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RECOMMENDED UNIFORM
EFFLUENT CONCENTRATIONS

EPA Region III
Enforcement Division

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PREFACE

This report is intended to meet the immediate needs of many programs of the Environmental Protection Agency. The information can be used by the professional staff of the Permits Branch in drafting industrial wastewater permit conditions, by the professional engineering and legal personnel of the Enforcement Division in seeking solutions to clean up the industrial, municipal and combined municipal-industrial discharges into our nation's surface waters, by Air and Water Programs Division in establishing effluent requirements, by the engineering staff of the Municipal Facilities Branch in approving plans and grants for municipal wastewater treatment systems, and by the administrative personnel in accomplishing the programs and objectives of the EPA.

The objectives of this work are to define the sources of certain pollutants, their effects within the aquatic environment for specified uses and the level of technology for treatment which is currently available and economically within reason and to recommend a uniform effluent level for the parameters covered. As such, very little dependence is made for the dilution effect. Rather, the ability of the waters to dilute pollutants is reserved for the many uncontrollable discharges such as surface runoff. Similarly, the toxicity of a pollutant on fish and aquatic life under a limited duration of one hour maximum is given more consideration than the effect of the pollutant during extended exposure.

In identifying the sources of each pollutant, both natural and manmade sources, outside and within the immediate scope of EPA programs, have been included. While there are many areas which need further investigation, the reader should at least gain a feeling for the magnitude of the problem.

Discussions of the effects of the pollutants within the aquatic environment include the following: a) the impact on man, domestic animals and wild life through consumption of water and food, b) the impact on man, domestic animals and wildlife by direct contact in

surface waters, c) the impact on plants by irrigation, d) the impact on fish and other aquatic life by direct contact, taking into account the duration of the exposure, the physical, chemical and biological characteristics of both the discharge and receiving waters as well as the concentration effect within the food chain.

The currently available methods of treatment have been described with respect to the influent loading, the achieved effluent concentration(s), and both the capital and operating cost. The heretofore nebulous description of treatment efficiency, in terms of percent removal, has been avoided wherever possible. The stoichiometry of chemical treatment processes is discussed in general terms.

The recommended uniform effluent concentrations are based on currently achievable concentrations for the particular waste under the worst waste condition reported. Many wasteloads are currently treatable to lower levels than those recommended as the uniform level. In fact, almost all wasteloads including even the worst, can be treated so that the average effluent concentrations will be lower than the recommended uniform concentration. The uniform effluent concentration is defined as the arithmetic average concentration (weight per unit volume - milligram per liter - mg/l) over a one hour period. Ideally, this should be measured by continuous composite sample proportional to the instantaneous flow, for a one hour period. Due to practical and economical limitation, however, the following are considered as acceptable alternatives.

1. At least 50% of the grab samples, collected at evenly spaced time intervals during any one hour period, should be less than the recommended concentration.

2. No single grab sample should exceed the recommended concentration for Hazardous Materials by more than 50 percent

3. No single grab sample should exceed the recommended concentration for any parameter by more than 100 percent.

In all situations the uniform effluent recommendations of this report apply to the treated process wastewaters prior to dilution with non-process or cooling waters.

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Every pollution problem must be evaluated on a case-by-case basis. This report defines an effluent level which can be reached now by almost all dischargers. In many cases the discharge levels can be much lower. In all situations the most stringent levels must be used, be they federal, state or local regulations.

SUMMARY OF RECOMMENDATIONS

<u>Parameter*</u>	<u>Max.Stream Conc. to Protect Water Uses</u>	<u>Effluent</u>		<u>Concentrations</u>	
		<u>Unif.Eff.Conc.</u>	<u>Max.</u>	<u>Design Goal</u>	
Arsenic	0.010	0.050	0.075	0.030	
Cadmium	0.010	0.100	0.150	none	
Chromium	0.050	0.100	0.150	none	
Lead	0.010	0.100	0.150	0.010	
Mercury	none	0.005	0.005	none	
Barium	1.0	2.0	4.0	< 1.0	
Copper	0.02	1.0	2.0	0.03	
Iron, Total	0.1	2.0	3.0	< 1.0	
Iron, Dissolved	0.1	1.0	2.0	< 0.3	
Manganese	0.05	0.1	0.2	0.05	
Nickel	0.5	1.0	2.0	< 0.5	
Selenium	0.010	0.010	0.020	< 0.010	
Silver	0.003	0.100	0.100	< 0.010	
Zinc	1.0	1.0	2.0	0.1	
Cyanide	0.01	0.025	0.050	none	
Fluoride	1.0	1.5	1.5	0.5 - 1.0	
Oil and Grease	0.3	10.0	10.0	1.0 - 2.0	
Phenolics	0.001	1.0	2.0	0.1	
Phosphorus	0.01	2.0	4.0	< 1.0	
Settleable Solids	none	0.2	0.4	none	
Surfactants	0.5	1.0	2.0	< 0.5	
Suspended Solids	none	30.0	30.0	<15	
BOD ₅	none	30 - 75	90.0	15	
Total Chlorine Residual	0.002	0.1	0.2	none	

* All units are mg/l except ml/l for settleable solids

CHAPTER I-ARSENIC

Arsenic is found in most natural waters as arsenate (AsO_4^{-2}) or arsenite (AsO_2^{-1}), occurring in sea water mainly as arsenite. Mineralogically, it may occur as elemental arsenic but it is usually found as the arsenides of the true metals or as pyrites. It is oxidized and recovered as a byproduct in the smelting of many ores. Table I-1 lists some of the naturally occurring levels of arsenic in the environment. A number of industrial sources of arsenic also exist. These are summarized in Table I-2 with the approximate concentrations to be expected in the various effluents.

ENVIRONMENTAL EFFECTS OF ARSENIC

Effect on Man

From a review of literature dealing with the biotic responses to arsenic and its pharmacology it is apparent that arsenic compounds can elicit a variety of responses from living organisms depending on its form, concentration and mode of exposure. In general the effects include chronic and acute syndromes and possible carcinogenicity. It is a cumulative poison in most life forms due to its low excretion rates. Schneider (83) reports that the human body constantly accumulates arsenic and that normal blood levels range from 0.2-1.0 mg/l of arsenic. Lambou and Lim (55) have reported that arsenic toxicity decreases in the following order depending on the mode of entry into the body-arsenides, arsenates, colloidal arsenic, atoxyl and cacodyl. Arsenicals (pesticides) also act locally as mild and slow corrosives. They systematically relax the capillaries and increase their permeability, thus creating inflammation.

The fatal dosage of arsenic compounds may vary with the solubility of the preparation. Table I-3 summarizes the human toxicity data available on arsenic. Lambou reports that trioxide is toxic at 5-50 mg and is usually fatal at 0.06-0.18 g (55). McKee and Wolf (66) report that arsenic concentrations of 0.21 mg/l-10.0 mg/l are sometimes poisonous to human beings; on the other hand concentrations of 0.05 mg/l-0.2 mg/l in drinking water can be safe for human consumption. The mortality rate of acute clinical arsenic poisoning has been reported to be 50-75% (55). Acute arsenic poisoning results in violent gastroenteritis which resembles cholera. It may also cause skin eruptions and liver or heart damage. The chronic or subacute symptoms include weakness, loss of appetite, gastrointestinal disturbances, hoarseness, coughing and laryngitis, peripheral neuritis, occasional hepatitis and skin disorders.

Schneider (83) reports that arsenic consumed in domestic water supplies would not be carcinogenic, a statement supported by Lambou and Linn (55). However, McKee and Wolf (66) report several incidents of cancer which may be attributable to consumption of arsenic in water. It is possible that the form of the compound may be the controlling factor. Potentially recognized possible sites of carcinogenic effects in humans are the skin, lung and liver. Other suspected sites include the mouth, esophagus, larynx and bladder (55).

Effect on Fish and Other Aquatic Life

The effects of arsenic on fish and other aquatic organisms are summarized in Tables I-4 and I-5. These tables give the toxic and tolerable levels found by various researchers. Some organisms have been found to concentrate arsenic from the surrounding water. Marine

TABLE I-1

CONCENTRATION OF ARSENIC IN NATURAL ENVIRONMENT

<u>Source</u>	<u>Concentration</u>	<u>Reference</u>
Soils	up to 500 mg/kg	(83)
Earth crust	1.8 mg/kg	(55)
U.S. surface water	0.01-0.1 mg/l	(55)
Sea water	0.003 mg/l	(6)
Normal blood	0.2-1.0 mg/l	(83)
Molluscs, Coelenterates and Crustaceans	up to 0.3 mg/kg	(83)
Marine plants (highest in the Brown algae)	up to 30 mg/kg	(83)
Marine animals	0.005-0.3 mg/kg	(83)
Shellfish	over 100 mg/kg	(66)
Fish oils (15 species):	Average 11.8 mg/l	
	Range 1.20-60-10	(33)

TABLE I-2

SOURCES AND SOME KNOWN CONCENTRATIONS OF ARSENIC
IN INDUSTRIAL WASTEWATERS

<u>Source</u>	<u>Concentration</u>	<u>Reference</u>
Manufacture of Parisgreen Calcium meta-arsenate Insecticides (Arsenical)	362 mg/l (as an Arsenious oxide)	(76)
Industrial or municipal discharge of pre-soak household detergent	up to 70 mg/l	(55)
Laundry products (currently available)	up to 36 mg/l	(55)
Laundry detergents discharged into Kansas sewage system	0.002-0.01 mg/l	(15)
Mineral rock; waste from industry and mining activity; residues from pesticides in major U.S. River Basins (1962-7)	mean-0.034 max -0.336	(15)
Herbicides and pesticides manufacture	significant amount of arsenic compound	(61)
Glassware and ceramic products		(76)
Tannery operations		(76)
Fish processing plant		(76)
Sulfuric acid made from sulfide ores		(55)
Acid mine drainage (active and abandoned mines)		(55)
Fly ash scrubber drainage		(55)
Storm runoff from power plant		(55)
Metallurgical industry		(61, 76, 55)

plants, specifically brown algae, have been found to contain concentrations up to 30 mg/l. Accumulations of up to 0.3 mg/l have been reported in some molluscs, coelenterates, and crustaceans. Some reported accumulation factors are shown in Table I-6.

TABLE I-3

TOXIC EFFECTS OF ARSENIC ON HUMANS

<u>Form</u>	<u>Conc(or Dose)</u>	<u>Effects</u>	<u>Reference</u>
Undefined	130 mg	Lethal	(59)
Undefined	130 mg	Severe poisoning; cumulative toxic effect; small eruptions on hands and soles of feet, sometimes developing into cancer; possible liver damage and heart ailments, causal factor for Hoff's disease.	(59)
Elemental	Ingestion of un- specified concentra- tions	Sub-acute and acute symptoms	(59)
Trioxide	5-50 mg	Toxic	(55)
Trioxide	60-180 mg	Fatal	(55)
Sodium Arsenite	325 mg	Lethal	(66)
Undefined	Prolonged ingestion at low conc.	Chronic, sub-acute symptoms	(59)
Undefined	Non-oral dose	positive, epidermal cancer	(59)
Undefined	Oral, drinking water	possible carcinogen to skin and liver.	(66)
Undefined	Normal exposure to workers in arsenical industry	no significant increase in cancer mortality.	(59)
Undefined	0.21 mg/l	poisonous over a long period of time	(66)
Undefined	0.3-1.0 mg/l	"	(66)
Undefined	0.4-10.0 mg/l	"	(66)
Undefined	12 mg/l	Death	(66)

The Green Book reports that arsenic is moderately toxic to plants and highly toxic to animals, especially as AsH_3 (6). They also report that fish food organisms can tolerate an application rate of 2 mg/l of As_2O_3 . A level of 15 mg/l has been reported to be toxic to certain fish eggs, including Lepomis macrochirus and Micropterus dolomieu. The eggs of these two species survived 7 and 6 days, respectively following exposure. The effluent from nuclear reactors may contain appreciable concentrations of arsenic-76 which may be concentrated somewhat in the aquatic food chain (55).

It is possible that arsenic will replace phosphorous in the bottom muds or even in plankton (55). Should further study confirm this hypothesis it would amplify the importance of controlling arsenic in effluents wherever the soluble phosphorous concentration is sufficient to produce a heavy aquatic growth.

Effect on Plants and Animals

Arsenic at very low concentrations appears to stimulate plant growth, however, the presence of any excess soluble arsenic will reduce crop yields. The mode of action appears to be the destruction of chlorophyll. McKee and Wolf (66) report that old orchard soils in the state of Washington were found to be unproductive when a concentration of 4 to 12 mg/kg of arsenic trioxide, was reached in the top soil. They also reported that fruits and vegetables, however, have been found to contain arsenic compounds due to natural conditions alone (66). Table I-7 summarizes some effects of arsenic on specific species of plants.

Sickness and death of cattle have been reported to result from consumption of arsenic naturally present in water supplies (66). The lethal dose of arsenic is believed to be approximately 20 mg/lb of animal weight. The dosages of arsenic toxic to various animals are given in Table I-8. Arsenic has been used in drinking water to counteract selenium poisoning in cattle, pigs, dogs and rats.

TABLE I-4

CONCENTRATIONS OF ARSENIC TOXIC TO FISH AND AQUATIC ORGANISMS (66)

<u>Type of Organisms</u>	<u>Concentration of Arsenic (mg/l)</u>	<u>Time of Exposure</u>
fish	1.1	---
pike perch	1.1-2.2	2 days
bleak	2.2	3 days
carp	3.1	4-6 days
eels	3.1	3 days
crabs	4.3	11 days
bass	7.6	10 days
minnows	11.6	36 hours
crappies and bluegills	15	---
minnows	17.8-234	---
Chironomus	<u>Concentration of Arsenic trioxide (mg/l)</u>	
	1.96	---
fish food organisms	2-4	---
pink salmon	5.3	8 days
fish	10	---
bass	10	10 days
bass, bluegills, crappies	10	---
mussels	16	3-16 days
flatworms	40	---

TABLE I-5

CONCENTRATIONS OF ARSENIC TOLERATED BY FISH AND AQUATIC ORGANISMS (66)

<u>Type of Organism</u>	<u>Concentration of Arsenic, mg/l</u>	<u>Time of Exposure</u>
pike perch	0.7-1.1	48 days
fish	0.76	---
bleak	1.1-1.6	11 days
fish	1.5-5.3	1-7 days
carp	2.2	13 days
eels	2.2	13 days
crabs	3.1	90 days
fish	5.3	24-148 hours
bass	6.0	232 hours
trout	7.6	30 days
minnows	13.0	1 hour
	<u>Concentration of Arsenic trioxide mg/l</u>	
chironomus larvae	1.9	---
food organisms	2	---
bass, bluegills, crappies	2-6	---
fish	2-7	1-7 days
mayfly nymphs	3-14	---
some zooplankton	5	---
trout, bluegills, sea lamprey	5	24 hours
fish	5	---
coho salmon	5-10	15-30 minutes
fish	7	24-148 hours
mussels	8	---
trout	10	1 month
insect larvae	10-20	---
minnows	17.1	1 hour

TABLE I-6

ACCUMULATION OF ARSENIC IN AQUATIC ORGANISMS (55)

<u>Organism</u>	<u>Concentration Factor</u>
Benthic Algae	2000
Mollusc (muscle)	650
Crustacean (muscle)	400
Fish (muscle)	700
Various species seaweed	200-600

TABLE I-7

CONCENTRATIONS OF ARSENIC TOXIC TO PLANTS (66)

<u>Plants</u>	<u>Form</u>	<u>Concentrations</u>	<u>Effect</u>
Beans, cucumbers (sensitive) turnips, cereals, grasses (relatively tolerant)	Arsenic Trioxide	1 mg/l	Blackening of vascular bundles
Lemon plants	Arsenite, Arsenate	1 mgm/l	root growth stimulated
Lemon plants	Arsenate	5 mgm/l	toxic to root and top growth
Lemon plants	Arsenite	10 mgm/l	toxic to root and top growth
Sugar beets	Arsenate	23 mgm/l	slightly injurious

