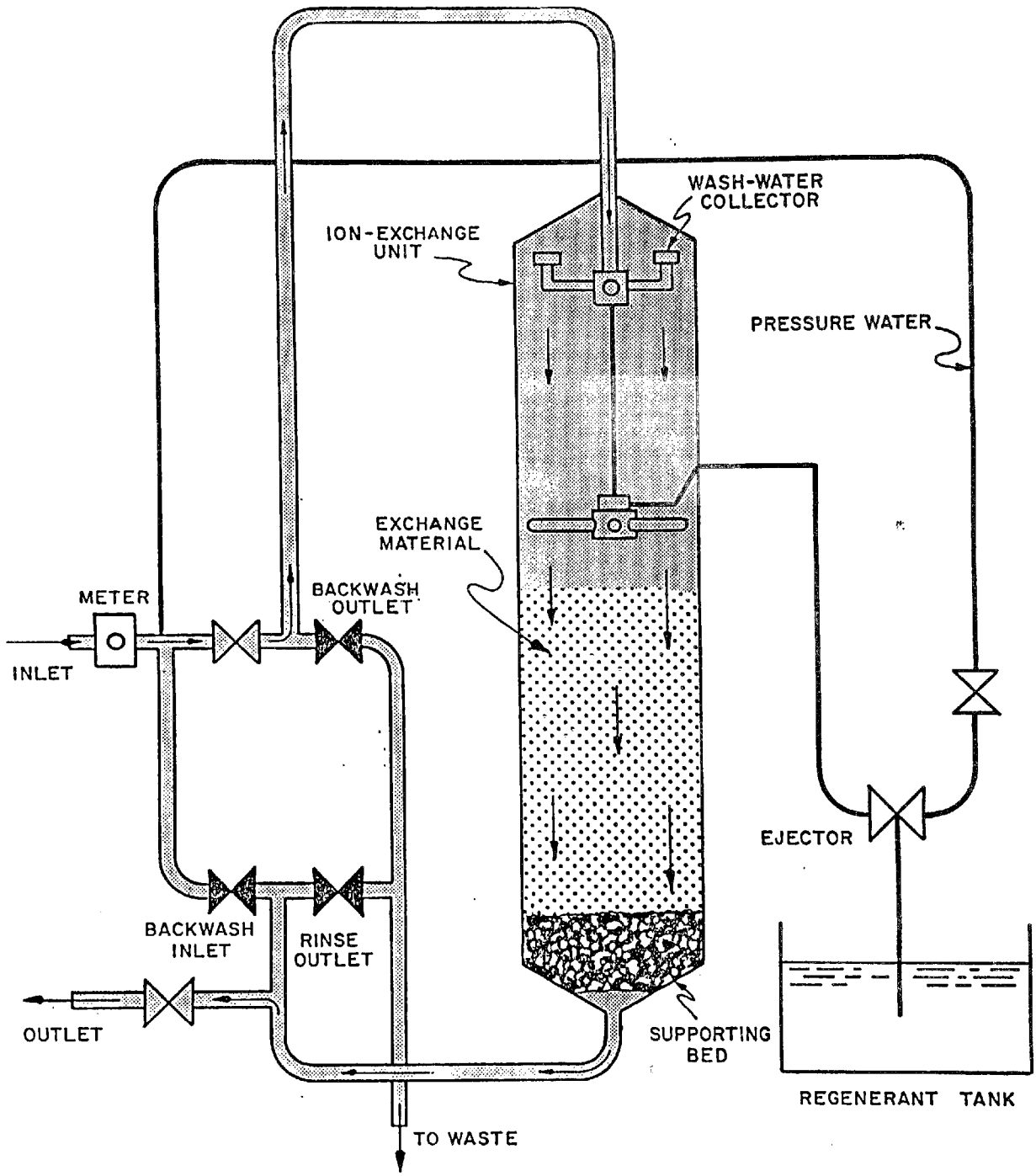
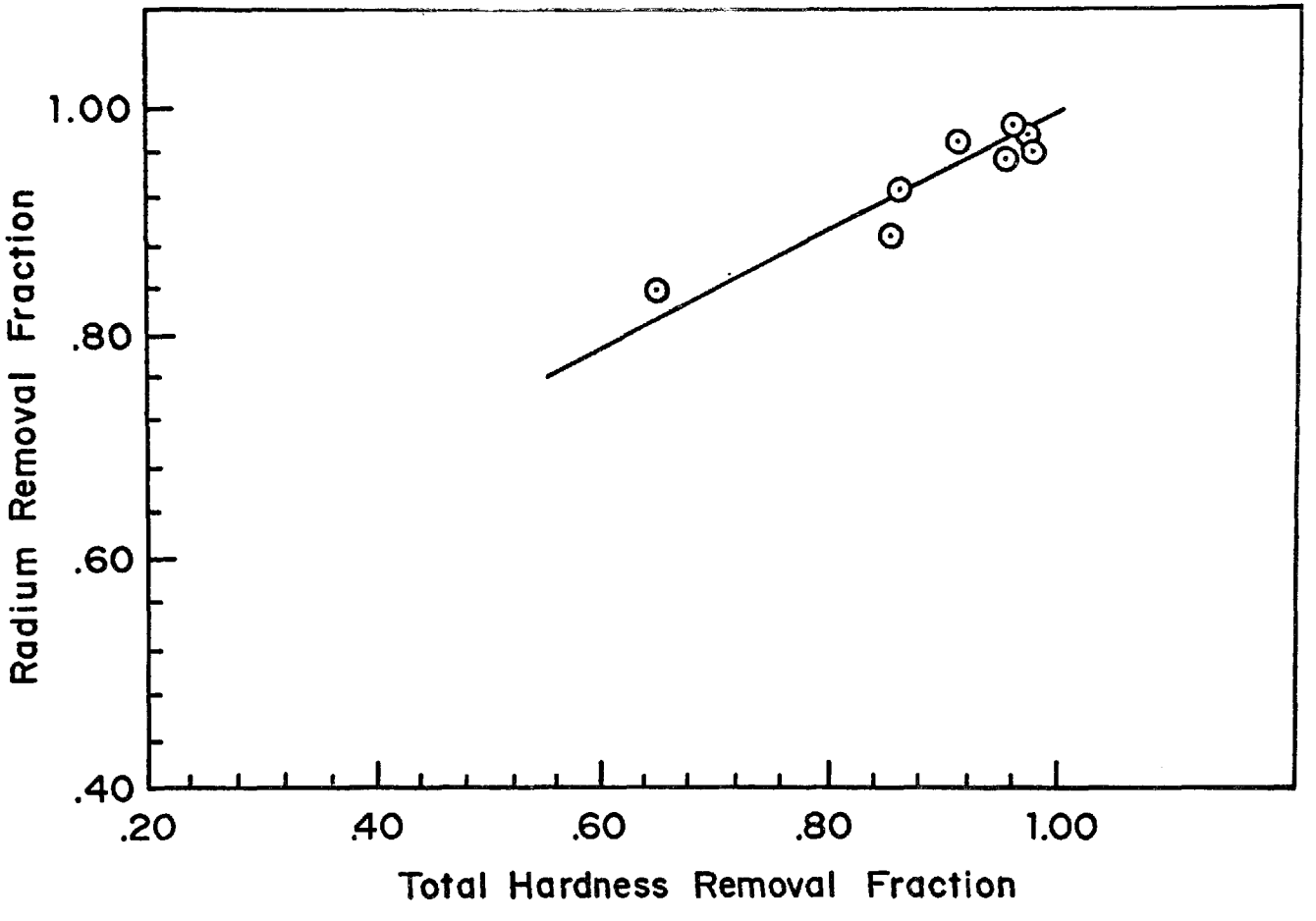


DIAGRAM OF TYPICAL ION EXCHANGE UNIT



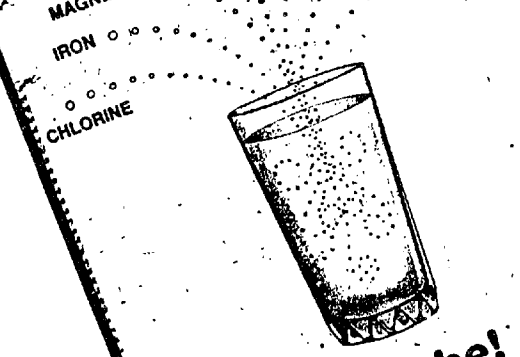
RADIUM REMOVAL FRACTION VS. TOTAL HARDNESS REMOVAL FRACTION IN ION EXCHANGE PLANTS (BEFORE BLENDING)

you can't
SEE THEM
SMELL THEM
or
TASTE THEM
and they can
KILL YOU!

THMs

THE DEADLY THMs in your DRINKING WATER!

Would You drink this?



But You may be!

It seems unbelievable, but it's true! E.P.A. and G.A.O. Federal studies have shown that most city water treatment plants do not effectively remove chemical and mineral contaminates from your water ... the water you drink ... cook with ... bathe with ... launder with. The RainSoft Classic Apollo Phase Four Water Treatment System softens, filters, decontaminates, and treats every drop of water in your home. Call today for a free in-home water analysis. We want you to drink only clean, sparkling, healthy, money saving water.

684-9411
PALM BEACH COUNTY
RainSoft Water Services, Inc.

RainSoft. What water was meant to be.

Guess Who Has Started Worrying About Quality of California Water

By Scot J. Paltrow
Staff Reporter of The Wall Street Journal

BEVERLY HILLS, Calif.—This wealthy city has long prided itself on having a high level of practically everything. And now it's about to be told that it may also have a high level of carcinogens in its water.

A campaign is underway to convince residents that their water contains a suspected carcinogen. But the campaign's booster isn't a group of environmentalists or concerned citizens. It is Evian Waters of France Inc.—which is about to introduce its bottled Swiss Alps spring water to Southern California.

Evian says it will hold a news conference disclosing that "an independent lab has found in Beverly Hills water amounts of trihalomethanes, which are "suspected carcinogens." Dr. Samuel A. Kunin, a Los Angeles biologist and surgeon, will present the laboratory results.

Unknown

Evian's conference invitation doesn't say Evian itself commissioned the analysis, conducted by laboratories of Pasadena.

Evian's medical spokesperson" for Evian, concedes in a telephone interview that Beverly Hills water contains fewer than 100 parts per million of trihalomethanes, the level the Environmental Protection Agency has established as safe.

Dr. Kunin also concedes there hasn't been any totally conclusive proof of a link between the chemical and cancer. But he says residents of one southern town, whose water had levels of the chemical significantly higher than 100 parts per million experienced exceptionally high levels of bladder and intestinal tract cancer. "Too little is known, really," he adds.

City's Advice

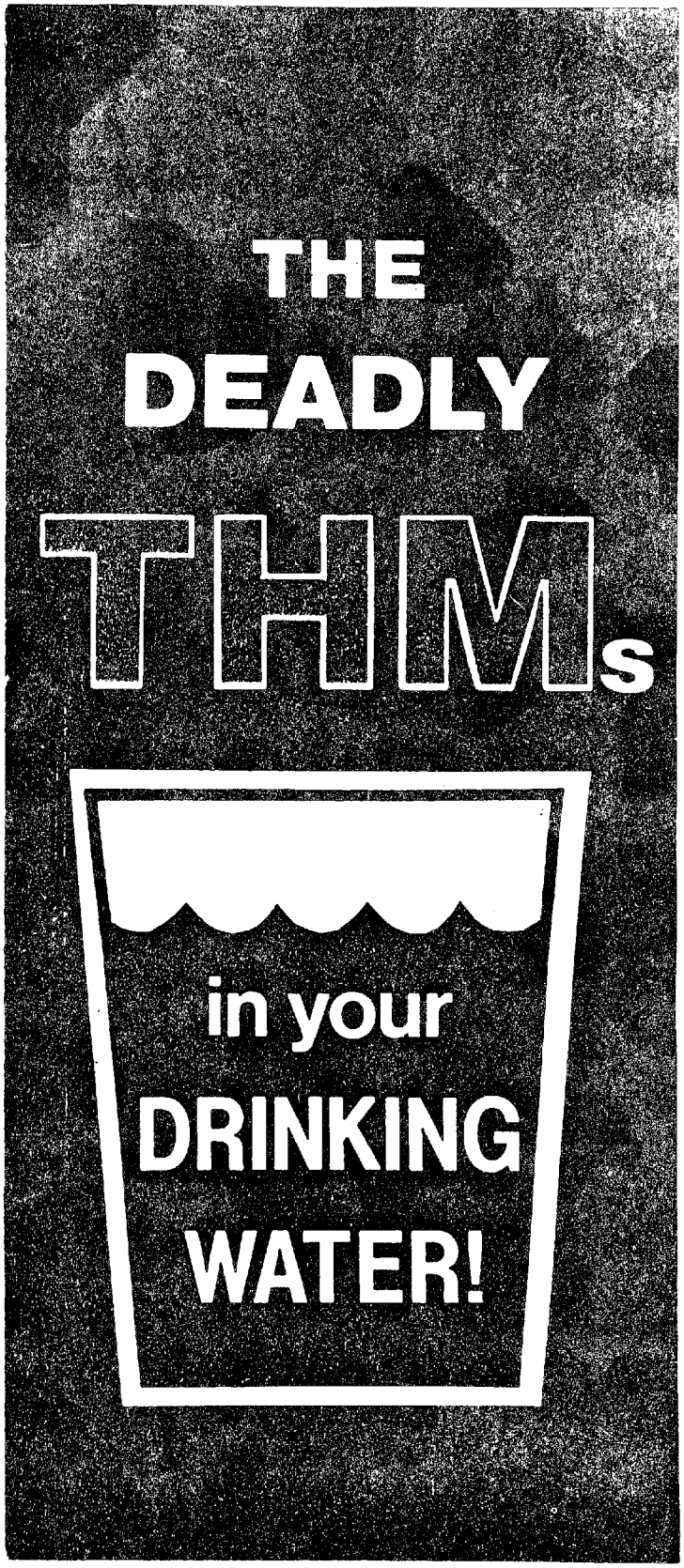
The Evian test purportedly shows that Beverly Hills has a higher level of the chemical than other communities in the area. But Mel Odom, Beverly Hills director of public service, says the city and most communities in the region get their water from the same source, and its chemical content should be uniform. He says the water meets all testing requirements, and he wouldn't advise residents "to stop drinking it with their Scotch."