TABLE I-8

CONCENTRATIONS OF ARSENIC TOXIC TO ANIMALS

<u>Species</u>	<u>Dose</u>	<u>Form</u>	<u>Effects</u>	<u>Reference</u>
Laboratory animals	5-100 mg/kg	arsenic	Lethal	(66)
Dog	100-200 mg/kg	---	Toxic	(55,66)
Swine	500-1000 mg/kg	---	Toxic	(55,66)
Sheep, goat, horse	10,000-15,000 mg	---	Toxic	(55,66)
Cow	15,000-30,000	---	Toxic	(55,66)
Rats, Mice	15.1-214 mg/kg	Arsenic Trioxide	96hr. LD(50)	(66)
Chickens	324 mg	---	Lethal in 24hr.	(66)
Fowl	50-100 mg	---	Toxic	(55,66)
Guinea Pigs	14-30 mg/kg	---	Lethal	(105)
Mouse	5 mg/l for life (0.50 mg/kg/day)	Sodium Arsenite	Significant decrease in survival and longevity	(105)
Laboratory animals	0.5 mg/kg/day	---	Change in conditioned reflexes	(105)
Laboratory animals	2.5 mg/kg/day	---	Morphological changes in blood and impairment of kidney function; cumulative in organs	(105)
Rats (cancer sensitive strain)	0.1 ml of 1% lanolin suspension in paranasal sinuses (3 times).	---	11 of 20 developed a total of 15 tumors of 7 types. Control: 8 of 20 developed a total of 8 tumors of 4 types	(105)

TABLE I-9

ARSENIC TREATMENT METHODS AND REMOVAL EFFICIENCY

<u>Treatment</u>	<u>Concentration mg/l</u>		<u>%Removal</u>	<u>References</u>
	<u>Initial</u>	<u>Final</u>		
Lime Softening	0.2	0.03	85	(55,76)
Charcoal Filtration	0.2	0.06	70	(76)
Ferric Sulfide Filter Bed	0.8	0.05	94	(76)
Coagulation with Ferric Sulfate	25.0	5 or less	80 or more	(76)
Coagulation with Ferric Chloride	3.0	0.05	98	(76)
Precipitation with Ferric Hydroxide	---	0.6	--	(76)
Precipitation with Ferric Hydroxide by Ferrous Sulfate & Lime Coagulation with Settling only	362 (as Arsenic Oxide)	15-20 (as Arsenic Oxide)	94-96	(76)
Ferrous Sulfide Filter Bed, Bone Carbon & Settling	0.8	0.05	94	(76)
Ferrous Sulfide Filter Bed, followed by Sand & Coke Filtration	0.5	trace		(76)
Chemical Coagulation, Sedimentation, and Filtration		0.05-0.5	80-95	(97)
Activated Sludge Removal /Biomass	0.0028+0.0004 0.040 +0.01 0.133 +0.023	0.0010+0.0005 0.0228+0.009 0.056 +0.01		(103)

TREATMENT TECHNOLOGY - ARSENIC REMOVAL

Currently available treatment technology consists of cold-lime softening and the more standard procedures of coagulation, settling and filtration. Complexation of the arsenic compounds with heavy metals has been reported as a potential removal mechanism not only in the above processes, but as a third treatment method.

The 1970 works of Magnusen et al, reviewed and discussed by Lambou and Lim (55) and Patterson and Minear (76) show that lime softening will reduce an initial arsenic complex concentration of 0.2 mg/l to approximately 0.03 mg/l, thus achieving an 85% removal. Simple filtration through a charcoal bed can reduce arsenic from 0.2 mg/l to a final effluent level of 0.06 mg/l of arsenic (55,76). Arsenic removal has also been accomplished by passage of the wastewater through a ferrous sulfide filter bed followed by bone carbon settling and filtration (76). Coagulation with iron salts (ferric sulfate, ferrous sulfate, ferric chloride) and subsequent rapid sand or multi media filtration of the ferric hydroxide precipitate is another arsenic removal process (76). When the arsenic bearing wastewaters are acid, lime is normally used to adjust the pH to alkaline conditions (pH = 10).

Arsenic compounds have been reported to be removed upon sediments. Lund (61) proposes that arsenic may be precipitated from wastewaters bearing heavy metals by complexation of the arsenic with the heavy metal ions. He has reported approximately 90% removal of the initial arsenic concentration by complexation with heavy metals, when the heavy metals were removed by chemical precipitation.

This complexation of arsenic compounds appears to be one of the mechanisms involved in the ferric hydroxide precipitation.

A tabulation of the currently available methods for treating arsenic compounds and their degree of removal is given in Table I-9. The cost of arsenic removal will be similar to that of routine water treatment. The chemical cost associated with this method will be that of the coagulant and lime needed for precipitation. A summary of treatment processes, their effectiveness and cost, by Weston (97) has shown the capital cost (in millions of dollars) to be approximately 0.3 for a one MGD facility, 1.3 for a ten MGD plant, and 4.6 for a fifty MGD facility. These cost estimates do not include the cost of sludge or lime disposal.

Three figures illustrating the treatment cost for arsenic are included here (76). Figure I-1 indicates the total cost of treatment by coagulation, sedimentation and rapid sand filtration. Figure I-2 gives the operating cost for lime neutralization and, Figure I-3 shows the capital cost for 21.0 MGD lime neutralization plant.

In summary, it has been shown that coagulation, sedimentation, and filtration are the most common and effective means of treating arsenic bearing wastes. Where the arsenic wastewaters are acidic, pH adjustment to alkaline conditions will be required for effective removal. The cost of treatment will depend on the volume of wastes to be treated and their initial water quality parameters, especially the acidity.

Figure 1-1

Total cost of treatment by coagulation, sedimentation and rapid sand filtration. Cost includes capital investments for 30 years at 4%, labor, power, chemicals, maintenance and repair, and heating of building (76).

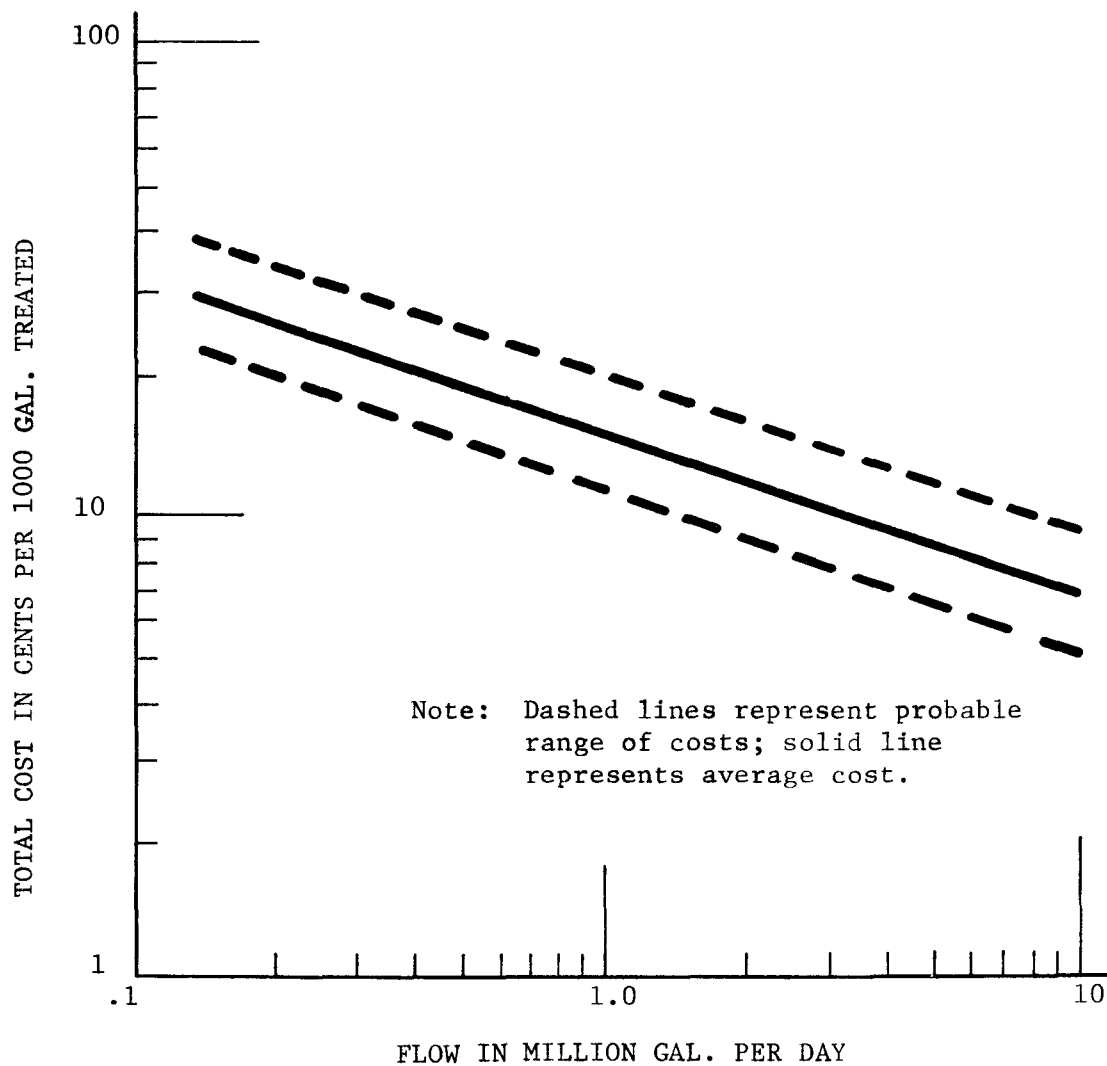


Figure 1-2

Operating costs for lime neutralization,
including sludge dewatering by vacuum filtration (76).

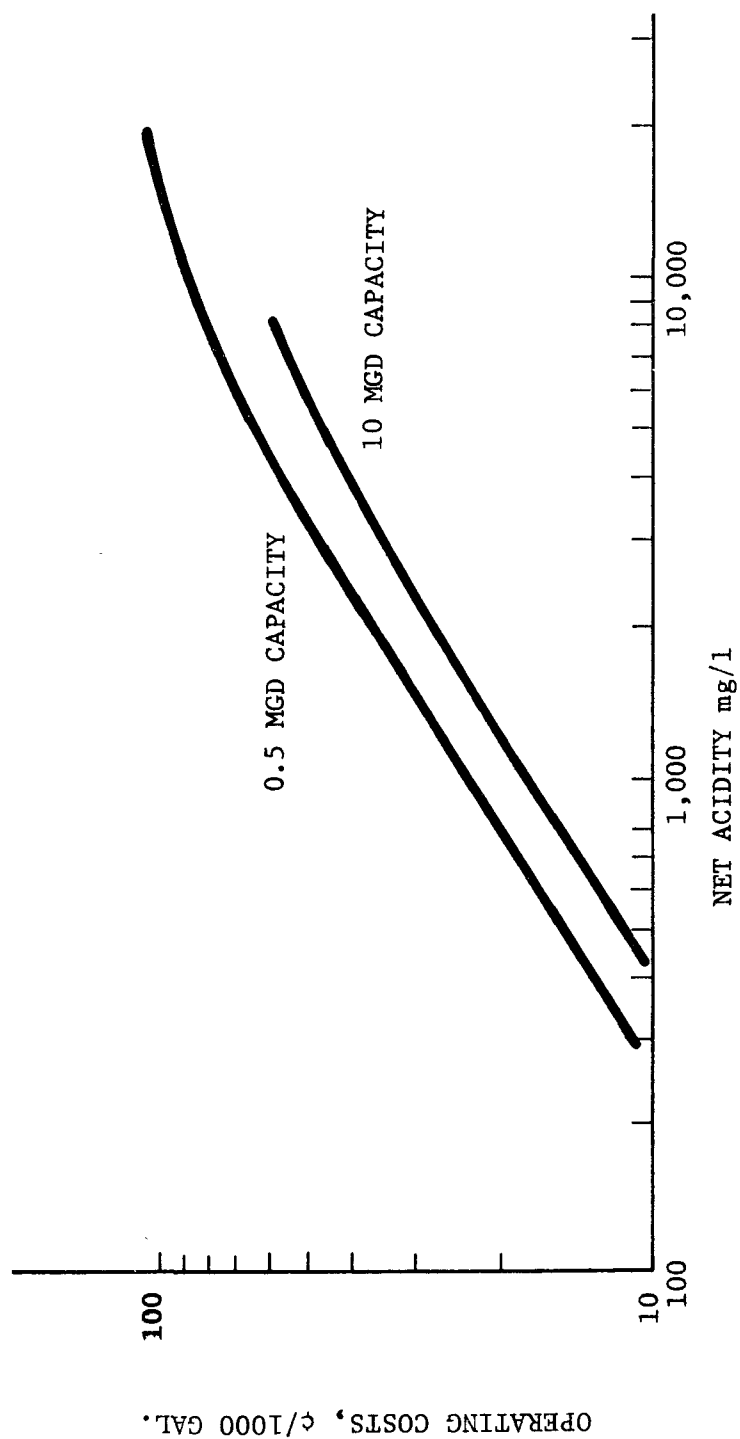
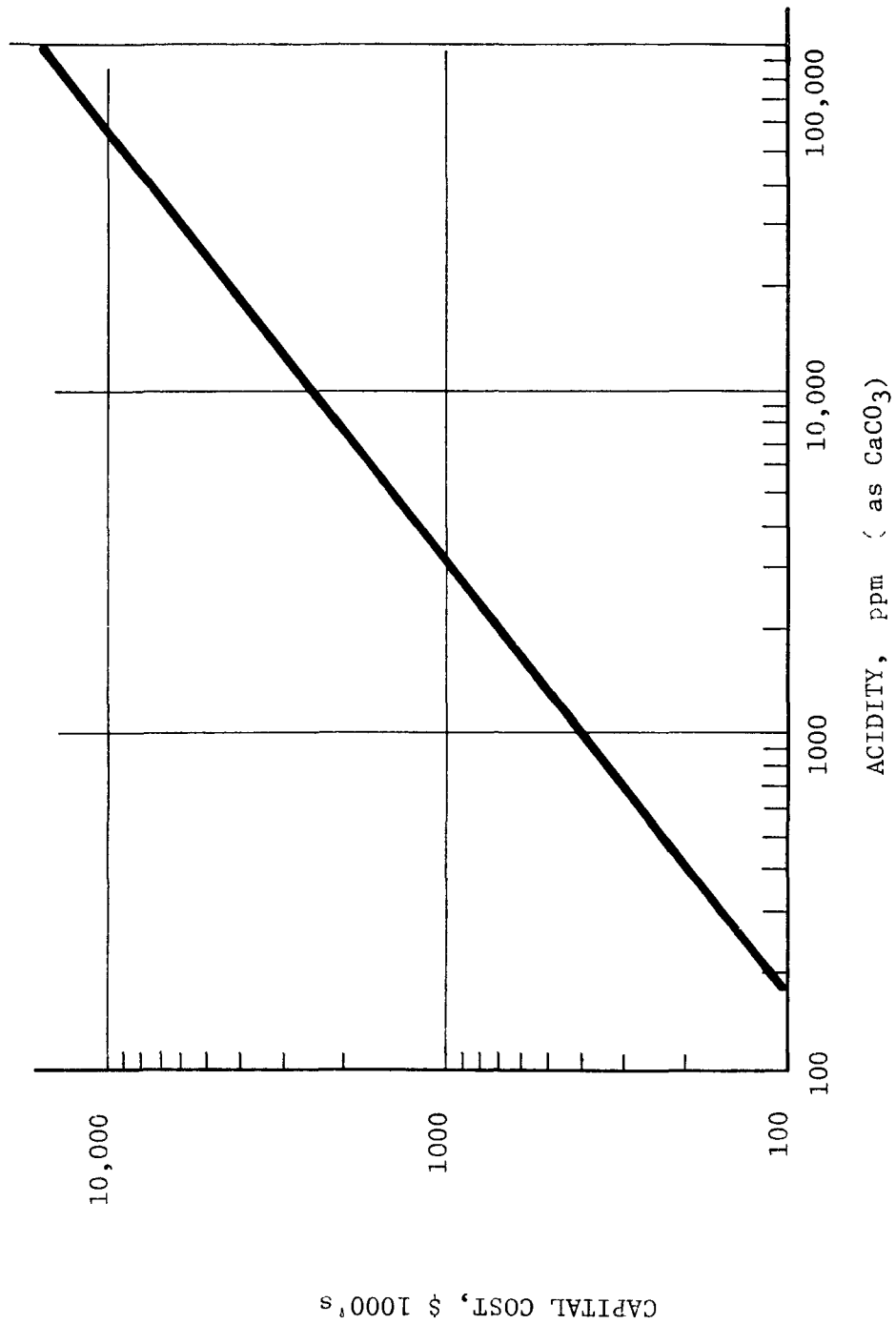


Figure 1-3

Capital cost for a 1 MGD lime neutralization plant, including sludge disposal (76).