But Dr. Kunin says levels of the trihalomethanes can vary—and that Evian's water contains lower levels of the chemical than several competing bottled waters.

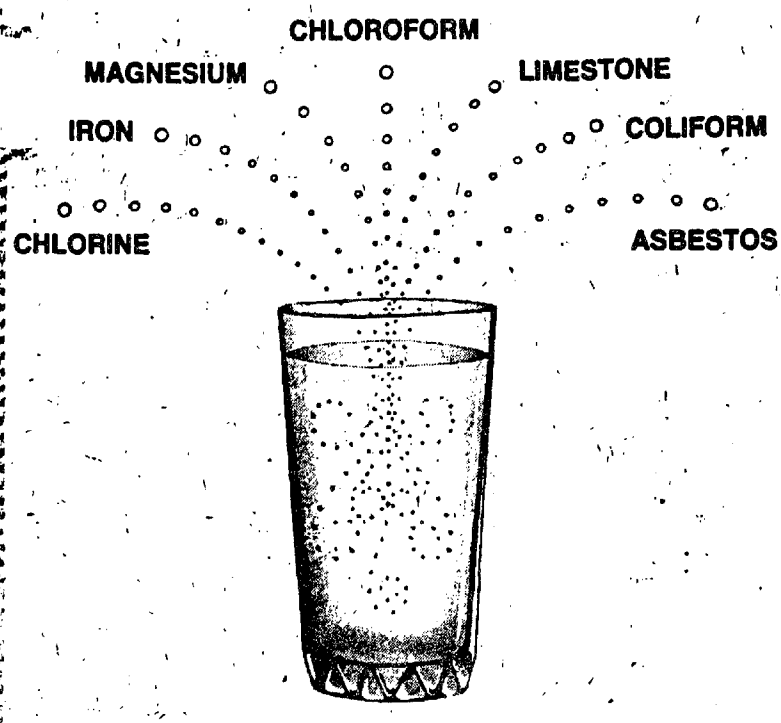
you can't
SEE THEM
SMELL THEM
or
TASTE THEM
and they can
KILL YOU!

THMs

The TRIHALOMETHANES (THM's) found in drinking water are organohalogen compounds that are named derivatives of methane, formed when three of the four hydrogen atoms have been replaced by three atoms of chlorine, bromine or iodine. Ten distinct compounds can be formed from the possible combinations of three hydrogenated atoms, one hydrogen atom, and one carbon atom. Current analytical methodology applied to drinking water has thus far led to the detection of chloroform (trichloromethane), bromodichloromethane, dibromochloromethane, bromoform (tribromomethane), and dichloroiodiomethane. Monitoring methods are currently available for the brominated and chlorinated THM's, but not for the iodinated types because of their chemical instability. EPA has promulgated an interim standard of 0.1 mg/l (100 ppb) for THM's.



Would You drink this?



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'Too Little Is Known'

But Evian's press conference invitation doesn't say that Evian itself commissioned and paid for the analysis, conducted by Montgomery Laboratories of Pasadena.