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SUMMARY AND RECOMMENDATIONS

The following conclusions can be drawn from the above data.

1. Arsenic and arsenic compounds are apparently tolerated by man and other organisms at the levels found normally in the environment except in a few locales with high arsenic containing mineralogy.
2. The above review indicates that arsenic compounds are cumulative throughout the entire food chain and are possibly concentrated upon bottom sediments. While man, fish, plants, and wild life are capable of tolerating most natural arsenic concentrations all are sensitive to toxic effects at relatively low dosage.
3. Currently available treatment for arsenic and arsenic compounds is capable of maintaining an effluent concentration of 0.05 mg/l. While higher effluent concentrations are reported for some wastes, filtration of the settled effluent should be capable of maintaining a final concentration of 0.05 mg/l.
4. Further literature review and research is needed to define the best available treatment technology.

Arsenic and arsenic compounds may be contributed to the aquatic environment, and to its food chains, by the precipitation of arsenic-bearing atmospheric particulates. This represents a source of arsenic uncontrollable by effluent standards, and necessitates the strictest possible limits on the controllable effluents. It is essential that the concentration of arsenic compounds in our nation's waters be kept to an absolute minimum. Even with minimum achievable

levels in receiving waters, arsenic may still be concentrated to a certain degree upon bottom sediments. This of itself necessitates the use of filtration where arsenic is a potential problem in a discharge.

It is, therefore, recommended that a uniform effluent limit of 0.05 mg/l be adopted at this time. When improved treatment technology becomes available, it should be applied to maintain arsenic levels at the lowest level possible. An arsenic concentration of 0.05 mg/l should be safe for human consumption.

CHAPTER II-BARIUM

Salts of barium are found naturally in soils and unweathered rock, hence, small concentrations are found in rivers and sea water. Barium salts are used extensively in the metallurgical, glass and ceramics, rubber, dye, explosives, concrete, and paint industries (66,76).

Table II-1 shows some naturally occurring levels of barium. The range in drinking water is from less than 0.0006 mg/l to as high as 3.0 mg/l.

Table II-2 is a list of the most commonly used barium salts in agricultural and industrial establishments. Also listed in that table is the maximum solubility of the salt between 10°C and 90°C (61,66).

ENVIRONMENTAL EFFECTS OF BARIUM

Effect on Man

The alkaline earth metal, barium, and its salts are toxic to man, animals, fish and other aquatic life in varying degrees. Table II-3 lists some of the toxic levels of various salts. Unlike other metals and toxic substances, barium has been studied extensively with respect to toxicity levels and time of exposure. It can be seen that a dose of 550-600 mg of barium is fatal to man.

The salts of barium are muscle stimulants, especially of the heart. Barium acts by constricting the blood vessels creating an increase in blood pressure. Barium sulfate when aspirated may cause granuloma of the lung and other sites in man. It is further reported

that deposition of insoluble forms of barium in sufficient amounts at localized sites may cause chronic irreversible changes in tissues (94).

According to McKee and Wolf (66), the fact that barium is excreted more rapidly than calcium indicates that there is little chance of a cumulative effect within the human body. Actual studies confirm that barium does not accumulate in the bone, muscle, kidney, or other tissue (66,94).

TABLE II-1

NATURALLY OCCURRING LEVELS OF BARIUM (59)

<u>Source</u>	<u>Conc.</u>
Various River Basins	0.015 - .090 mg/l
Rivers, selected	0.009 - .152 mg/l
N. Atlantic Slope Basin	0.010 - 0.150 mg/l
Drinking Water	0.0006 - 3.000 mg/l

TABLE II-2

COMMONLY USED BARIUM SALTS (66)

<u>Salt</u>	<u>Solubility</u>	<u>Industry Use*</u>
Barium Acetate	588 g/l	3, 4, 5
Barium Carbonate	22 mg/l	1, 2
Barium Chloride	393 g/l	2, 3, 4, 5
Barium Nitrate	50 g/l	6, 7, 8
Barium Sulfate	1.15 mg/l	2, 3, 4, 5, 9
Barium Silica Fluoride	260 mg/l	10, 11

* Industry Use is defined as follows:

1. Natural rock weathering
2. Chemical industry
3. Dry and Tanning
4. Textiles
5. Paint
6. Electronic
7. Pyrotechnic
8. Petroleum
9. Rubber
10. Glass
11. Metal Manufacture

On the basis of the threshold limiting values in industrial atmospheres, an estimate of the amount adsorbed into the bloodstream, and daily consumption of two liters of water, it is estimated that consumption of barium should be limited to 2.0 mg/l (66). McKee and Wolf (66) and the Drinking Water Standards (94) have recommended a limit of 1.0 mg/l to provide a safety factor and to allow for possible accumulation in the body.

Effect on Plants

According to the data provided by McKee and Wolf, barium is present in most soils, however, it is not utilized by most plants. Barium is considered to be poisonous to them (66).

Effect on Fish and Other Aquatic Life

The lethal concentration of barium in fish and aquatic life varies according to the form in which it is found. The lethal concentration limit of barium for sticklebacks is 400 mg/l (66). Goldfish have a concentration factor of approximately 150 for barium. While none of the other data reviewed indicates that other fish or aquatic life concentrate barium, it should be considered as a possibility.

A review of the effect of various barium salts on fish and aquatic life as reported in McKee and Wolf is summarized below (66):

Barium acetate at a concentration of 5 mg/l was found to have no effect on rainbow trout, bluegill sunfish, and sea lamprey during a 24-hour exposure.

Barium carbonate was found to have a 96-hour TLm greater than 10,000 mg/l for mosquito fish. However, it was noted that the limiting solubility of barium carbonate is 22 mg/l.

Barium chloride is reported to have harmed the nervous system of young silver salmon after a 72-hour exposure at a concentration of 50 mg/l. Barium chloride in Lake Erie water at 20-25°C was found to have threshold concentrations of 12 mg/l for Leptodora kindtii and 29 mg/l for Daphnia magna. Barium chloride was also found to have a lethal concentration of 10 mg/l on the aquatic plant, Elodea canadensis, and 11.1 and 14.3 mg/l on two different species of snails.

Barium nitrate has been found to be lethal in concentrations of 20 mg/l for two species of snails, 10 mg/l for Elodea canadensis and 200 mg/l for goldfish. In investigations of Lake Huron water at 12°C, a 24-hour exposure to Barium nitrate at a concentration of 5.0 mg/l had no effect on rainbow trout, bluegill sunfish, or the sea lamprey.

Barium sulfide at a concentration of 5.0 mg/l was investigated in Lake Huron water at 12°C and no effect on rainbow trout, bluegill sunfish, or the sea lamprey was indicated after a 24-hour exposure.

On the basis of the above data, McKee and Wolf recommended a maximum concentration of 5.0 mg/l of barium for fish and other aquatic life (66).

TREATMENT TECHNOLOGY - BARIUM REMOVAL

While there is not an extensive amount of literature available on the treatment of barium, Patterson and Minear (76) and Weston (97) have proposed the following methods for barium removal. The most likely method, according to both sources, is coagulation and precipitation of barium as barium sulfate. Weston indicates that filtration may be desirable for effluent polishing. Precipitation with sodium and ferric sulfate have also been reported as effective. Patterson and Minear pointed out that maximum theoretical solubility of barium sulfate is 1.4 mg/l (as barium). Ferric sulfate has been effectively used in removing the finer non-settleable barium sulfate precipitate and could eliminate the need for final filtration.

Other methods reported by Patterson and Minear include the use of adsorption by activated carbon, ion exchange, and electrodialysis. While no efficiency was reported for adsorption on activated carbon, an operating cost of 20 cents per thousand gallons was given. Removal of barium from nuclear waste was reported as 99.99% efficient and an efficiency of 99% removal from non-nuclear wastewaters was achieved. Electrodialysis similarly was reported as 99.9% efficient in the removal of barium.

While little cost data are available, Weston has indicated that coagulation and precipitation of barium with sodium sulfate followed by settling and filtration is capable of achieving a final barium effluent concentration of 1-2 mg/l at a capital cost of \$200 per thousand gallons for a 1 MGD plant; \$128 per thousand for a 10 MGD plant, and \$92 per thousand gallons for a 50 MGD plant. In relation

to the capital costs of a typical secondary sewage treatment facility, these capital costs range from 3-6 times less.

SUMMARY AND RECOMMENDATIONS

On the basis of the data discussed above, the following statements can be made:

1. It is apparent that barium may be found in the industrial wastewater from several industries including, but not limited to, metallurgy, glass manufacture, textiles and dyes, vulcanization of rubber, paints, tanning, embalming, electronics, pyrotechnics, and radioactive wastewaters.
2. Barium is toxic to man, animals, fish and aquatic life.
3. Based on the known toxicity to man, the maximum allowable concentration should be 1.0 mg/l. Based on barium's toxicity to fish and aquatic life, barium should not be discharged in concentrations greater than 5.0 mg/l.
4. Treatment by coagulation, precipitation, and filtration has been reported to reduce barium concentrations to an effluent level of 1-2 mg/l. Treatment by activated carbon, ion exchange, and electrodialysis has been reported to have high percentages of removal (over 99%). Removal of barium from industrial wastes by coagulation, precipitation, settling, and filtration are achievable at capital costs 3-6 times less than the cost of a typical secondary sewage treatment facility.

On the basis of the above statements, it is recommended that a

maximum uniform effluent criteria for barium be set at a concentration of 2.0 mg/l. Where an industrial or a municipal discharge containing barium is located immediately upstream from a domestic water supply intake, it is recommended that treatment be employed to maintain effluent concentration below 1.0 mg/l.

TABLE II-3

TOXIC EFFECTS OF BARIUM ON MAN AND ANIMALS (105)

<u>Compd</u>	<u>Species</u>	<u>Dose</u>	<u>Effect</u>
Ba ⁺⁺	Human	500-600 mg	Lethal
BaCO ₃	Human	800 mg	"
BaCO ₃	Rabbit	170-300 mg/kg	"
BaCO ₃	Rat	50-200 mg/kg	
BaCO ₃	Rat	800 mg/kg	LD ₅₀
BaCO ₃	Rat	1,480±340 mg/kg	LD ₅₀
BaCO ₃	Mouse	200 mg/kg	Lethal
BaCO ₃	Rabbit	170-130 mg/kg	LD ₅₀
BaCO ₃	Guinea Pig	1,000 mg/kg	LD ₅₀
BaCl ₂	Human	100 mg/kg	Lethal
BaCl ₂	Rat	250 mg/kg	LD ₅₀
BaCl ₂	Dog	90 mg/kg	LD ₅₀
BaCl ₂	Mouse	7-14 mg/kg	Lethal
BaCl ₂	Rat	355-533 mg/kg	"
BaCl ₂	Dog	90 mg/kg	"
BaCl ₂	Horse	800-1,000 mg/kg	"
BaCl ₂	Rabbit	170 kg	"
Ba F ₂	Guinea Pig	350 mg/kg	LD ₅₀

TABLE II-3

TOXIC EFFECTS OF BARIUM ON MAN AND ANIMALS (105)

<u>Compd</u>	<u>Species</u>	<u>Dose</u>	<u>Chronic Effect</u>
Ba ⁺⁺	Human	None reported	vaso-constriction elevation of BP, muscle stimulant, especially heart
BaCl ₂	Rat	20 mg/kg/day 10 mg/kg/day for 6.5 mos.	changes in conditioned reflexes, slight tissue structure changes slight decrease in cholinesterase activity
Cl ₂	Rabbit	5, 2.5, +1 mg/kg/day 13.2 mos.	Decrease in cholinesterase activity at 5 mg/kg. No changes at other doses.

TABLE II-4

TOXIC EFFECTS OF BARIUM ON FISH AND AQUATIC LIFE

<u>Salt</u>	<u>Species</u>	Concentration, mg/l	<u>Reference</u>
BaCl ₂	Silver Salmon	158 72 hr LD ₉₀	(66)
BaCl ₂	Silver Salmon	282 100% kill in 23 hrs.	(66)
BaCl ₂	Plants (Elodea)	10 Lethal threshold	(66)
BaCl ₂	Snails	11.1 Lethal threshold	(66)
BaCl ₂	Snails	14.3 Lethal threshold	(66)
BaF ₂	Tinca vulgaris	10,000 Lethal threshold	(66)
BaNO ₃	Snail	20 Lethal threshold	(66)
BaNO ₃	Elodea	10 Lethal threshold	(66)
BaNO ₃	Goldfish	200 Lethal threshold	(66)
BaCO ₃	<u>Gambusia affinis</u>	10,000 Lethal threshold	(15)
BaCl ₂	<u>Daphnia magna</u>	83 immobilization threshold (48 hrs)	(15)
BaCl ₂	<u>Daphnia magna</u>	29 immobilization threshold (64 hrs)	(15)
BaCl ₂	<u>Gambusia affinis</u>	3,200 Lethal threshold	(15)
BaCl ₂	Rana sp. (eggs)	24,430 Lethal threshold	(15)
BaNO ₃	<u>Gasterosteus aculeatus</u>	400 Lethal threshold	(15)
BaCl ₂	Mosquito fish	1640 96 hr. TL _m	(66)
BaCl ₂	Young eels	2083 36 hr. TL _m	(66)

CHAPTER III

BIOCHEMICAL OXYGEN DEMAND AND SUSPENDED SOLIDS

IDENTIFICATION OF THE PARAMETERS

Biochemical oxygen demand (BOD) and suspended solids (SS) are two of the most commonly used parameters to describe effluent qualities.

The decay of organic matter washed into streams during a rainfall will exert a BOD. Natural erosion may result in a suspended solids concentration. In addition to natural sources, domestic and industrial wastewater discharges also contain substantial amounts of BOD and suspended solids. Various sources and concentrations found in the material studied are summarized in Table III-1.

BOD

The BOD test is a measurement of the oxygen required by living organisms (bacteria) to decompose organic material under aerobic conditions. It is a laboratory procedure, which is intended to represent, in a controlled environment, that which would occur under normal stream conditions. The oxygen demand is exerted by three classes of materials: carbonaceous organic material, that which is utilized by bacteria under aerobic conditions as a source of food; nitrogenous organic material (or oxidizable nitrogen of nitrite, ammonia, and organic nitrogen) that which serves as food for the specific Nitrosomonas and Nitrobacter bacteria; and reducible inorganic compounds (such as ferrous iron, sulfite, and sulfide).

TABLE III-1

SOURCES OF BOD AND SUSPENDED SOLIDS

<u>Source</u>	<u>Flow (MGD)</u>	<u>BOD (mg/l)</u>	<u>SS (mg/l)</u>	<u>Reference</u>
<u>Domestic Waste</u>				
Strong	---	300	500	(11)
Medium	---	200	300	(11)
Weak	---	100	100	(11)
Digester Supernatant	---	---	17,100	(80)
Digester Supernatant	---	---	740	(80)
<u>Food Industry</u>				
Cannery, Soup	---	616	263	(43)
Dairy, Cheese	.0072	840-1380	---	(84)
Dairy, Cheese	.0072-.072	1530-2220	---	(84)
<u>Seafood</u>				
General Fish Processing		2700-3440	2200-3020	(87)
Bottom Fish Processing		1726 192-640	---	(87)
Fish meal: cooling water		621	---	(87)
process water		1005	---	(87)
Herring Pump Water		---	---	(87)
Stickwater	--- 56,000-112,000		---	(87)
Rendering Waste		42,000	19,700	(87)
Salmon Cannery	.043-.046	3660-3900	508-4780	(87)

TABLE III-1 (Cont.)