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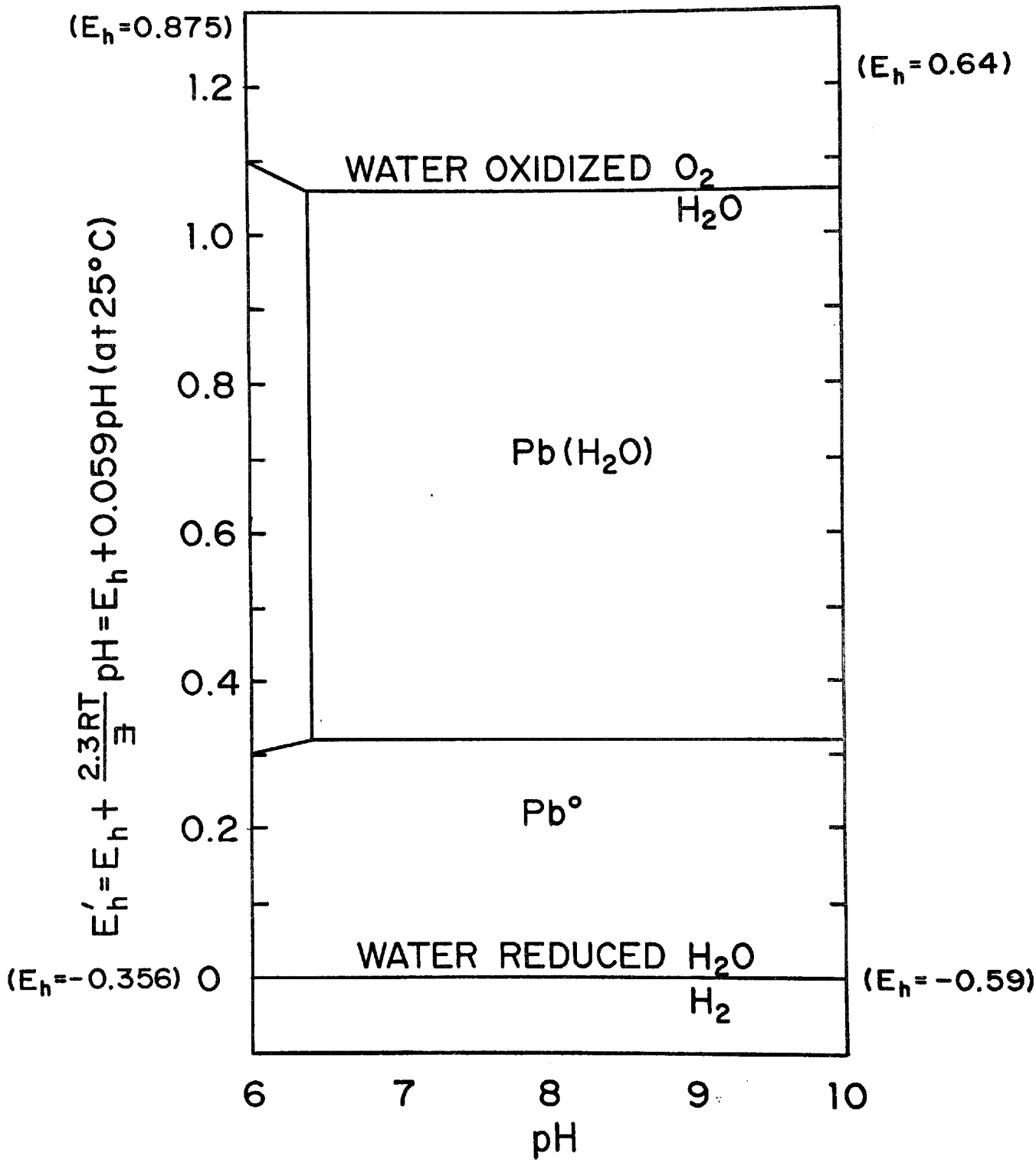
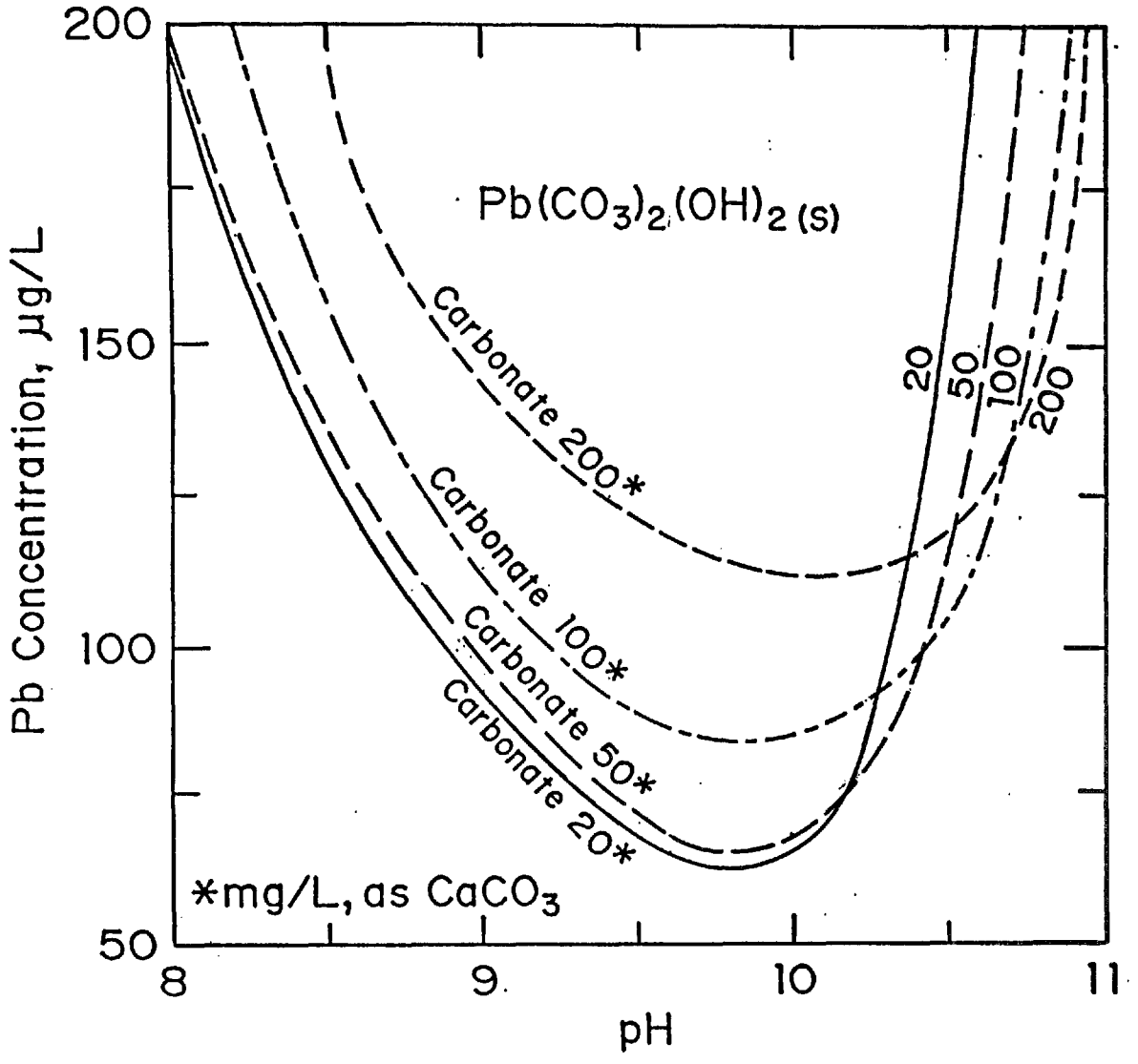
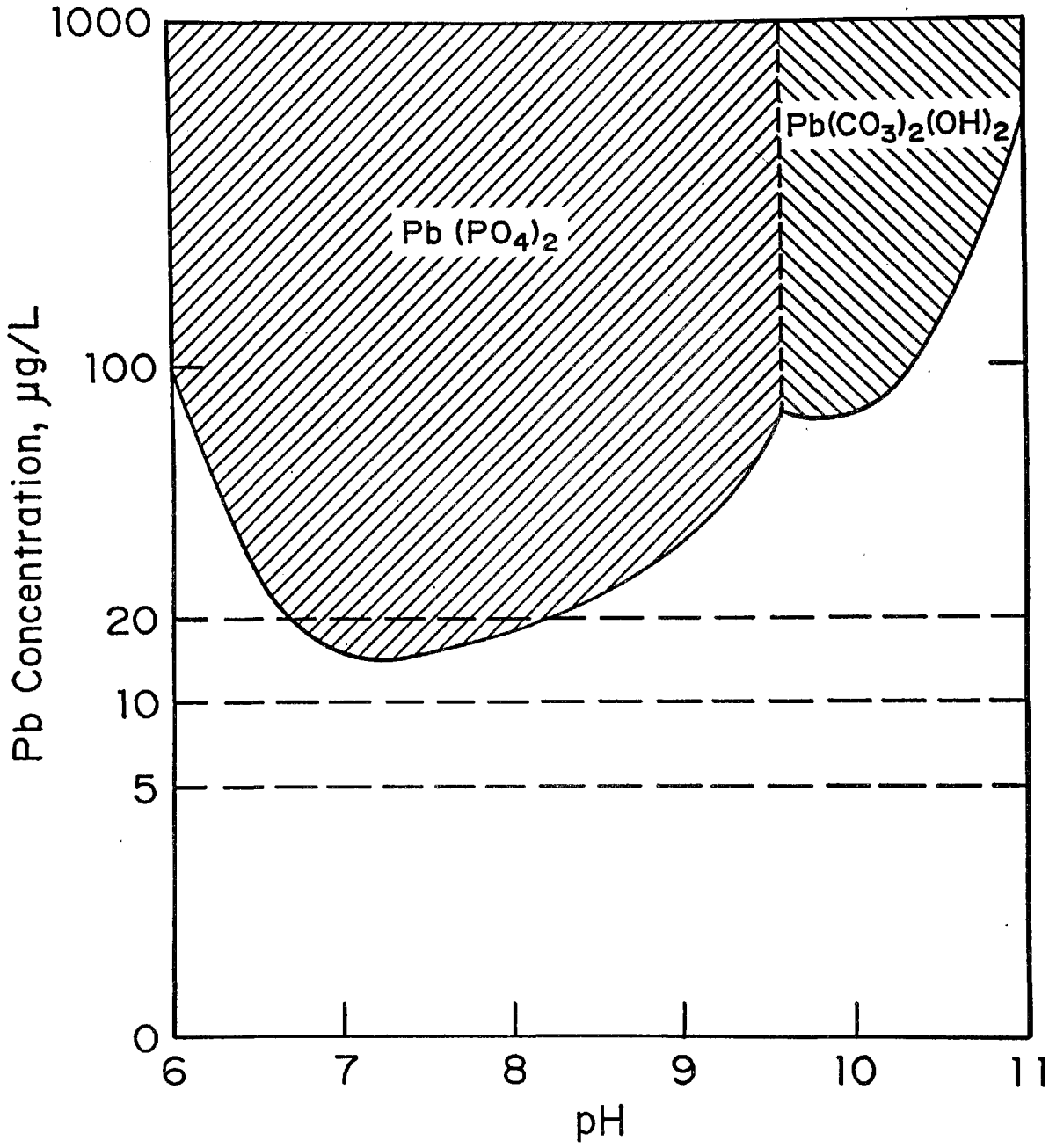


MODIFIED POURBAIX DIAGRAM FOR LEAD IN WATER



Solubility of Lead as a Function of pH and Carbonate. (Adapted from AWWARF/EBI, 1985)



Solubility of Lead in the Presence of 50mg/L (as $CaCO_3$) DIC. (Adapted from Schock (AWWARF/EBI, 1985).

ORDER OF ACTIVITY OF COMMON METALS

MAGNESIUM

ZINC

ALUMINUM

MILD STEEL

WROUGHT IRON

CAST IRON

LEAD

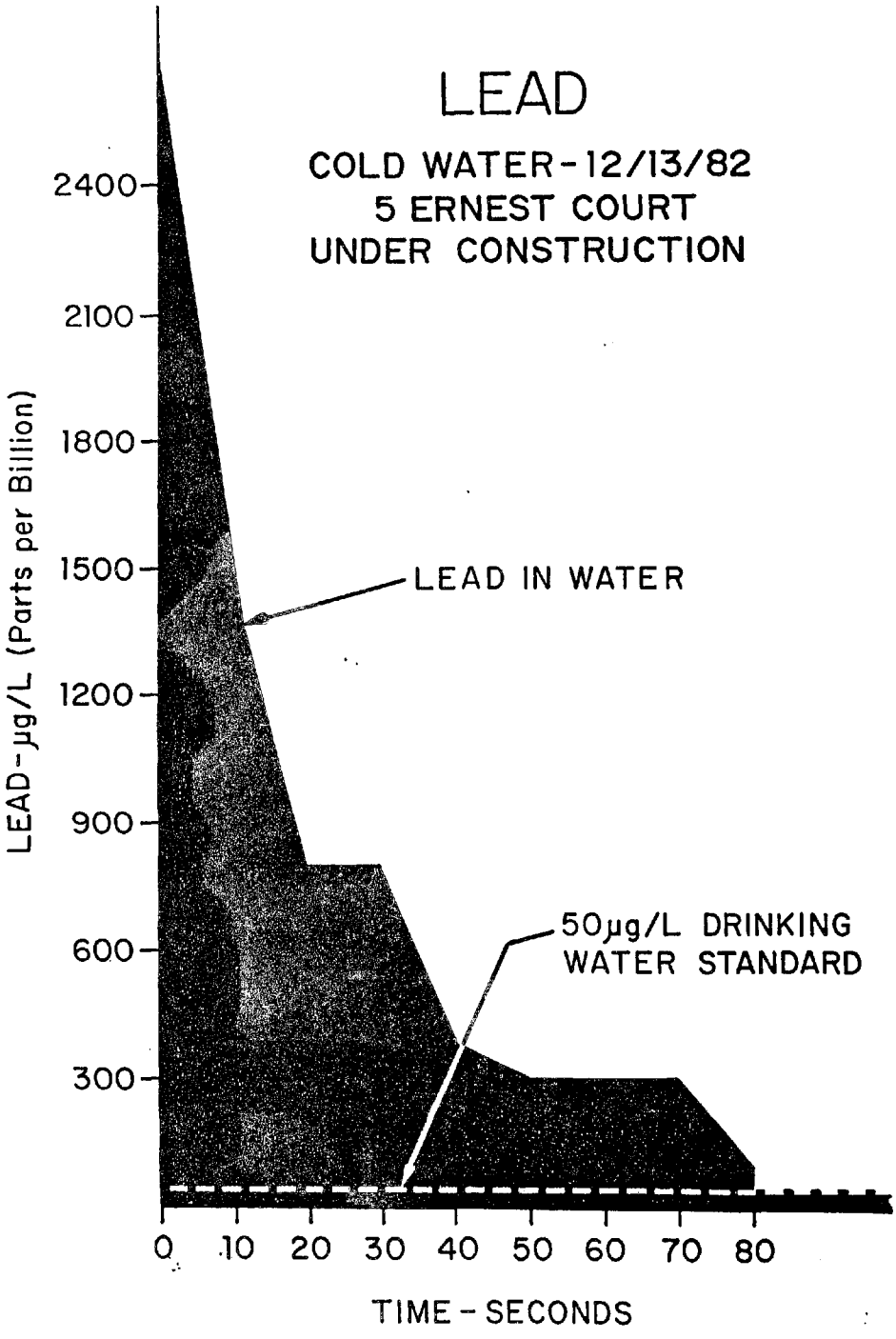
TIN

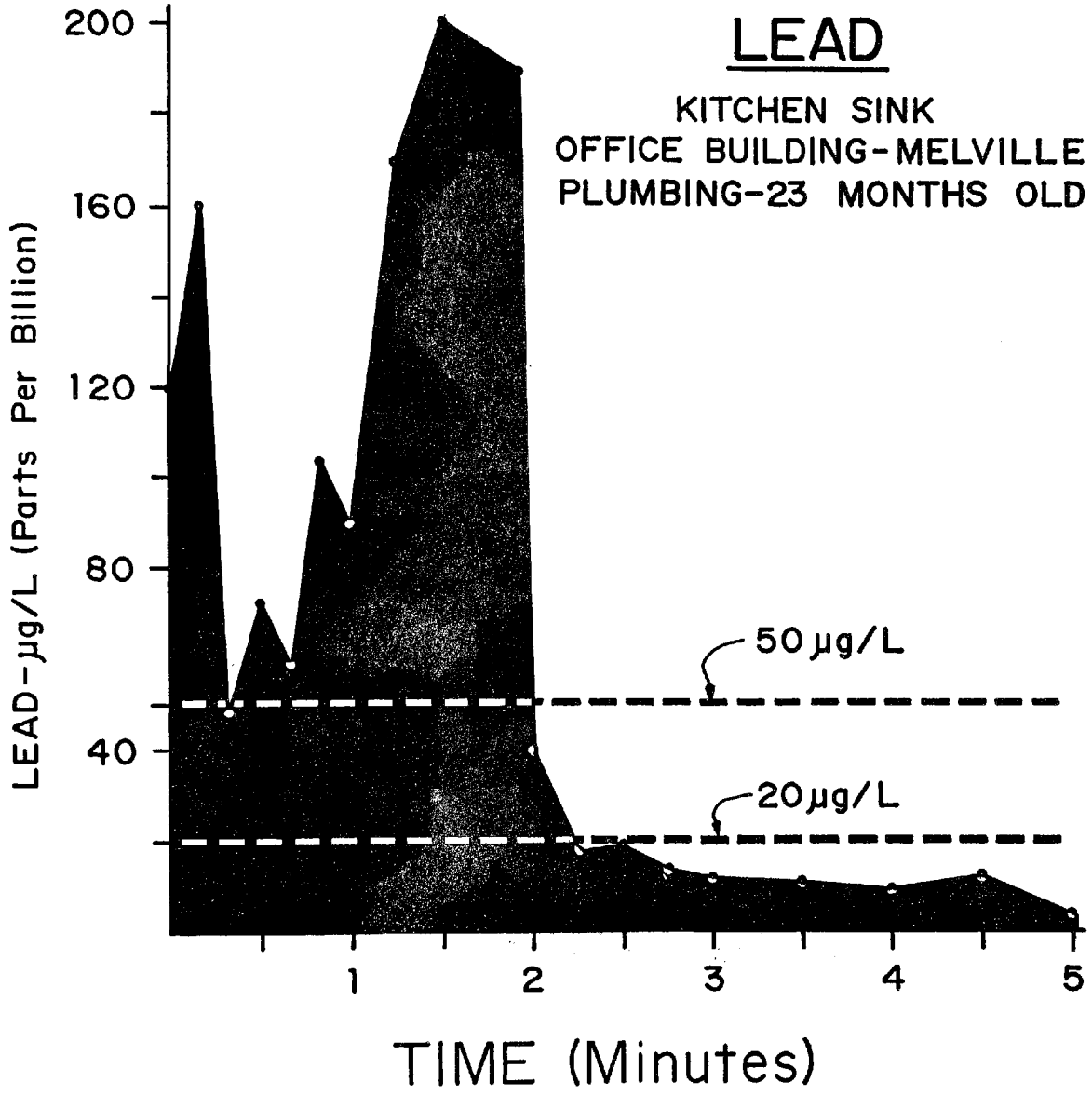
BRASS

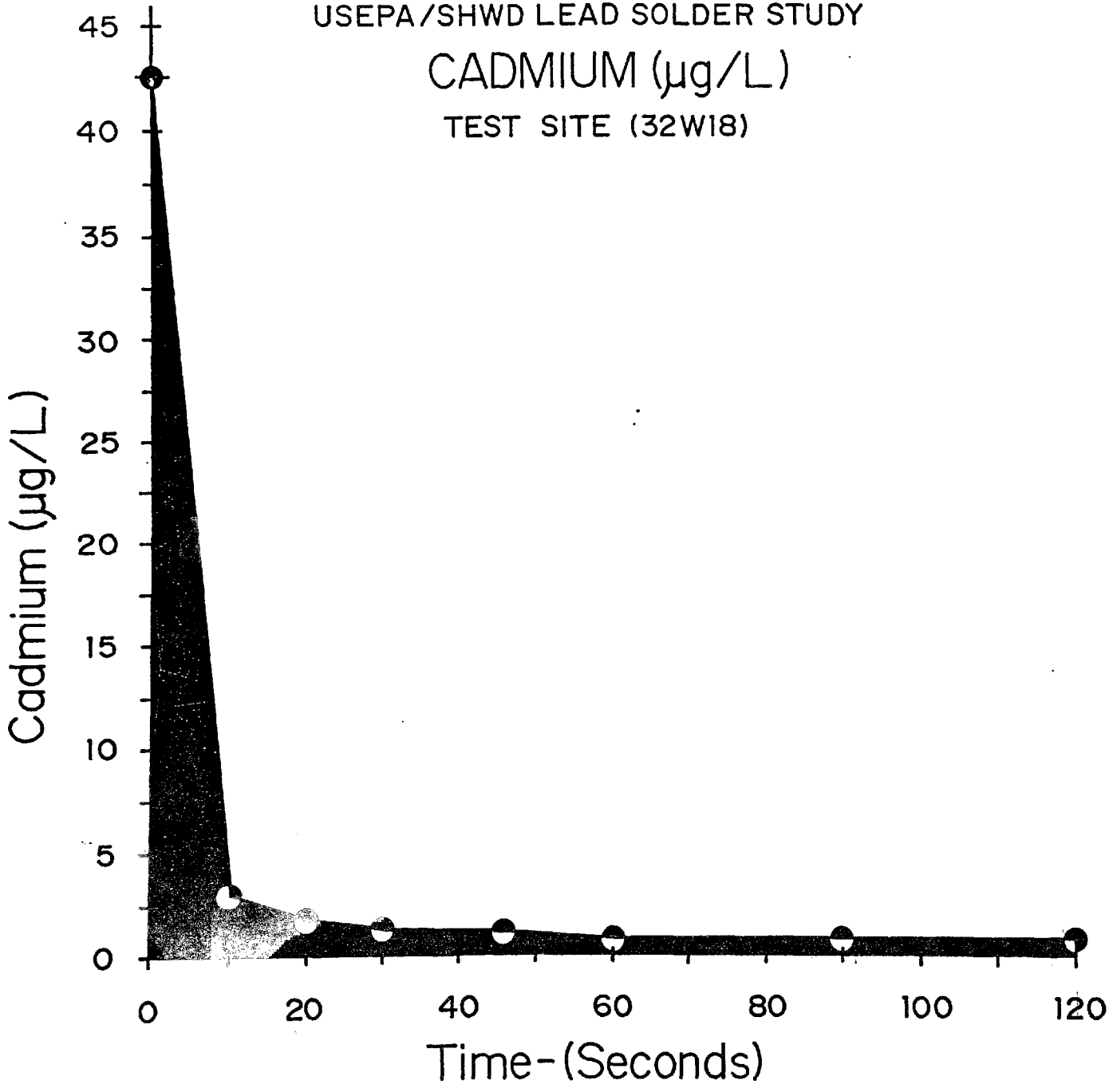
COPPER

STAINLESS STEEL

MORE ACTIVE


LEAD
COLD WATER - 12/13/82
5 ERNEST COURT
UNDER CONSTRUCTION
LEAD - µg/L (Parts per Billion)
2400
2100
1800
1500
1200
900
600
300
LEAD IN WATER
50µg/L DRINKING
WATER STANDARD
0
10
20
30
40
50
60
70
80
TIME - SECONDS


LEAD
KITCHEN SINK
OFFICE BUILDING-MELVILLE
PLUMBING-23 MONTHS OLD
LEAD-µg/L (Parts Per Billion)
200
160
120
80
40
50µg/L
20µg/L
1
2
3
4
5
TIME (Minutes)


USEPA/SHWD LEAD SOLDER STUDY
CADMIUM (µg/L)
TEST SITE (32W18)
Cadmium (µg/L)
45
40
35
30
25
20
15
10
5
0
0
20
40
60
80
100
120
Time-(Seconds)

LEAD (FIRST DRAW)

NASSAU COUNTY HEALTH DEPT. TEST

LOCATION	LEAD µg/L	pH	HARDNESS mg/L	% LEAD SOLDER	AGE
LOCUST VALLEY	17000	7.0	41	60.3	0
PORT WASHINGTON	4400	6.8	49	61.7	1
MANORHAVEN	3500	6.8	49	47.9	0
WOODBURY	2900	7.3	64	58.4	0
NORTH PORT WASH.	930	7.0	49	50.3	0
NORTH HILL	750	6.7	23	56.2	0
NORTH HILL	530	6.7	23	60.0	0