SOURCES OF BOD AND SUSPENDED SOLIDS

<u>Source</u>	<u>Flow (MGD)</u>	<u>BOD (mg/l)</u>	<u>SS (mg/l)</u>	<u>Reference</u>
Salmon Cannery	.33	3860	2470	(87)
Salmon Curing	.011-.66	173-3082	40-1824	(87)
Transport Flume Water		200-1150	400	(87)
Waste Flume		100-2200	100-2100	(87)
Tuna Processing	---	895	1091	(87)
Fruits & Vegetables	---	840-2400	---	(61)
Citrus Plant	2.0	1170	---	(53)
Cannery Waste: (screened)				
Pear	0.01-1.87	1600-2040	770	(35)
Peach	0.30-2.02	860-1810	830	(35)
Apple	0.43-0.60	950-1390	470-540	(35)
Municipal-Cannery	2.0	141-424	---	(46)
Meat Processing	---	1000	---	(98)
Poultry	---	150-2400	100-1500	(61)
Poultry		712	530	(25)
Packing House	---	400-3000	230-2000	(61)
Slaughterhouse	---	200- 800	930-3000	(61)
Slaughterhouse	0.0235	1700	---	(50)
<u>Petrochemical Industry</u>	---	10-250,000	---	(44)
Mixed Chemicals	---	1950	27-60	(45)
Refinery, Detergent Alkylate		345	121	(45)
Refinery, Butadiene, Butyl Rubber		225	110	(45)

The five-day BOD as determined in the laboratory, generally represents from 44%-94% of the ultimate BOD, depending on the rate constant (K). Recent investigations of pulp and paper mill waste papers, however, have indicated that due to the extremely low rate of biological attack on lignin, less than 50% of the ultimate BOD is found in the 100 day period (77).

The BOD₅ test is performed at a constant temperature of 20°C, which is well within the range of natural stream temperature. Similarly, the dilution water used is enriched and buffered with potassium, phosphate, calcium, magnesium and ammonium salts solutions to maintain favorable nutrient and pH conditions throughout the test.

SUSPENDED SOLIDS

The 13th edition of Standard Methods (1) defines suspended solids (non filtrable) as that portion of material in a liquid sample which is retained on a filter. In general terms, suspended solids may be considered to be the colloidal material or the difference between total solids and dissolved material.

Standard Methods points out that the principal factors involved in the analytical procedure are: the chemical and physical nature of the material in suspension, the pore size of the filter, the area and thickness of the filter mat, and the amount and physical state of the material being retained on the filter. Because the residue determination is subject to several variables it does not have the accuracy of some analytical procedures. The temperature at which the residue is dried is important because the weight of the sample may be increased or decreased accordingly. For example, volatili-

zation of organic matter, water of crystallization and gases from heat-induced chemical decomposition may be responsible for losses in weight, while oxidation and absorbed atmospheric moisture may cause a gain in weight.

ENVIRONMENTAL EFFECTS OF BOD AND SUSPENDED SOLIDS

The basic effect of both suspended solids and BOD discharges on receiving waters is (1) the reduction of the dissolved oxygen level in the receiving waters through immediate and short term oxygen demands, (2) the deposition of solids which through decomposition of benthic deposits exert a continuous oxygen demand and (3) the concentration of toxic compounds. Biological flocculation can cause solids to settle out in streams, creating sludge banks, septic conditions, odors and general unsightliness. While BOD may enhance the growth of some viruses and bacteria, it will have a deleterious effect on other aquatic organisms, through depletion of the dissolved oxygen in the stream. The concentration effect of some trace metals such as arsenic, cadmium and mercury is discussed in other chapters.

Effect on Man

The presence of biological suspended solids and associated BOD₅ is an indicator of the potential presence of pathogens. It is recommended (6) that domestic water supplies have a dissolved oxygen level of 4 mg/l on the average, and never less than 3 mg/l. High concentrations of BOD₅ reduce the dissolved oxygen of the stream and thus indicates the presence of organic pollution. Suspended

solids are easily monitored continuously and can be used to control possible turbidity and trace metal concentrations.

Effect on Plants

There is insufficient information available on which to base definite limits on BOD or dissolved oxygen levels for irrigation water (6). It is noted, however, that the utilization of waters having high BOD or COD values are capable of aggravating conditions, by further depletion of the available oxygen and by production of conditions in the soil which may reduce trace metals. When the dissolved oxygen level is decreased, elements such as iron and manganese may be reduced to the more soluble divalent forms. Reduced forms of some metals are toxic.

It is known that suspended solids are capable of interfering with the flow of water in conveyant systems and other structures. In general, suspended solids are known to precipitate and settle when the velocity decreases to two feet per second. Suspended solids can decrease the storage capacity of reservoirs and create excessive abrasion on structures, pipes and pumps. Suspended solids can cause crust formations on soils, thereby reducing the infiltration rate and the emergence of seedlings. The beneficial use of BOD and suspended solids, however, have been well documented with respect to the irrigation of sandy soils of low organic matter. The effect of BOD and suspended solids on soils and plants varies with respect to the permeability and type of soil which receives the discharge.

Effect on Domestic Animals and Wildlife

For animals and wildlife (as for man), it is important to control BOD and suspended solids to maintain an adequate dissolved oxygen level in the water and to insure a minimum concentration of disease producing organisms. Areas used by waterfowl, for example, must be kept aerobic to suppress Botulinus organisms which have been reported to have killed millions of waterfowl (6).

Effect on Fish and Aquatic Organisms

As with many pollutants, the discharge of BOD and suspended solids to receiving waters has a major impact upon the fish and aquatic life present in those waters. The discharge of raw domestic sewage and certain improperly treated industrial discharges (such as from paper and pulp and sugar industries) have been shown to stimulate growth of Sphaerotilus bacteria. Heavy growths of Sphaerotilus are well known for fouling fishing lines, clogging nets, and generating unsightly conditions. The metabolic demands of both living and decomposing Sphaerotilus impose a high BOD load on the stream. Large populations of Sphaerotilus may render the habitat noxious to animals, thereby excluding desirable fish and invertebrates.

Most of the research concerning oxygen requirements for fresh water organisms deal with fish (6), however, it is logical to assume that a requirement for fish would also serve the rest of the aquatic community. On the basis of investigations of the various effects of low dissolved oxygen on fish life, it was recommended (6) that for

diversified warm water biota, including game fish, the daily dissolved oxygen concentration should be greater than 5 mg/l. Due to expected daily and seasonal fluctuations, a dissolved oxygen level between 4 and 5 mg/l can be withstood for short periods, though. Similarly, for cold water biota the dissolved oxygen concentration should be near saturation. It is noted that this is especially important in spawning areas, where the dissolved oxygen concentration should not be less than 7 mg/l at any time. On the basis of supporting growth and propagation of trout, salmon and other cold water species of the biota, a dissolved oxygen concentration of at least 6 mg/l should be provided at all times. With respect to dissolved oxygen levels of small and large oligotrophic lakes, it was recommended that the hypolimnion not contain less than 6 mg/l oxygen at any time.

Investigations of the marine environment revealed that satisfactory survival and growth of marine organisms are supported by a dissolved oxygen level ranging between 5 and 8 mg/l. Studies on marine animals have shown that a dissolved oxygen level less than 1.25 killed most of the marine test animals within a very few hours. It was therefore recommended that the surface dissolved oxygen concentration of coastal waters be not less than 5 mg/l, except for natural variations (6). With respect to estuaries and tidal tributaries, it was recommended that the dissolved oxygen level should not be less than 4.0 mg/l at any time, except for natural variations.

TREATMENT TECHNOLOGY - BOD AND SUSPENDED SOLIDS

In reviewing current engineering text, one is readily cognizant that flowing streams have an ability to recover from biological load-

TABLE III-2

RELATIVE EFFICIENCIES OF SEWAGE TREATMENT (37)

<u>Treatment Operation or Process</u>	Percent Removals	
	<u>BOD</u>	<u>SS</u>
Fine Screening	5-10	2-20
Plain Sedimentation	25-40	40-70
Chemical Precipitation	50-85	70-90
Trickling filter preceded and followed by plain sedimentation	50-95	50-92
Activated sludge preceded and followed by plain sedimentation	55-95	55-95
Stabilization ponds	90-95	85-95

ings. The ability to utilize self purification of streams as a safety factor, has been aptly discussed by Fair, Geyer & Okun (37). Their report includes the following quotation: "The removal of 90-95% of the suspended solids, BOD, and COD of wastewaters before the discharge of effluents into receiving waters is not considered enough, nor is a subsequent natural purification of receiving waters for reuse by man accepted as sufficiently rigorous to assure the safety and palatability as well as the general usefulness of such waters." We are thus faced with the question of not what can the river take and survive, rather, what can be done with currently applicable technology within reasonable cost to enhance the quality of our resources.

Removal of BOD and suspended solids from industrial and municipal wastewaters may be achieved by physical, chemical and biological operations and/or processes or a combination of all three. The respective removal efficiencies which one can anticipate from various treatment operations and processes are summarized in Table III-2 from Fair, Geyer and Okun (37).* As may be seen from the table the greater efficiency of both BOD and suspended solids removal is achieved through biological processes. A report by Stewart (92) on the various modifications of activated sludge indicates that biological processes may be loaded over a wide range with respective degrees of removal. A tabulation of the twelve more common modifications of the activated

* One should realize, however, that when the data in this table were prepared, many of the newer process and operation modifications were not in use.

sludge process are summarized in Table III-3.

In addition to the standard procedures of Tables III-2 and 3, treatment technology for BOD and suspended solids removal during the last several years has made substantial improvements. Among these are the tube settlers, microscreens, ultrafiltration, multi-media filtration, upflow clarifiers, and moving bed filters. A summary of these improvements and their effectiveness for removal of BOD and suspended solids, in the form of additional treatment steps and as substitutes for secondary type treatment, is given in Table III-4 from the work of Convery (26) and the EPA Technology Transfer Manual on Suspended Solids Removal (23).

Suspended solids are associated not only with biological process waste, but also with chemical treatment. As a great deal of the suspended solids are found in the colloidal state, one should consider the mechanisms of removal which are described by Nemerow (72) and Rich (78,79). Colloidal solids may be removed by chemical coagulation, neutralization of the electrical charge, and adsorption. Removal of colloidal solids by chemical coagulation requires the formation and precipitation of insoluble metal hydroxides and oxides or interaction with organic polymers having charged sites. Neutralization of the electrical charge involves lowering of the zeta potential and/or neutralization of the colloidal charges with an excess of oppositely charged ions. In the presence of an excess of oppositely charged ions, hydrous oxides are formed which enhance both chemical coagulation and adsorption. Adsorption is a surface phenomenon in which organic and/or inorganic matter is adsorbed on a material.

TABLE III-3

EFFICIENCY OF ACTIVATED SLUDGE MODIFICATIONS (92)

<u>Process</u>	<u>Loading Factor</u> <u>Lb. BOD/Day/1000 cu. ft.</u>	<u>Percent Removal</u> <u>BOD₅</u>
Extended Aeration	20	75-85
Conv. Activated Sludge	35	95+
Tapered Aeration	35	95+
Step Aeration	50+	90-95
Activated Aeration	50+	80-85
Contact Stabilization	70	85-90
Hatfield Process	70+	85-90
Kraus Process	100	85-90
High Rate	100	60-75
Modified Aeration	100	60-75
Rapid Bloc	150+	90-95
Supra Activation	400	55-65

Good adsorbents have active or activated surfaces with a high surface to volume ratio.

In addition to the interrelationships of chemical coagulation, neutralization, and adsorption processes for the removal of colloidal solids, a polishing step such as rapid and/or multi-media filtration is beneficial. Other methods utilized for the removal of suspended solids include flotation and microscreening.

From the above discussion, it is apparent that BOD and suspended solids may be removed from municipal and industrial wastewaters. Typical percentages of BOD removal range from 75-95%. Suspended solids removal in terms of percentage is found to parallel the percentage removal of BOD. Likewise, as the suspended solids are reduced, so are the levels of many other pollutants. A summary of the data found in the literature with respect to industrial waste and information from "Deeds and Data" (4) is shown in Figure III-i. It is apparent from the data plotted in Figure III-i that a relationship does exist between the effluent BOD and effluent suspended solids levels. In a well designed and operated biological treatment system, the soluble portion of the BOD in the effluent will be extremely small with respect to the portion of BOD which is associated with the suspended solids. Thus, by removal of the suspended solids after biological treatment and clarification, one can expect that not only will the suspended solids be greatly reduced, but the BOD will also be reduced.

By referring to Figure III-i it is apparent that for a biological effluent with a suspended solids level of 60 mg/l, a BOD of approximately 80 mg/l would be expected, however, it could possibly range

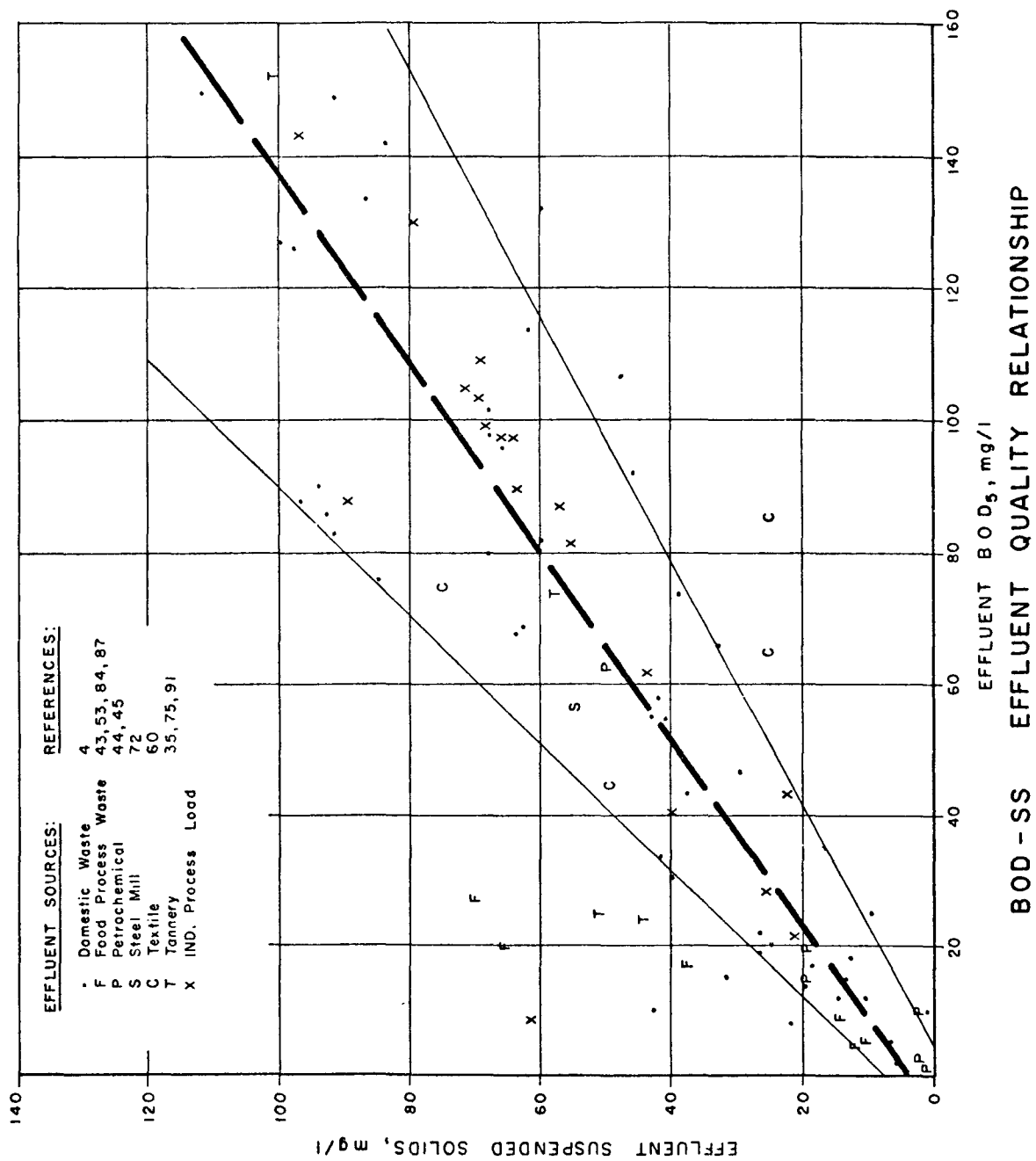


FIGURE III - i

between 50 and 120. In the lower portion of the figure, the suspended solids appear to vary more widely than does the BOD. This indicates that at a lower range of BOD one is speaking almost strictly of a soluble BOD which has not been removed by biological treatment, rather than one associated with suspended solids. It also appears that as the suspended solids approach zero, the remaining BOD is soluble and not suspended. It, therefore, appears logical to conclude that should the waste with a suspended solids level of 60 mg/l and a BOD level of 80 mg/l be further treated for the removal of suspended solids to a level of 20-30 mg/l, the associated BOD will also be removed with only the soluble BOD remaining. From the figure, a residual BOD of 10-30 mg/l could be expected.