MINNESOTA
DEPT. OF HEALTH

46 COMMUNITIES LESS THAN 3 YEARS OLD

COMMUNITY	first draw lead ug/L
Winona	1500
Randolph	860
Mankato	790
New Trier	300
New Germany	270
Prinsburg	260
Red Wing	200
Madelia	140
Norwood	130
Watertown	120
Minnetonka Beach	110
Barnum	95
Waconia	80
Young America	63
Spring Lake Park	61
Fridley	57
Becker	54

25 COMMUNITIES NEW CONSTRUCTION

COMMUNITY	first draw lea ug/L
Mankato	33000
Kinckley	15000
Rice	8800
Park Rapids	4600
Northfild	4100
Eveleth	3800
Winsted	2400
St Peter	1900
Brainerd	1100
Waconia	1100
Rushford	640
Willmar	450
Zumbrota	400
Elk River	350
New Ulm	310
Backus	290
Rochester	150

VS 50 ug/L DRINKING WATER STANDARD

PERCENTAGE OF TEST SITES WITH LEAD IN DRINKING WATER GREATER THAN 20 ug/L AT LOW pH (6.4 & LESS)

Age Of Test Site (Years)	First Draw	10 Sec	20 Sec	30 Sec	45 Sec	60 Sec	90 Sec	120 Sec
0 – 1	100%	100%	100%	100%	100%	86%	86%	88%
1 – 2	100%	71%	86%	57%	57%	29%	43%	14%
2 – 3	86%	86%	57%	57%	43%	43%	43%	29%
3 – 4	100%	86%	100%	71%	71%	71%	29%	29%
4 – 5	86%	57%	29%	43%	43%	43%	14%	0%
6 – 7	78%	44%	33%	33%	11%	11%	11%	0%
9 – 10	71%	29%	14%	14%	14%	14%	0%	0%
15 – 16	57%	14%	14%	14%	14%	14%	14%	14%
20 & Older	86%	27%	29%	0%	14%	0%	14%	0%

PERCENTAGE OF TEST SITES WITH LEAD IN DRINKING WATER GREATER THAN 20 ug/L AT MEDIUM pH (7.0-7.4)

Age Of Test Site (Years)	First Draw	10 Sec	20 Sec	30 Sec	45 Sec	60 Sec	90 Sec	120 Sec
0-1	100%	90%	90%	60%	30%	20%	10%	10%
1-2	80%	60%	30%	10%	20%	0%	10%	0%
2-3	40%	20%	10%	10%	10%	0%	0%	0%
3-4	50%	20%	20%	30%	20%	30%	30%	20%
4-5	30%	10%	10%	0%	10%	0%	0%	0%
6-7	10%	0%	0%	0%	0%	0%	0%	0%
9-10	20%	0%	0%	0%	0%	0%	0%	0%
15-16	40%	20%	20%	10%	0%	0%	0%	0%
20 & Older	20%	0%	0%	0%	10%	0%	0%	0%

PERCENTAGE OF TEST SITES WITH LEAD IN DRINKING WATER GREATER THAN 20 ug/L AT HIGH pH (8.0 & GREATER)

Age Of Test Site (Years)	First Draw	10 Sec	20 Sec	30 Sec	45 Sec	60 Sec	90 Sec	120 Sec
0-1	100%	100%	60%	10%	20%	10%	20%	0%
1-2	67%	22%	11%	11%	11%	0%	11%	0%
2-3	30%	10%	10%	0%	0%	0%	0%	0%
3-4	25%	0%	0%	0%	0%	0%	0%	13%
4-5	30%	10%	0%	0%	0%	0%	0%	0%
6-7	20%	0%	0%	0%	0%	0%	0%	0%
9-10	10%	0%	10%	0%	0%	10%	0%	10%
15-16	33%	22%	11%	11%	0%	0%	0%	0%
20 & Older	20%	0%	0%	0%	0%	0%	0%	0%

RESULTS FROM HOUSEHOLD LEAD STUDY FIRST DRAW SAMPLES

pH	% of Homes Exceeding 50 ug/L
6.2	58.7
6.2-8.2	26.6
78.2	24.4

SOLDER TEMPERATURES

NORMAL COMPOSITION %				MELTING RANGES	
TIN	LEAD	ANTIMONY	SILVER	SOLIDUS°F	LIQUIDUS°F
95	—	5	—	452	464
95	—	—	5	430	473
30	70	—	—	361	491
35	65	—	—	361	471
40	60	—	—	361	460
45	55	—	—	361	441
50	50	—	—	361	421
60	40	—	—	361	374

SOLDER

Common Usage

Type	Percentage	Liquid Temp.	Range	Solid Temp.	*April 1984 Wholesale Cost
Tin/Lead	50/50	421° F	60° F	361° F	$4.50/lb.
Alternates					
Tin/Antimony	95/5	464° F	12° F	452° F	$8.00/lb.
Tin/Silver	95/5	473° F	43° F	430° F	$20.00/lb.

ASTM Standards - Part 8 - B32

*estimated by plumbers at less than 1 pound SOLDER required per residence

USEPA/SEATTLE STUDY

Tin Antimony Solder

UNIVERSITY OF WASHINGTON BUILDINGS

BUILDING	YEAR OCCUPIED	SAMPLE	ANTIMONY µg/L
OCEANOGRAPHY TEACHING	1969	MECH. ROOM	<0.6
		STANDING	<2.0
SOUTH CAMPUS CENTER	1969	MECH. ROOM	<0.6
		STANDING	<0.6
HEALTH SCIENCES WING T	1973	MECH. ROOM	<0.6
		STANDING	<0.6
CONDON	1974	MECH. ROOM	<0.6
		STANDING	<0.6
WATER FRONT ACTIVITIES	1977	MECH. ROOM	<0.6
		STANDING	<0.6
HALL HEALTH CENTER	1978	MECH. ROOM	<0.6
		STANDING	<0.6
LOEW	1979	MECH. ROOM	<0.6
		STANDING	<0.6
ENGINEERING LIBRARY	1969	MECH. ROOM	<0.6
		STANDING	<0.6

COPPER LEACHING IN FOUR PIPE LOOPS

pH	SOLDER	COPPER (mg/L)
5.5	TIN/SILVER	3.80
5.5	TIN/ANTIMONY	4.28
5.5	TIN/COPPER	4.50
5.5	TIN/LEAD	4.28

- AGE OF THE PLUMBING
- CORROSIVE WATERS
- GALVANIC CORROSION
- FLUX USED

CORROSION CONTROL

- pH ADJUTMENT ALONE
- ADJUST ALKALINITY AND pH
- STABILIZE WATER (CALCIUM CARBONATE BALANCE)
- ADD CORROSION INHIBITORS

SEATTLE CORROSION CONTROL PROGRAM

- SERVICE LIFE ECONOMICS
  - LOSS $7.8 MILLION/YEAR
- AESTHETICS
  - RED & BLUE STAINS
  - METALLIC TASTE COMPLAINTS
- HEALTH
  - LEAD ABOVE MCL