In consideration of the data shown in Figure III-i, and the achievable final effluent levels associated with suspended solids, the soluble portion of the BOD in the effluent may be expected to vary with respect to the activated sludge or other biological treatment process. For example, a treatment plant utilizing a high rate biological system could have a substantially greater amount of soluble BOD in the effluent than one using the contact stabilization or extended aeration modification of activated sludge.

TREATMENT SUMMARY:

From the above discussions, it is apparent that the technology does exist for the removal of BOD₅ and SS. It is rather a matter of the application of the technology. Some industries as shown in the previous section, have accepted the challenge and are currently

achieving treated effluents with BOD₅ less than 30 mg/l and SS less than 30 mg/l.

It is recognized that, in general, biological processes lose their peak efficiencies during cold winter weather. They are capable of maintaining a final effluent of less than 75 mg/l, however. As streams naturally have higher D.O. levels, due to greater oxygen transfer in the winter, slightly higher BOD₅ loadings may be handled without creating problems. Weather, however, does not affect the impact of suspended solids on the receiving waters. Therefore, the suspended solids level of all discharges should be maintained below 30 mg/l year around.

It is also recognized that natural conditions such as, surface runoff may add significant loads of suspended materials on the receiving waters. This must not be an excuse to add further to the problem through industrial and municipal discharges. Rather, it is the reason and need to improve management practice of agricultural lands, urban storm runoff, etc.

SUMMARY AND RECOMMENDATIONS

On the basis of the literature reviewed and the above discussions, the following conclusions are drawn.

- 1) Material which exerts a biochemical oxygen demand and suspended solids are found in surface waters from many natural and man-made sources.
- 2) The major impact of BOD is through the depletion of oxygen in the receiving waters.

- 3) Suspended solids exert an impact on the receiving waters by creating sludge banks, general unsightliness, acting as an adsorbent for toxic chemicals, destroying of fish spawning grounds, creating excessive wear on transport facilities, and by depleting the storage capacities of impoundments.
- 4) Domestic water supplies should contain neither BOD nor SS as both can be associated with disease producing organisms and virus.
- 5) Waters used on plants should not contain excessive amounts of BOD or SS.
- 6) Sandy soils may be used effectively for waste disposal. The extent of this use depends upon the organic content of the soil and its permeability.
- 7) BOD and SS must be kept to a minimum to insure adequate dissolved oxygen to suppress Botulinus organisms.
- 8) BOD and SS must be maintained at minimum levels to ensure adequate dissolved oxygen for fish and aquatic life in both fresh and marine waters.
- 9) The technology currently exists to remove 5 day BOD and SS to effluent concentrations less than 30 mg/l, each.
- 10) Cold temperatures may decrease the performance of biological treatment processes. However, an effluent level of 75 mg/l should be attainable by biological means during cold weather.
- 11) Removal of suspended solids from biologically treated waste effluents will also remove the associated BOD of the flocculant solids.

- 12) Effluent BOD₅ below 20 mg/l will most likely be in a dissolved state and may not be further removed with SS unless treated further.
- 13) Removal of colloidal suspended solids from chemically treated wastewaters is often necessary to maintain low effluent levels of trace metals.
- 14) The removal of oil and grease residuals after biological treatment can be improved through better suspended solids removal.

On the basis of these conclusions and the text of this report, it is recommended that the following effluent limits be adopted:

Suspended Solids: Maximum level of 30.0 mg/l at all times.

Biochemical Oxygen Demand-5 Day: The BOD₅ shall not exceed a 24 hour average of 30 mg/l for three (3) consecutive days, except during winter when the 24 hour average shall not exceed 75 mg/l for three (3) consecutive days

For EPA Region III it is recommended that "winter" apply to the months of December through February in the southern area and November through March in the northern most areas.

It is further recommended that the BOD₅ not exceed a concentration of 90 mg/l at any time.

TABLE III-4

EFFICIENCIES OF NEW PROCESSES & OPERATIONS FOR BOD₅ AND SS REMOVAL (23,26)

Process or Operation	Flow MGD	SUSPENDED SOLIDS		BOD ₅	
		Conc. (mg/l)	Percent Influent Effluent Removal	Conc. (mg/l)	Percent Influent Effluent Removal
Tube Settlers	0.13	50-80	5-30		
Hopewell, Pa.	0.13	60-70	27 ave		
Ontario, Ca.			28 ave		
Microsereens					
Screen size	3.6			55	30
microns	7.2			66	32
	0.3			80	
	0.1			57	54
	2.0			71	74
	Pilot			89	81
	Pilot			73	61
	0.165			99	96
Ultrafiltration		129	0	100	1
Multi-Media Filtration				285	99
Highrate Trickling Filter Eff.			10-20		
2-Stage Trickling Filter Eff.			6-15		
Contact Stabilization Eff.			6-15		
Conv. Activated Sludge Eff.			3-10		
Extended Aeration Eff.			1-5		
Step Aeration & Coagulate Eff.	30		8		
Upflow Filters					
Moving Bed Filter			less than	85	
on Raw Domestic Waste			5		
Primary Effluent	156	27		115	19
Unsettled Trickling Filter Eff.	77	11		67	12
Clarified Trickling Filter Eff.	86	7		55	4
2-Stage Lime: Wash. D. C.	50	15		65	12
		15		139	42
					69.7

TABLE III-4 (cont)

Process or Operation	Flow MGD	SUSPENDED SOLIDS		BOD ₅	
		Conc. (mg/l)	Percent Influent Effluent Removal	Conc. (mg/l)	Percent Influent Effluent Removal
w/Filter				139	28
w/carbon				139	4
1-Stage Lime:					
w/Filter	85	10		76	25
w/carbon	85	1		76	10
					67
					87

CASE STUDIES OF BOD₅ & SS REMOVAL

A. Food Industry

A new addition to the realm of biological treatment processes is the BIO-DISC. The BIO-DISC system consists of closely spaced, round discs mounted on a horizontal shaft. Functionally, it combines the principles of trickling filters and activated sludge. It has been reported by Antonie (10) to be effective both in pretreatment and as a secondary treatment process. Treatment efficiencies BOD₅-removal are summarized in Table III-5. As a biological process it is capable of achieving a final BOD₅ effluent in the range of 17-55 mg/l.

In treating dairy cheese waste for a cheese factory in Hilbert, Wisconsin, in a two stage aerobic "Cavitator" system, Schulze (84) reported the following efficiencies:

1. A BOD₅ concentration of 840-1380 mg/l was reduced to an effluent of 12-18 mg/l. The loading was 80 lb. BOD/D, detention 20 hr. and flow 7200 GPD.
2. A BOD₅ concentration of 1530-2220 mg/l was reduced to an effluent of 15-29 mg/l. The loading was 140 lb BOD/D, detention 12 hr. and flow 7200-72,000 GPD.

A report by Soderquist, et al. (87) discussed the treatment of fish processing wastes by coagulation, flotation, and activated sludge. Clarification with 4000-5000 mg/l F-FLOK coagulant on Salmon process waste reduced total solids from approximately 2000 mg/l to about 800 mg/l. Eighty to 92% of the protein was also recovered by this method. Breaking of fish oil emulsions with clay, lime, alum, and ferric chloride has been reported as 75% effective in BOD removal. The

chlorination required prior to sedimentation reduced suspended solids to about 200 mg/l and BOD to 400 mg/l. Flotation with coagulant aids on salmon processing wastes was also reported as partially effective in BOD and solids removal. The results are summarized in Table III-6. An activated sludge pilot plant treating fish process waste reduced suspended solids from 320 mg/l to 12-70 mg/l, BOD₅ from 1000 mg/l to 5-27 mg/l, and Total N from 70 mg/l to 35-51 mg/l.

By utilizing spray irrigation on terraced land, Gilde (43) reports that food processing waste from Campbell Soup Company was treated to the following effluent characteristics.

<u>Parameter</u>	Mean Concentration, mg/l	
	<u>Wastewater</u>	<u>Effluent</u>
Total Suspended Solids	263	16
Total Organic Carbon	264	23
BOD ₅	616	9
Total Phosphorus	7.6	4.3
Total Nitrogen	17.4	2.8

The design criteria from the Paris, California, study (43) included a slope recommendation of greater than 2% but less than 6%, with a 150-175 foot zone between the sprinklers and the effluent collection berm. The application rate was 0.25 inch per day in winter and 0.50 inch per day in summer. The plots were planted with Reed Canary grass. In a recent report on fruit processing waste, Exvelt 35 reported that raw waste loads in the range of 860-2040 mg/l BOD₅ can be reduced by aerobic treatment to an effluent of less than 10 mg/l when the unit is loaded at 0.5 mg BOD removed/mg MLVSS-Day.

TABLE III-5

BIO-DISC OPERATING EFFICIENCY (10)
BOD₅ Conc, mg/l

<u>WASTE WATER</u>	<u>Influent</u>	<u>Effluent</u>	<u>Percentage REMOVAL</u>	<u>Residence TIME, hr.</u>
Dairy:				
Fresh	1000	300	70	0.3
		30	97	2.5
Septic	1100	55	95	5.0
	850	17	98	2.9
Brewery:	600	300	50	0.2
		30	95	0.5
Bakery:	2000	350	85	2.8
Septic	1200	480	80	2.2
Combined Domestic & Industrial	600	30	95	1.1
Distillery:	800	40	95	0.7
Piggery: Septic	500	50	90	2.2

TABLE III-6FLOATATION WITH COAGULANT AID (87) ON SALMON WASTE WATERS

<u>COAGULANT</u>	<u>BOD</u>		<u>TS</u>		<u>SS</u>	
	<u>INF.</u>	<u>EFF.</u>	<u>INF.</u>	<u>EFF.</u>	<u>INF.</u>	<u>EFF.</u>
Alum 47 mg/l	-	-	5400	1560	-	-
" "			2290	1200	-	-
Ferric Chloride 60 mg/l	-	-	5580	2400	-	-
" " "	-	-	2860	950	-	-
" " 133 mg/l	-	-	1800	1180	-	-
F-FLOK 1000 mg/l	-	-	5900	1200	-	-
Aluminum Hydroxide 75 mg/l	1775	425	2685	1505	640	1305
Zetol A 1 mg/l	1275	381	2441	1625	697	200
Alum 375 mg/l plus lime 75 mg/l	2833	633	4268	2162	1993	397

It is apparent from Exvelt's report that good solids removal is mandatory for low BOD in the effluent. The results of Exvelt's studies are summarized in Table III-7 below. The new plant was put into operation between the 1968-69 season. The last 3 data sets are the most significant.

Graham and Filbert 46 have reported that a combined municipal cannery waste with a combined BOD₅ concentration of 141-424 mg/l has been reduced to an effluent of 16 mg/l or less, 96 percent of the time. Treatment consists of aeration basins with sludge return, clarification, and chlorination. They also report an effluent of 3.2 mg/l orthophosphate (as PO₄) which was a reduction over the influent. The average flow was 2.0 MGD.

In treating slaughterhouse waste, Hopkins and Dutterer (50) noted a BOD₃ removal from 1700 mg/l-10 mg/l. The 23,499 GPD plant utilized screening grease separation by air flotation and skimming, agitation, activated sludge, chlorination, and ponding.

Merrill 68 reported settleable solids removal from 3788 and 3339 mg/l to 561 and 38 mg/l, respectively from frozen meat packing wastes. Treatment by air flotation of grease, alum (Al₂(SO₄)₃) coagulation extended aeration, clarification and chlorination yielded a final effluent of 17 mg/l (85-95% removal).

A poultry processing plant in West Germany is reported by Wieferig 98 to have reduced 1000 mg/l BOD₅ from its wastewater to an effluent of less than 25-30 mg/l. Treatment consisted of surface aeration after removing fat, feathers and solids.

TABLE III-7

AEROBIC TREATMENT OF CANNERY WASTE (35)

Fruit Processed	Screened Waste			Effluent		SS mg/l
	Flow MGD	BOD mg/l	COD mg/l	BOD mg/l	COD mg/l	
A. <u>Aerated Lagoon Effluent:</u> Cost \$0.041/#BOD Removed						
1967 Pear	1.03	2040	3050	370	1040	770
1967 Peach	1.36	1810	2150	340	-	830
1967 Apple	NOV DEC	0.60	1230	1520	190	760
1968 Apple	JAN FEB	0.52	950	1400	110	620
B. <u>Activated Sludge:</u> Cost \$0.061/#BOD Removed						
1968 Pear	0.21	2040	3050	250	490	375
1968 Peach	0.30	1810	2150	360	-	370
1968 Apple	MAR APR MAY	0.40	1390	1830	130	570
1969 Peach	2.02	860	1510	20	120	66
1969 Pear	1.87	1600	2290	9	55	15
1969 Apple	0.43	1190	1500	5	28	11
C. <u>Contact Stabilization:</u> Cost \$0.067/#BOD Removed.						
1969 Pear	1.58	2150	2910	4	23	6

Camp (25) ,in describing in-house changes for a poultry process in Florida, reported that by improving plant operating practices the average flow rate was decreased from 422 gpm to 357 gpm. The BOD₅ was also reduced from 712 mg/l to 263 mg/l. Improvements included cleaning of traps and separators, reducing spills and improving dry clean-up procedures prior to wash down.

TABLE III-8

ACTIVATED SLUDGE TREATMENT OF PERTOCHEMICAL WASTES
from Gloyna & Ford (44)

Product and/or Process	Flow (MGD)	In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)	Organic Loading lb BOD ₅ / day	Nutri- ents Read.
Refinery, Natural Gas Liquids, Chemical Specialties Sanitary Sewage	4.87	90	20	78	200	90	55	0.1	None
Phthalic Anhydride, Phenol, Salicylic Acid, Rubber Chem, Aspirin, Phenacetin	2.54	45.7	6.1	86.7				0.031	None
Refinery, Detergent Alkylate	2.45	345	50- 100	71- 85.5	855	150- 200	76.6- 82.5	0.08	PO ₄
Butadiene Maleic Acid	2.0	2,000	25	98.8	2,990	480	84	0.24	NH ₃
Butadiene Alkylate	1.5	1,960	24	98.8	2,980	477	98.3		
Butadiene, Maleic Anhydride Fumaric Acid Tetrahydrophthalic, Anhydride, Butylene Isomers, Alkylate	1.5	1,960	24	98.8	2,980	51	84	0.24 (MLVSS)	NH ₃

TABLE III-8(Con't)

ACTIVATED SLUDGE TREATMENT OF PERTOCHEMICAL WASTES
from Gloyna & Ford (44)

Product and/or Process	Flow (MGD)	In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)	Organic Loading lb BOD ₅ / day	Nutri- ents Read.
Ethylene Propylene, Benzene	1.44	600	90	85	700	105	85		None
Naphthalene, Butadiene, Phenol, Acrylonitrile, Sodt Detergent Bases, Resins, Other Aromatics	0.43	500	60	85- 90	600	90	80- 85	1.5	NH ₃ PO ₄
Phenol, 2, 4-D Aniline, Nitro- Benzene, Rubber Chem., Polyester Resins Misc. Chem.	0.97	370	76	76.2				0.4	NH ₃ PO ₄
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oils	0.63	85	10	99	200	75	62.5		
Refining Processes	0.51- 0.63	125	15- 25	80- 88				0.28- 0.4	PO ₄
Nylon	0.4	1,540	250	83.8					
Petroleum Products	0.27	440	5	98.8	500	60	88		

TABLE III-8(Con't)
ACTIVATED SLUDGE TREATMENT OF PETROCHEMICAL WASTES
from Gloyna & Ford (44)

Product and/or Process	Flow (MGD)	In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)	Organic Loading lb BOD ₅ /day	Nutri-ents
Acrylic Fibers	0.252	2,260	118-226	90-95				0.4	
Acetone, Phenol p-Cresol, Diterp.-Butyl-p-Cresol Dicumyl Peroxide	0.216	3,560-4,400	1,030-750	71-83				0.89-1.1	
Resins-Formalin, Aminoplasts, Phaeonol-Formald., Epoxy Resins, Textile Aux.	0.2	890	444-266		50-70			0.8-1.2	
Ethylene and Propylene Oxides, Glycols, Morpholines, Ethylene-Diamines, Ethers, Piperzine	0.15	1,950	20	99	7,970-8,540	5,120-5,950	25-40	0.51	None
2, 4-D 2, 4, 5-T (Acid Wash Wastes)	0.1	1,670	125	92.5	2,500	500	80	0.78 (MLVSS)	NH ₃
Cracking, Isomerization of Butane and Naphthene, Alkylation,		1,100	55-110	90-95				0.5	

TABLE III-8(Con't)

ACTIVATED SLUDGE TREATMENT OF PERTOCHEMICAL WASTES
from Gloyna & Ford (44)

Product and/or Process	Flow (MGD)	In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)	Organic Loading lb BOD ₅ / day	Nutri- ents Read.
Benzene, Toluene, Alcohols, Ketones, Cresylic Acids									
Ethylene, Acetylene	20							0.23- 0.33	PO ₄
Nylon Manuf,- Adipic Acid				95			85	1.0	PO ₄
Aaidonitricz Alk. Organics								3.0	NH ₃

TABLE III-9

TRICKLING FILTER TREATMENT OF PETROCHEMICAL WASTES from GLOYNA & FORD (44)

Product and/or Process	Flow (MGD)	BOD			COD			Organic loading lb BOD ₅ /day 1,000 ft ³	Deficient Nutrients
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)		
Phenol, Salicylic Acid, Rubber Chem, Aspirin, Phenacetin, Phthalic Anhydride	2.59	190	58	69.5				40.5	None
	2.59	58	34	41.5				11.8	None
Plastics, Amines, Enzymes	1.06	1,960	37	98.1	2,660	230	91.5		
Ethylene, Propylene, Butadiene, Benzene, Polyethylene, Fuel Oil	0.63	170	85	50	400	200	50	89	None
Aliphatic Acids, Esters, Alcohols, Aromatics, Amines, Inorganic Salts	0.57- 0.86	1,100 2,300	23- 470	57- 99				42.1- 82 (Both fibers combined)	None
Theylene, Propylene, Butadiene, Benzene, Naphthalene, Phenol, Acrylonitrile, Saft Detergent Bases, Resins	0.43	1,300			1,500	450	60- 70	140	NH ₃
Pentaerythritol	0.118	5,080-	225-	95-				1st stage	NH ₃
Waste contains Formaldehyde, Sodium Formate, Methanol, Pentaerthritol		5,800	232*	96*				65	PO ₄ Yes

TABLE III-9

Product and/or Process	Flow (MGD)	In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)	Organic loading lb BOD ₅ /day 1,000 ft ³	Defi- cient Nutri- ents
Resins-Formaum, Aminoplasts, Phenol-Formal, Epoxy Resins, Textile Aus.	0.17			82.6				11.7	None
	0.03			89.3				14.6	None
Acrylic Fibers	0.32		13	30- 70	49	30- 70		50 84 1st stage 85 (as phenol)	NH ₃ PO ₄
Synthetic Resins- Phenol, Formalde- hyde, Fatty Acids, Phthalic Acid, Maleic Acid, Glycerol, Pentaerythritol, H.C. Solvents				95- 98				2nd stage 11.6-18.2 gpd/ft ³	

TABLE III-10

AERATED LAGOON TREATMENT OF PETROCHEMICAL WASTES from GLOYNA & FORD (44)

Product and/or Process	Flow (MGD)	BOD			COD			Organic loading lb BOD ₅ Acre day	Nutrients Required
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)		
Refinery Butadiene, Butyl Rubber	19.1	225	100	55	610	350	43	4,630	PO ₄
Refinery, Detergent Alkylate	2.45	345	50- 100	71- 85	855	150- 200	77- 83	6,300	PO ₄
Cyclohexane, p-Xylene, Benzene, Para- finic Naphtha, o-Xylene Gasoline Nylon Fibers	0.51	100	25	75				400	
Chemicals for Lubricating Oils	0.2	465	180	61	1,050	600	43		

Following the inplant reductions a treatment plant was designed and constructed to use segregated wastewater collection, surface settling, extended aeration, final settling and a four acre polishing pond. Operation record revealed a final clarifier effluent of 15 mg/l BOD₅ maximum, 8 mg/l average (98.5-99.5% removal) and a suspended solids level of 10 mg/l maximum, 6 mg/l average. The polishing pond effluent showed a BOD₅ of 8 mg/l maximum and 3 mg/l average.

B. Petrochemical Industry

The treatment of various petrochemical wastewaters was reported by Gloyna and Ford (44,45). Tables III-8,9,10 and 11 summarize their findings on BOD₅ removal efficiencies by activated sludge, trickling filters, aerated lagoons, and waste stabilization ponds, respectively.

C. Pulp and Paper Industry

A review of recent literature indicates that while activated sludge is the major method of treating pulp and paper wastewaters, chemical treatment is being tested in full scale facilities with success. In treating 125 kg/ton BOD by anerobic fermentation and aeration, Grishina and Izotova (47) report that the BOD₅ was reduced from 1000 mg/l to 20 mg/l. The effluent COD remained high, however, and a BOD:M:E ratio of 100:3:0.5 was necessary.

Dobolyi 29 reported a final effluent of 25 mg/l BOD and 430 mg/l COD for an intergrated mill pulping straw by the Kraft process. The waste was pre-treated by coagulation with 400 mg/l Fe SO₄ and 600 mg/l Ca(OH)₂ prior to biological treatment. In using activated sludge

TABLE III-11

WASTE STABILIZATION POND TREATMENT OF PETROCHEMICAL WASTES

Product and/or Process	Flow (MGD)	BOD			COD			Organic loading lb BOD ₅ Acre day	Nutrients Required
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)		
Refinery, Butadiene Butyl Rubber	19.1	100	50	50	350	200	43	Primary pond 91; Total ponds 46	None
Resins, Alcohols, Amines, Esters,	5	500- 1,000	400- 700	20- 60				96	None
Styrene, Ethylene	5	400- 700	25- 50	88 96				164	None
		25- 50	35- 30	40- 90				5	None
Butane, Propane, Nat. Gas, Ethanol, Ethyl Chloride, Polyethylene, Ammonia, H ₂ SO ₄	3.25	150	7-	90-	260			75	None
Refinery, Detergent Alkylate	2.45	50- 100	20- 50	50- 80	150- 200	120	20-	95	None
Plastics	1.69	686	186		1,681	590	65		

TABLE III-11 (cont)

Product and/or Process	Flow (MGD)	BOD			COD			Organic loading lb BOD ₅		Nutrients Required
		In (mg/l)	Out (mg/l)	Rem (%)	In (mg/l)	Out (mg/l)	Rem (%)	Acre	day	
Ethylene and Pro- pylene Oxides, Glycols, Morpho- lines, Ethylene- diamines, Ethers, Piperazine	0.15	20			5,120-	4,610-	10	25		None
					5,950	4,450	25			
Mixed Petrochemicals								75-	100	
								96		

on a Kraft mill waste, Ganczarzyk (40) reported BOD₅ removals of 85% for 25-65 mg/l in the effluent. The COD removal of 50% gave an effluent of 220-440 mg/l. In a report on water reuse optimization for a Kraft mill, Lyons and Eckenfelder 62 present the following summary, Table III-12.

D. Tanneries

Stanley 91 reported that typical standard raw waste loads (SRWL) from chrome tannery wastes range from 253-1323 mg/l BOD₅ and 100-1255 mg/l SS. The effectiveness of various biological processes are summarized below. The SRWL shown were after primary treatment.

Type Process	<u>BOD</u>	<u>SS</u>
	SRWL _ EFF	SRWL - EFF
Aerobic Lagoons	525 - 104	526 - 312
Anerobic - Aerobic Lagoons	1146 - 152	408 - 105
Activated Sludge	250/450 - 25/75	50/100 - 25/100
	Unknown - 25	Unknown - 52
	732 - 101	556 - 398
Trickling Filters	180 - 74	143 - 58
	124 - 24	90 - 45

Eye 36 reported that suspended lime was removed from vegetable tannery beam house waste by clarification with polyelectrolytes in the 10 mg/l range. Suspended Solids were reduced from 3000-5000 to 200-500 mg/l. The clarification step prior to further treatment also reduced the COD by about 50%. Blended clarified beam house wastes

and vegetable tanning waste contain 1000-1500 mg/l BOD₅; 2000-8000 mg/l COD, and total Kjeldahl nitrogen of 150 mg/l. Treatment by an anerobic-aerobic lagoon yielded an effluent with 20-330 mg/l BOD (200 mg/l aver.), 300-1700 mg/l COD (900 mg/l aver.), and total Kjeldahl nitrogen of 100 mg/l (aver.). In a similar study, Parker (25) reported the treatment of vegetable tannery waste by activated sludge. The results of his study are summarized in Table III-13. They show the affect of different loadings and detention.

E. Textiles

A report by the A.D. Little Company (60) discussed the treatment of textile wastes. The SRWL for BOD₅ was reported to range from 270-1000 mg/l. Very little removal of total dissolved solids is accomplished by conventional activated sludge, extended aeration or lagoons. Total dissolved solids of the textile waste reported ranged from 500-3000 mg/l. The effectiveness of biological treatment on textile wastes is summarized in Table 14.

F. Steel Industry

In a 1954 paper on the treatment of flue dust waste from the U.S. Steel Fairless Works, Henderson and Baffa 49 reported that primary thickening, flocculation with lime, followed by clarification is capable of reducing the influent suspended solids from 2000 mg/l to less than 50 mg/l.

In treating combined once through cooling water and concentrated coolant wastes at a 12:1 ratio, Armco (2) found the following oil removals with 195 mg/l alum, 43 mg/l lime, 32 mg/l clay, and 1 mg/l

TABLE III-12
EFFLUENT QUALITY & COST (62)*

<u>PROCESS</u>	<u>BOD mg/l</u>	<u>COD mg/l</u>	<u>SS mg/l</u>	<u>COLOR (Units)</u>	<u>TDS mg/l</u>	<u>Cumulative Cost ¢/1000 GAL</u>
Influent	284	1600	440	2000	1450	--
Primary Eff	277	1440	38	2000	1450	3 to 4
Biological						
Aerated Lagoon	63	700	50	1800	1450	902
Activated Sludge	20	410	20	1800	1450	10
Massive Lime	15	400	20	200	1200	20
Sand Filtration	10	400	1	200	1200	23
Carbon Absorption	2	10	1	10	1100	23
Ion Exchange	nil	5	1	nil	nil	77

*Based on 1969 ENR Const. Cost
Example Discharge of 24.3 MGD.

TABLE III-13

EFFLUENT DATA FOR BLENDED BATE POOL & TANNINS FROM Parker (75)

<u>PARAMETER</u>	<u>AVE. RAW WASTE</u>	<u>I</u>	<u>II</u>	<u>PHASE III</u>	<u>IV</u>	<u>V</u>
Flow, GPM	-	15	20	33	69	127
Detention, days	-	49.6	37.4	16.2	7.8	4.2
BOD Load, lb/1000 ft 3/D	-	1.8	2.4	4.5	9.4	17.3
% BOD Removed	-	97	96	84	67	63
% COD Removed	-	76	65	42	38	37
BOD ₅ , mg/l	1043	35	47	187	270	315
COD, mg/l	4470	1135	1650	2740	2930	3000
ORG-N, mg/l	40.6	15	30	36	18	25
NH ₃ N, mg/l	47.1	25	28	34	18	43
TKN, mg/l	87.8	40	59	70	36	68
TS, mg/l	9190	6000	7600	2500	2000	2400
TDS, mg/l	6500	5500	6600	1400	800	1200
TVS, mg/l	2710	900	1100	1000	1400	1200
SS, mg/l	539	500	900	500	500	450
Set. S., ml/l	15.1	20+	40	3	1	2
pH	6.0	7.0	7.2	7.3	7.1	6.8
T. Sulf., mg/l	1.5	0	0	0	0	0.4
TP, mg/l	6.83	2.3	7.7	5.6	5.8	3.6

TABLE III-14

BIOLOGICAL TREATMENT OF TEXTILE WASTE FROM A. D. Little (60)

<u>TREATMENT PROCESS</u>	<u>BOD</u> <u>SRWL - EFF</u>	<u>SS</u> <u>SRWL - EFF</u>
a) Modified Activated Sludge-Cotton & Polyester	760-120	105-270
b) Extended Aeration - Cotton & Polyester & Rayon	450-85	50-25
c) Extended Aeration - Printing	650-45	175-50
d) Extended Aeration - Cotton & Polyester & Rayon	560-75	200-75
e) Extended Aeration - Polyester & Synthetics	450-65	25-25
f) Extended Aeration - Cotton	570-33	- -
g) Activated Sludge - Cotton & Synthetics	to { 600-25 1000-75 }	to { 100-5 300-70 }
h) Extended Aeration - Polyester & Rayon	300-50	- -
i) Aerated Lagoon - Wool	164-64	- -
j) Aerated & Natural Lagoons - Average of 8 Plants Fabric Unknown or Cotton & Nylons with Dyeing and Finishing	360-45	112-121

cationic polymer.

<u>Parameter</u>	<u>SRWL</u>	<u>Effluent</u>	<u>% Removal</u>
Total Oil, mg/l	1276	76	91
BOD ₅ , mg/l	893	57	93
COD, mg/l	6320	441	89
Suspended Solids, mg/l	770	55	93

The report also concluded that the pH needed to be maintained above 6.0 for efficient treatment and that flow equalization was an absolute must.

The cost of treating combined once through cooling water and concentrated coolant oily waste was between \$0.046-0.051/1000 gallons of waste. Treatment included coagulation and air flotation. Although the recovered oil scum had no potential as fuel oil, it was sold to municipalities for use as road oil (2).

G. General.

The performance of surface-aerated basins on BOD₅ removal prior to clarification has been summarized by Beychok (18). Table III-15 shows some of his data.

TABLE III-15

INDUSTRIAL WASTE TREATMENT by SURFACE AERATED BASINS (18)

<u>Industry</u>	<u>BOD, mg/l</u>		<u>Remarks</u>
	<u>Inf</u>	<u>Eff</u>	
Pulp & Paper	254	93	Single Basin
Pulp & Paper	239-93-33		Two Basins in series
Oil Refinery	85.5-57-45		" " " "
Pulp & Paper	225-119-78.5		" " No Nutrients
Pulp & Paper	225-62-40.5		" " w/Nutrients
Petrochemical	600	90	Two Basins in Parallel
Pulp & Paper	131	92	Single Basin
Pulp & Paper	526	95	Two Sections in Series
Pulp & Paper	402	74	Single Basin
Textiles	200	100	Single Basin
Distillery	550	94	Single Basin
Fiberglass	933-98-78.5		Two Basins in Series
Oil Refinery	270	72	" " " "
Petrochemical	2500	200	Single Basin
Oil Refinery	160-120-40		Two Basins in Series
Wood Treating	2200	200	Single Basin
Cannery	360	21	Lit. Rev.
Cannery	980	50	" "

Further treatment of effluents of this quality would be needed prior to discharge. However, application of one of the methods described in the previous section could easily provide an effluent with a BOD₅ and SS of less than 30 mg/l each.

While BOD₅ per se is not associated with trace metals and hydroxide sludges, suspended solids are. In this regard, filtration of settled chemically treated wastewaters is often necessary to maintain desired effluent levels for the trace metal.

In treating electroplating wastes, McDonough and Steward 64 reported that the use of the Lancy Intergrated treatment system yielded a final effluent of less than 10 mg/l suspended solids.

In testimony to the Illinois Pollution Control Board (97) Weston cited filtration as a polishing step in the removal of arsenic, barium, calcium, copper, iron, manganese, nickel, and zinc. As discussed in the chapter on "Oil and Grease," the removal of biological floc and suspended solids by filtration from biological effluents will improve the removal of oils. For further details refer to the individual chapters for the parameter in question.

CHAPTER IV-CADMIUM

SOURCES OF CADMIUM

Cadmium, like many other metals, occurs naturally in soil, fresh and salt waters, consequently in our food and bodies.

In the natural aquatic environment it occurs as soluble Cd^{+2} salts, soluble inorganic and organic complexes and insoluble precipitates. At a pH of greater than 7, cadmium hydroxides and carbonates will precipitate.