(Courchene, J.E. & Hoyt, B.P. "Benefits of Corrosion Treatment in Seattle" CA/NV AWWA Seminar, 1985)

SEATTLE CORROSION CONTROL PROGRAM

INSTITUTED MATERIAL SELECTION PROGRAM

- PLASTIC PIPE
  - ALLOWED PB AND CPVC IN BOTH HOT AND COLD
  - REQUIRED DIELECTRIC INSULATORS
  - ENCOURAGED TYPE K AND L COPPER PIPE
  - DISCOURAGED GALVANIZED PIPE
  - < 0.2% LEAD IN SOLDERS

(Courchene, J.E. & Hoyt, B.P. "Benefits of Corrosion Treatment in Seattle" CA/NV AWWA Seminar, 1985)

SEATTLE CORROSION CONTROL PROGRAM

WATER TREATMENT PROGRAM

TOLT

2 mg/L CaO

9 mg/L Na_2CO_3

CEDER

2 mg/L CaO

(Courchene, J.E. & Hoyt, B.P. "Benefits of Corrosion Treatment in Seattle" CA/NV AWWA Seminar, 1985)

SEATTLE CORROSION CONTROL PROGRAM

RWQM* OVERNIGHT STANDING SAMPLES, ALL CEDAR AND TOLT GROUPS

Parameter	Average Concentration			%>MCL	
	Before	After	%Reduction	Before	After
Pb, µg/L	10.6	4.0	63	5	0.4
Cd, µg/L	0.76	0.41	46	0	0
Cu, mg/L	0.28	0.09	68	11	0
Fe, mg/L	1.21	0.99	18	75	67
Zn, mg/L	0.60	0.33	45	0	0

* Residential Water Quality Monitoring – 300 residences

(Courchene, J.E. & Hoyt, B.P. "Benefits of Corrosion Treatment in Seattle" CA/NV AWWA Seminar, 1985)

SEATTLE CORROSION CONTROL PROGRAM

LEAD LEVELS

	% BEFORE		% AFTER	
SOURCE	>20*	>50*	>20*	>50*
TOLT	12.5	5.9	3.9	0.6
CEDAR	9.8	4.3	2	0

* µg/L

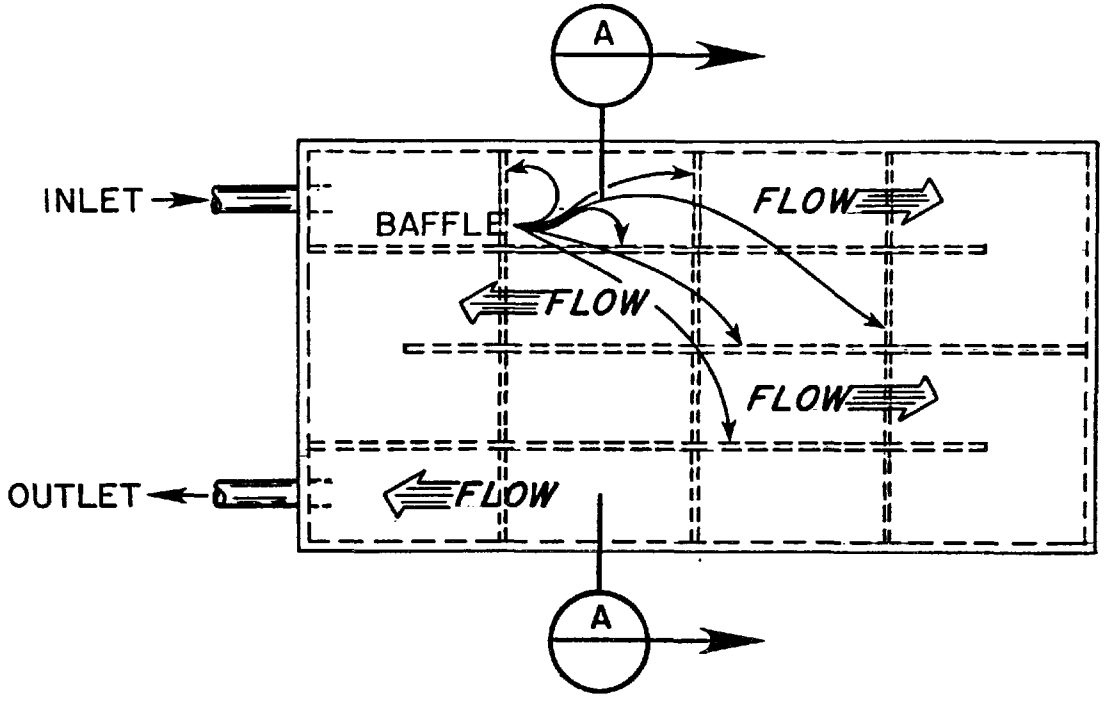
(Courchene, J.E. & Hoyt, B.P. "Benefits of Corrosion Treatment in Seattle" CA/NV AWWA Seminar, 1985)

SEATTLE CORROSION CONTROL PROGRAM

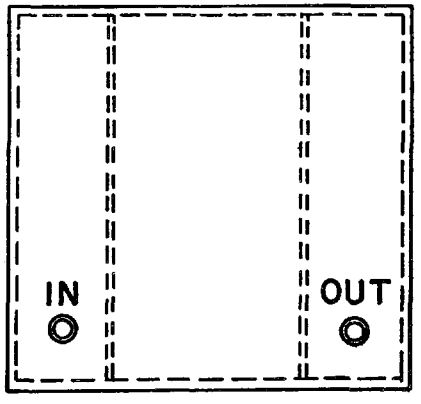
WATER QUALITY CHANGES SINCE TREATMENT

Water Characteristic	Cedar		Tolt	
	Before	After	Before	After
pH	7.2	8.2	6.0	8.2
Tot. Alkalinity, mg/L $CaCO_3$	16	19	2.5	13.5
Carbon Dioxide, mg/L	2.7	0	6.0	0
Hardness, mg/L $CaCO_3$	21	24	8	11
Sodium, mg/L	1.8	1.8	1.0	4.8
Tot. Diss. Solids, mg/L	46	48	25	36
Spec. Conductance, µmhos	55	59	27	42
Larson's Ratio	0.65	0.55	3.9	0.8

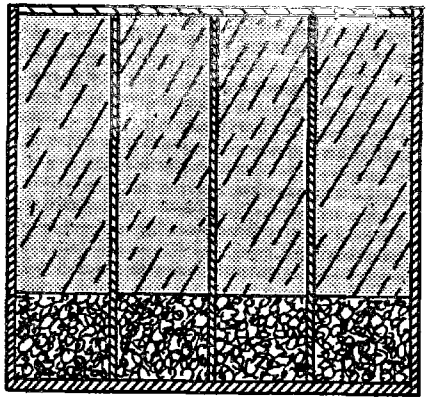
(Courchene, J.E. & Hoyt, B.P. "Benefits of Corrosion Treatment in Seattle" CA/NV AWWA Seminar 1985)



PLAN VIEW



INLET/OUTLET ELEVATION



SECTION A A

LIMESTONE CONTACTOR