Friberg et.al. (39) report that cadmium in the environment is particularly associated with zinc, lead and copper concentrations. In areas not known to be polluted with cadmium, natural conditions in the soil are reported to be less than 1 ppm. Normal levels of cadmium in food are reported to be less than 0.05 ppm. Similarly, McKee and Wolf (66) have reported that a normal concentration of cadmium for many plant and animal tissues is about 1 mg/kg. Table IV-1 lists some naturally occurring concentrations of cadmium.

While cadmium is normally present in the environment, its concentration in water is being increased by many industrial discharges. Since it is associated with the refining of zinc, lead, copper, and the alloying of copper, lead, silver, aluminum, and nickel, it is very likely that cadmium pollution started as early as the first use of any of these metals. Industrial activities which contribute to increased concentrations of cadmium are shown in Table IV-2. Friberg et.al. (39) also reported that the burning of oil and waste and scrap metal treatment may contribute to the cadmium concentration. Their work also showed that agricultural fertilizers, either as chemicals or as sludge from sewage treatment plants, contain cadmium which may be

TABLE IV-1

NATURALLY OCCURRING CONCENTRATIONS OF CADMIUM

<u>Source</u>	<u>Concentration</u>	<u>Reference</u>
Soils*	1 mg/kg	(39)
Food (normal level)	0.05 mg/kg	(39)
Many plant and animal tissues	1 mg/kg	(66)
Some natural waters	0.010 mg/l	(39)
Sea water	0.08 mg/l	(6)
Marine plants	0.4 mg/l	(6)
Marine Animals	0.15-3mg/l	(6)
Air (Manhattan)	Yearly mean 0.023 mg/m ³	(39)
Air (non-urban New York)	Yearly mean 0.003 mg/m ³	(39)

TABLE IV-2

INDUSTRIAL SOURCES AND CONCENTRATIONS OF CADMIUM

<u>Industrial Source</u>	<u>Cadmium Concentration (mg/l)</u>	<u>Reference</u>
Alkaline accumulators		(39)
Automobile heating control manufacturing	14-22	(76)
Ceramic manufacturing		(61,66,76)
Chemical Industries		(61,76,66)
Pigment Works		(76,39)
Textile printing		(61,76,66)
Plastics		(39)
Lead mining		
Acid drainage	1,000	(76)
Metallurgical alloying (on copper, lead, silver, aluminum, and nickel)		(61,66,76)
Plating		
Plating rinse waters	15 average	(76)
(large installations)	50 maximum	
0.5 GPH drag-out	48	
2.5 GPH drag-out	240	
Plating bath	23,000	
Electroplating waste	<2-4	(14)

released to the aquatic environment. Lund (61) reported that cadmium is a by-product of nuclear reactor operations. Salts of cadmium are also used in insecticides and as anti-parasitic agents.

ENVIRONMENTAL EFFECTS OF CADMIUM

Effect on Man and Animals

Table IV-3 lists the physiological effects of cadmium upon animals. The consumption of water containing cadmium has been found to result in cumulative poisoning in mammals. McKee and Wolf (66) have reported that cadmium tends to concentrate in the liver, kidneys, pancreas and thyroid of humans and animals.

In general, for humans there are two principal mechanisms of absorption: respiration and ingestion (39). For this report the primary concern is the gastrointestinal mode of ingestion. Friberg et.al. (39) reported that in human newborns, the total body content of cadmium is small, less than .001 mg. Their studies, and those which they reviewed, indicated that the placenta of the mother apparently acts as a shield to the fetus, even for those mothers who had been exposed to excessive cadmium concentration prior to the child's birth.

The concentration of calcium has been found to play an important role in the assimilation of metals from the intestines. While the hardness of the water itself is not the most important factor, a low calcium diet has been shown to allow up to 50% more concentration of cadmium in the liver and kidneys of rats. Similarly, a low protein diet, irrespective of the calcium content within the diet, was found to give considerably higher levels of cadmium in the kidneys, livers, and whole bodies of rats.

Friberg et.al. has shown that cadmium in the human body may cause hypertension and arteriosclerotic heart disease, bone damage, sterilization, liver, and renal damage.

Cadmium together with vanadium has also been correlated with mortality by heart disease. Bone damage can occur under relatively short periods of exposure to only moderate concentrations of cadmium when the calcium content of the individual's diet is low. The report by Friberg et.al. also concluded from studies on animals that cadmium and cadmium compounds can give rise to malignant tumors. With respect to the potential carcinogenic effect of cadmium on man Friberg stated, "the carcinogenic evidence of cadmium in human beings is by no means conclusive as yet but fully motivates further and intensive studies in groups exposed industrially as well as those through food and ambient air".

Normal daily intakes of cadmium in human diets as reported by Friberg et.al. (39) varied between 0.004 and 0.06 mg in five different countries studies. Table IV-4 gives suggested maximum cadmium concentration in drinking water.

TABLE IV-3

PHYSIOLOGICAL EFFECTS OF CADMIUM UPON ANIMALS

<u>Species</u>	<u>Dose</u>	<u>Effect</u>	<u>Reference</u>
Human	150 mg/kg	Lethal in 1.5 hrs.	(66)
Human	14.5 mg	Nausea and vomiting	(66)
Human	From water - "High conc."	Disorders of renal function, "Itai itai" disease	(39)
Human	From water and food	Hypertension linked to increased retention of Cd in kidneys	(39)
Rabbits	0.3-0.5 g/kg 0.1-50.0 ppm in drinking water	0/16 animals with tumors	(39)
Dogs	0.15-0.3 mg/kg	Fatal	(39)
Hamster	High	Positive teratogenicity	(39)

Friberg, et.al. (39) concluded from experiments on animals that an absorption rate of less than 10% of the actual oral dose would be normal and that in most cases a 2% absorption could be expected. However, there were large individual variations. In considering the absorption for a "standard man" with an estimated 50 years intake, they estimated a normal absorption rate between 3 and 8%. They recommended, however, that an absorption rate of 10% should be considered as quite possible until clarified by further studies. The research indicated that normally the highest concentration of cadmium will be found in the kidneys. Based upon experiments on animals, Friberg et.al. has determined that a concentration of about 200 ppm wet weight is a critical concentration in the renal cortex. At an assumed 10 percent absorption rate over a fifty year period, for example, a daily consumption of 0.05-0.075 mg/l cadmium would result in renal dysfunction. (At a 5% absorption rate over the same period of time a daily consumption of 0.1-0.15 mg/l would have the same result.) Friberg et.al. concluded that a concentration of 0.01 mg/l in a water supply would contribute little to the daily intake of man (assuming the standard consumption of 1-2 liters of water per day). A concentration of 0.02 mg/l, however, would increase the cadmium consumption from 0.02-0.04 mg per day. This then approaches a critical concentration at a 10% absorption.

In discussing the possible biological half-life of cadmium in man, Friberg, et.al. (39) concluded "...it is conceivable that cadmium will be retained for many years in man once it has been absorbed. This is supported by findings in autopsies of workers which indicate

a very slow decrease in liver levels after exposure ceased."

Effects on Plants

Friberg et.al. (39) identified rice and wheat as two food products which are capable of concentrating cadmium from the soil. In general, they found that wheat accumulated cadmium to a slightly greater extent but both concentrations were around 1 ppm. Rice and wheat grown in most parts of the world will normally contain less than 0.1 ppm of cadmium in the grain.

Effects on Fish and Other Aquatic Life

Table IV-5 shows that the acute lethal level of cadmium with respect to fish varies from a low of 0.01-10 mg/l, depending upon the organism, the hardness of the water, the temperature, and the time of exposure. McKee and Wolf (66) and others (15) show that cadmium toxicity increases with water softness for all the forms of fish life studied. As hardness increases, thereby increasing the chance of a higher calcium diet for aquatic life, the toxicity of the cadmium compounds decreases. Several authors have reported a synergistic effect with respect to toxicity of cadmium compounds in the presence of zinc, copper, selenium, and cyanide (6,15,66).

In investigating the concentrations of cadmium in seafood, Friberg et.al (39) reported that oysters from the East Coast of the United States contain 0.1-7.8 ppm (wet weight) whereas West Coast oysters contain only 0.2-2.1 ppm (wet weight).

Cadmium, like other trace metals, has been reported to be concentrated upon suspended particles and in bottom sediments (39).

In the literature reviewed by Friberg et.al. (39) one particular case indicated that 500 meters downstream from a factory discharging cadmium, only 0.004 mg/l of cadmium was found in the water, while 80 mg/l (dry weight) was found in the bottom sediments. Thus, we must be aware that even the lack of detection of cadmium in the surface water does not preclude the possibility of relatively high cadmium concentrations being available to biota of the stream.

TABLE IV-4

CADMIUM STANDARDS PROMULGATED (66)

<u>Agency</u>	<u>Maximum Conc. (mg/l)</u>
U S.P.H.S. Drinking Water Stds. in the U.S.-1962	Mandatory 0.01
1961 WHO European Std. for Drinking Water	Excessive 0.05
USSR Max. Permissible Conc. in Reservoir Waters	General Sanitary 0.01
Surface Water Criteria for Public Water Supplies in the U. S.	Permissible 0.01

TABLE IV-5

ENVIRONMENTAL EFFECTS OF CADMIUM UPON FISH AND AQUATIC ORGANISMS

<u>Species</u>	<u>Dose</u>	<u>Effect</u>	<u>Reference</u>
<u>Daphnia magna</u>	0.10 mg/l as CdCl ₂	Threshold	(66)
<u>Daphnia magna</u>	0.0026 mg/l as CdCl ₂	Immobilization	(66)
Flathead Minnows	0.90 mg/l as CdCl ₂	Toxic in Soft water	(15)
Flathead Minnows	5.0 mg/l as CdCl ₂	Toxic in Hard water	(66)
Flatworm	2.7 mg/l as CdNO ₃	Toxic	(6)
Goldfish	0.0165 mg/l as CdCl ₂ in 8.5 to 18 hrs.	Very sensitive in Soft water	(66)
Strickleback	0.20 mg/l as Cd	Lethal	(6,66)

Where cyanide or other complexing agents are not present, the cost of removing cadmium may be expected to be equivalent to that of conventional treatment involving coagulation, settling, rapid sand or multimedia filtration. As with many metal wastes, filtration is very important in removing the slow settling metal hydroxide floc. The total cost of treatment by coagulation, sedimentation, and filtration has been described in the report on arsenic.

The new system described by Patterson and Minear for precipitation of cadmium, for small electroplating wastes, is the Kastone process. Hydrogen peroxide is added to the wastewaters, which oxidizes the cyanide and forms an oxide of cadmium simultaneously. The cadmium oxide is claimed to be more easily removed than the cadmium hydroxide. This treatment system is believed to be suitable for plants with low flows. Filtration is still advisable.

Ion Exchange

The ion exchange process concentrates the cadmium, making recovery amenable. Patterson and Minear reported the recovery value of cadmium to be between \$1.20-\$6.00 per thousand gallons for a solution concentration of 50-250 mg/l (as cadmium). The recovered value of cadmium may be capable of offsetting the additional treatment cost within one-half to two years. Patterson and Minear did warn, however, that ion exchange is unsuitable for the recovery of cyanide solutions. No specific applications of ion exchange recovery of cadmium cyanide solutions were found.

On the basis of pilot plant work, reported by Patterson and Minear, removal of cadmium by a cation exchanger was 99% efficient,

and 99.9% efficient by a cation plus anion exchange column. The initial concentration was reported as a trace quantity. On this basis, one can only assume that the final effluent would be in the zero mg/l range prior to breakthrough.

In summary, it is apparent that cadmium has a significant environmental impact upon man, other animals, and aquatic life. It has been shown that the toxicity of cadmium will vary with the presence of calcium and protein in the diet of mammals and possibly that of fish, and with the presence of other trace metals. It has also been shown that once cadmium is absorbed by the human body it is retained. For this reason, Byerrum, as reported in McKee and Wolf (66), suggested that cadmium concentrations should not be allowed to exceed 0.1 mg/l.

TREATMENT FEASIBILITY - CADMIUM REMOVAL

A detailed review of current technology of cadmium removal has been prepared by Patterson and Minear (76) and others (46,61,66). In general, cadmium may be removed by ion exchange or chemical precipitation. Cadmium carbonate and cadmium hydroxide are insoluble under alkaline conditions and are therefore easily precipitated. It is also technically feasible to remove concentrated sources of cadmium by electrolytic or evaporative recovery. A new process for low flows has been discussed by Patterson and Minear (76).

Chemical Precipitation

The chemical precipitation of cadmium is dependent upon the pH of 8, an effluent of 1.0 mg/l may be expected; whereas at a pH of 10,

a final effluent of 0.1 mg/l may be expected. In Patterson and Minear's review, they stated that when iron is present in the waste with cadmium, "precipitation will yield complete removal" at a pH of only 8.5.

Complexing agents such as cyanide, as found in electroplating waste, must be removed before cadmium can be precipitated. Fortunately, cyanide may be readily removed allowing for cadmium precipitation. Patterson and Minear report the cost for removing complexed cadmium can be expected to be equal to that of cyanide removal.

SUMMARY AND RECOMMENDATIONS

The review of cadmium as a waste, its impact, and treatment has provided the following information:

1. Cadmium exists naturally in the soil and in the water but industrial and agricultural discharges contribute substantial loads when untreated.
2. Like arsenic, cadmium is concentrated and becomes cumulative in man, animals, and plants. Cadmium is toxic to animals and aquatic life.
3. Cadmium acts synergistically in the presence of other metallic ions increasing its toxicity.
4. Cadmium causes poor bone mineralization in humans with low calcium diets. Cadmium can cause liver and renal damage in man and animals. It has also been shown that with low calcium diets cadmium accumulation in the liver was about 50% more than in the kidneys of test animals. Cadmium

causes chronic kidney damage in man under continuous exposure, possibly as low as 0.012-0.020 mg/day. Cadmium levels were also shown to be higher in test animals when their diet was low in protein. Cadmium contributes to cardio-vascular disease in man.

5. Trace amounts of cadmium in water may concentrate on bottom sediments as much as 20,000 times the concentration in the water.
6. There appear to be technically feasible methods to reduce cadmium levels in wastewaters to levels lower than 0.1 mg/l. However, further study and research is needed to confirm the actual level which is currently obtainable by these methods.

It is readily apparent that the effluent level of all cadmium bearing wastewaters should be controlled to the lowest level possible. It is desirable that an effluent level for cadmium be set at 0.10 mg/l. Furthermore, it is recommended that literature reviews and research in this area be supported and continued to investigate other currently feasible methods of treatment, and to determine obtainable effluent levels for all discharges.

CHAPTER V-TOTAL CHLORINE RESIDUAL

The major discussion on the effects of chlorine residuals in the aquatic environment is a report by Brungs (20). It is important to note that Brungs work is directed at safe total chlorine residuals in surface waters. The references cited within this report are listed in Brungs' report.

Brungs has documented that the uniform total residual chlorine level in surface waters should not exceed 0.002 mg/l to protect most aquatic life. Intermittent discharges from certain facilities such as from power plant chlorination processes for slime removal, should not cause the receiving waters to reach a total residual chlorine concentration of 0.1 mg/l for more than 30 minutes, nor 0.005 mg/l for more than 2 hours.

When consulted on this report, Brungs (21) stated that he is continuing to document his studies. With respect to potentially safe effluent levels of total chlorine residuals, Brungs stated that a reasonable maximum level would be 0.1 mg/l. The stream, however, should never contain more than 0.002 mg/l. Therefore, discharges which will be diluted from a concentration of 0.1 mg/l-0.002 mg/l within 30 minutes could be tolerated provided the entire cross section of the stream is not affected. Brungs stressed that a channel past the discharge must be maintained if fish life is to exist in the stream. Waters containing as little as 0.001 mg/l total residual chlorine are avoided by rainbow trout.

Data on the effects of chlorine residuals over continuous and intermittent periods of exposure are summarized in Table V-1.

RESULTS OF BRIEF EXPOSURES OF FISH TO TOTAL RESIDUAL CHLORINE

<u>Species</u>	<u>Effect Endpoint</u>	<u>Time</u>	<u>Residual Chlorine Concentration(mg/l)</u>	<u>Brungs' References</u>
Misc	initial kill	15 min.	0.28	Truchan, 1971
Misc	erratic swimming	6 min.	0.09	Truchan, 1971
trout fry	lethal	instantly	0.3	Coventry,et.al 1935
chinook salmon	first death	2.2 hrs	0.25	Holland,et.al. 1960
white sucker	lethal	30-60 min.	1.0	Fobes, 1972
brook trout	median mortality	90 min.	0.5	Pyle, 1960
smallmouth bass	median mortality	15 hrs.	0.5	Pyle, 1960
rainbow trout	slight avoidance	10 min.	0.001	Sprague & Drury, 1969
rainbow trout	lethal	2 hrs.	0.3	Taylor & James 1928
fingerling rainbow trout	lethal	4-5 hrs.	0.25	Taylor & James, 1928
fathead minnows	TL50*	1 hr.	0.79	Arthur, 1972
fathead minnows	TL50	12 hrs.	0.26	Arther, 1972
yellow perch	TL50	1 hr.	0.88	Arther, 1972
yellow perch	TL50	12 hrs.	0.494	Arther, 1972
largemouth bass	TL50	1 hr.	0.74	Arthur, 1972
largemouth bass	TL50	12 hrs.	0.365	Arthur, 1972
brook trout	mean survival time	8.7 hrs.	0.35	Dandy, 1967
brook trout	mean survival time	14.1 hrs.	0.10	Dandy, 1967
brook trout	mean survival time	20.9 hrs.	0.05	Dandy, 1968
brook trout	mean survival time	24 hrs.	0.005	Dandy, 1967

* TL50 = median tolerance limit.

It is fully recognized that many state agencies either recommend or require minimum total residual chlorine levels in treated effluents. The states in Region III which currently require chlorination and/or a chlorine residual in at least some of their discharges are as follows:

- (1) Delaware - All domestic wastewaters must be chlorinated.
- (2) Pennsylvania - Effluent must be disinfected.
- (3) Virginia - 2.0 mg/l chlorine residual must be maintained for discharges into some waters.
- (4) West Virginia - Chlorination is required of all discharges 12 months of the year. (34)

Requirements for states in other regions are also reported in a summary of federally approved water quality standards. (34).

TREATMENT METHODS

Wastewaters are disinfected primarily to control bacteria and the organisms which are pathogenic. Indicators such as fecal coliforms are used for controlling the efficiency of the disinfection process. The means of attaining low levels of these indicator organisms is presently being reevaluated and many questions are arising as to the proper choice for disinfecting, be it chlorine, ozone, or other biological, physical, or chemical processes. Two promising processes are briefly discussed below.

"Closed-loop chlorination" has been reported by Thomas and Brown (93) to be an economical and effective means of controlling the rate of chlorination. According to the authors, closed-loop chlorination is applicable to any waste treatment facility. While the unit

costs about \$5,000 it rapidly offsets the cost of manpower needed to do the same job. Thomas and Brown stated that "financially, it is imperative that closed-loop chlorination equipment be provided to replace the four men who otherwise would be required to give effective chlorination. The cost of closed-loop chlorination equipment can be recovered in two to three months by payroll savings. Obviously, additional maintenance will be required; but this will be small - in the range of one hour a week to one hour a day".

The use of ozone for disinfection is also a possible alternative. It is widely reported to be in use in Europe and is gaining acceptance in the U. S.

RECOMMENDATIONS

On the basis of the above discussion and the report by Brungs (20), a maximum total chlorine residual in surface waters of 0.002 mg/l is recommended.

Where currently permissible under state and local laws and regulations, it is suggested that all discharges contain not more than 0.10 mg/l total residual chlorine, or where possible maintain a stream level at less than or equal to 0.002 mg/l after a 30 minute mixing period.

As an interim measure to limit the chlorine residual in a discharge, it is recommended that the discharge not contain more than 0.2 mg/l total chlorine residual above that required by state or local law and/or regulation.

CHAPTER VI-CHROMIUM

Unlike most toxic trace elements, chromium is not commonly encountered in the natural environment. Trace amounts of chromium have been found in food (66). However, this is only expected for food cooked in a stainless steel utensil. Trace amounts found from this source are not known to have any physiological effects upon man. Chromium has been found in trace amounts in soil and plants, however, there is no evidence that this chromium level is either detrimental or beneficial for plant nutrition.

Chromium may be found, apparently due to natural conditions, in sea water at a concentration of 0.00005 mg/l. Marine plants may contain chromium at concentrations of 1.0 mg/l, and marine animals between 0.2 and 1.0 mg/l (6).

Chromium is found in hexavalent and trivalent forms. The trivalent form (Cr^{+3}) normally consists of the hydrated or complexed cation in water. The prevalent forms of hexavalent chromium (Cr^{+6}) include chromate (CrO_4^{-2}) and dichromate ($\text{Cr}_2\text{O}_7^{-2}$). Chromium trioxide, a hexavalent form, is also referred to as "chromic acid" or "chromic acid anhydride".

Divalent compounds (Cr^{+2}) tend to oxidize to the trivalent form. The hexavalent chromium salts of sodium, potassium, and ammonium are quite soluble. As a result, for removal one normally considers reducing hexavalent chromium to the trivalent form. This may be done by heat, organic matter, or by reducing agents such as sodium metabisulfite. The trivalent chromic salts are soluble only as chloride, nitrate, and sulfate, and the hydroxide and carbonate chromic salts are quite

insoluble.

The industrial sources of chromium reported by Lund (61), Nemerow (72), and others are shown in Table VI-1. The most common sources are electroplating, metal finishing, tanning of leather, and cooling tower effluents. McKee and Wolf also reported prevalent sources of hexavalent chromium to include anodizing of aluminum, the manufacture of paints, dyes, explosives, ceramics and paper. Hexavalent chromium is more prevalent in these effluents, although some trivalent chromium may be present. Trivalent chromium salts are used as mordants in textile dying, in the ceramic and glass industry and in photography.

The major source of chromium in our surface waters appears to be from industrial and municipal discharges which contain industrial wastes rather than from natural sources.

ENVIRONMENTAL EFFECTS OF CHROMIUM

Effect on Man

The toxicity of chromium compounds in man is quite high. In 1946 the U.S.P.H.S. Drinking Water Standards set a maximum allowable limit of 0.05 mg/l. A justification for this limit at that time was that it was the current limit of detection. It was not set as a result of physiological effects. The 1962 Drinking Water Standards retained the same 0.05 mg/l limit.

Evidence indicates that man neither needs nor benefits from chromium salts in his diet. Chromium salts are rapidly and completely eliminated when ingested orally. It was reported that a Long Island family of two adults and two children revealed no abnormalities after

TABLE VI-1
SOURCES OF CHROMIUM

<u>Sources</u>	<u>Type</u>	<u>Concentration mg/l</u>	<u>Reference</u>
Chrome Plating	CrO_3^{-3}	4,170,000	(61)
Plating Waste	Cr^{+6}	0-555	(72)
	Total	0-612	
Electroplating	Total	11-41	(14)
Electroplating	Cr^{+3}	140	(76)
IBM Plant	Cr^{+6}	1300	(76)
Metal Finishing	Total	1-700	(16)
Brass & Copper Wire Mill	CrO_3	70-96.9	(96)
	Cr^{+3}	27	(96)
Acid Bath Waste	Cr^{+6}	122-270	(76)
	Cr^{+3}	37-282	(76)
Tannery Wastes	Total	30-70	(72)

consuming hexavalent chromium of 1.0 to 25.0 mg/l in their drinking water for a three year period. Another investigation reportedly found mild nausea from consumption of water with 5 mg/l on an empty stomach. Consumption of water with 2.5 and 3.5 mg/l, however, failed to produce any symptoms. McKee and Wolf concluded that man apparently may consume 5.0 mg/l hexavalent chromium with no deleterious physiological effects. However, concentrations above 1.5 mg/l may cause color and taste problems.

While the salts of trivalent chromium are not believed to be physiologically harmful, large doses of chromate may lead to corrosive effects in the intestinal tract and to nephritis. Approximately 0.5 grams of potassium bichromate has been reported to be toxic.

Effect on Plants

Chromium is shown to be toxic to plants (6,66) at concentrations of 3.4 mg/l or above. Table VI-2 summarizes toxicity data.

Effect on Animals

A limit of 0.05 mg/l for chromium in water used for stock watering has been proposed, but there apparently is little justification for the level (6).

McKee and Wolf report that the maximum non-toxic level in the drinking water of white rats is 500 mg/l as hexavalent chromium (66). They also reported that a drinking water concentration of 500 mg/l of potassium chromate would not affect the utilization of food by rabbits but that 10,000 mg/l of zinc chromate has markedly interfered with the digestion. The concentration of 5 mg/l of chromium in conjunction with 11 mg/l of selenium caused an increase in mortality among rats.

In other works reported by McKee and Wolf, white rats were fed potassium chromate at a dosage of up to 11 mg/l for one year. Other test rats received up to 25 mg/l of chromium as potassium chromate and 25 mg/l as chromic chloride. The study indicated that there was no significance in the difference of weight, food intake, water consumption, or blood analysis from the experimental group. However, the report did show that a concentration above 5 mg/l chromium was detected in all tissues, especially in the spleen. As a result, McKee and Wolf recommended that the concentration of chromium be maintained at or below 5 mg/l for all stock and wild life for watering purposes.

Effect on Aquatic Life

It is readily apparent that the lethal and toxic concentrations of

TABLE VI-2
CHROMIUM TOXICITY TO PLANTS (66)

<u>Form</u>	<u>Concentration, mg/l</u>	<u>Plant</u>	<u>Effect</u>
Trivalent	3.4-17.3	Various	Slightly Toxic
Potassium Dichromate	5	Oat	Slight Chlorosis
Potassium Dichromate	10	Oat	Marked Chlorosis
Potassium Dichromate	15-50	Oat	Reduced Growth
Trivalent & Hexavalent	5	Sensitive	Adverse

all forms of chromium vary with the species (66). Table VI-3 summarizes the experimental evidence available. McKee and Wolf report a general toxicity limit for fish of 5 mg/l. [A threshold toxic concentration for small prawn was reported to be less than 5 mg/l. Lower forms of aquatic life are much more sensitive to chromium compounds (66).] Under a two (2) year exposure oysters showed a chromium toxicity of 0.01-0.012 mg/l (6).

McKee and Wolf have also reported that fish are capable of withstanding from 10 mg/l to over 500 mg/l of various chromium compounds, depending on the time of exposure without detrimental effect. They noted that lower forms of aquatic life are capable of withstanding a chromium concentration of 5.0 mg/l for up to one hour without detrimental effect.

McKee and Wolf have reported that algae are capable of concentrating radioactive chromium 100 to 500 times. Similarly, Van den Berg and Daum (95) indicated that recent studies on a cooling water chromium discharge showed that chromium is concentrated in fish. Their investigation showed that the concentration within the fish is increased as both the total chromium concentration in the water, and time increased. While under continuous exposure, fish have shown detrimental effects to concentrations of 1.0 mg/l, while they are capable of survival with no significant damage at concentrations of 10 or more mg/l for short periods of time. Total chromium concentrations should be maintained at 0.05 mg/l for aquatic life under continuous exposure. They are capable of withstanding short exposures of up to 5.0 mg/l for as much one hour. Other factors such as temperature, pH, the species, the

TABLE VI-3

TOXICITY OF CHROMIUM TO FISH
AND AQUATIC ORGANISMS (66)

<u>Target Organism</u>	<u>Cr Form</u>	<u>Concentration mg/l)</u>	<u>Effect</u>
Brown Trout	hexa-	5.2	toxic
Carp	hexa-	7.1	unharmd
Silver Salmon	hexa-	10.0	freshwater, toxic
Silver Salmon	hexa-	17.8	seawater, toxic
Rainbow trout	hexa-	20.0	toxic, 18°C
Goldfish	hexa-	35.3	unharmd
Bluegills	hexa-	45.0	tolerated 20 days
Bluegills	hexa-	50.0	toxic limit, 30 days
Trout	hexa-	50.0	killed within 33 hrs.
Bluegills	hexa-	70.0	toxic limit, 1 week
Trout	hexa-	100.0	24 hr. TLm
Trout	hexa-	150.0	killed in 6 hrs.
Bluegills	hexa-	103.0	96 hr. TLm
Bluegills	hexa-	145.0	24 hr. TLm
Young eels	hexa-	130	tolerated 50 hrs.
Young eels	hexa-	520	killed 5-12 hrs.
Sticklebacks	tri-	1.3	survived 1 week
Sticklebacks	tri-	2.0	survived 2 days
Sticklebacks	tri-	2.4	lethal limit
Young eels	tri-	5.2	survived avg. of 187 hrs
Minnows	tri-	40.0	survived 6 hrs.
<u>Daphnia magna</u>	hexa-	0.016	toxic threshold
<u>Daphnia magna</u>	hexa-	0.05	killed in 6 days
<u>Microregma</u>	hexa-	0.21	toxic threshold
<u>Navicula</u>	hexa-	0.21	softwater TLm
<u>Navicula</u>	hexa-	0.25	hardwater TLm
<u>Daphnia magna</u>	hexa-	0.51	toxic threshold
<u>Scenedesmus</u>	hexa-	0.7	toxic threshold
<u>E. Coli</u>	hexa-	0.7	toxic threshold
<u>Grammarus pulex</u>	hexa-	1.4	total mortality
Snail	hexa-	17.3	softwater TLm
Midge fly larvae	hexa-	25.0	unharmd
Snail	hexa-	40.6	hardwater TLm
<u>Polycelis nigra</u>	hexa-	148.0	toxic threshold
<u>Daphnia magna</u>	tri-	42.0	toxic threshold
<u>Scenedesmus</u>	tri-	5.0	toxic threshold
<u>Microregma</u>	tri-	37.0	toxic threshold
<u>Polycelis nigra</u>	tri-	75.0	toxic threshold

hardness of the water, and possibly the valence of chromium may also influence its toxicity (66).

TREATMENT TECHNOLOGY - CHROMIUM REMOVAL

The currently available methods of chromium treatment consist of a reduction-precipitation process, a modification known as the Lancy Integrated System, and Ion Exchange. Other methods which have been researched by the Battelle Memorial Institute will be discussed, as well as the effects of chromium on biological treatment.

The theory and practice of treating chromium bearing plating wastes is presented in Nemerow (72) and Gurnham (48). The basic process consists of alkaline-chlorination, reduction, and precipitation followed by neutralization. Control of pH is very important, as is the time of reaction.

Alkaline Chlorination

Many chromium bearing plating wastes may also contain cyanide. This waste must be reduced and acidified to convert the hexavalent chromium to the trivalent form prior to precipitation. As chromium cannot be reduced until all of the cyanide is removed, the alkaline chlorination process is used for cyanide removal. The details of this method are discussed in the chapter on cyanide.

Reduction and Precipitation

After removal of cyanide from combined wastes, or upon separating chromium plating wastes, the hexavalent form of chromium must be reduced

to the trivalent form to permit precipitation. To accomplish this, sufficient free mineral acid is added to the waste to reduce the chromium by maintaining a pH of 3.0 or lower. After reduction of the chromium, alkali, usually in the form of a lime slurry, is added to neutralize the acid and then precipitate the trivalent chromium. One of the methods used to reduce the hexavalent form of chromium to trivalent is the addition of ferrous sulfate. Nemerow (72) summarized the chemicals needed to remove one mg of chromium as follows: 16 mg of copperas (ferrous sulfate), 6 mg sulfuric acid, and 9.5 mg lime. The chemical reactions will normally produce 2 mg of a chromic hydroxide and 0.4 mg of a ferric hydroxide sludge. In addition, about 2 mg of calcium sulfate will be produced, part of which may also precipitate. Disposal of these sludges is a major unsolved environmental problem.

Neutralization

In many plating waste operations the oxidized cyanide and reduced chromium wastes will be combined with the other wastes, which may contain metals, oil, and grease, for subsequent and perhaps final treatment. If the combined waste is still acidic, a lime slurry can be added to neutralize and precipitate the metals. This reaction normally produces a large and heavy coagulant sludge.

A 1968 report by the Battelle Memorial Institute (16) listed the following two conventional methods for chromium removal:

1. Hexavalent chromium may be reduced by the addition of sulfur dioxide, sulfates, and ferrous sulfate. The process is common among intermediate and large plants. The process involves reduction of the hexavalent chromium to the trivalent form under

low pH (2.0-3.0) followed by precipitation of the trivalent form with alkali. Clarification is mandatory for efficient removal of the trivalent chromium, copper, nickel, and iron when waste pickle liquor is used for the reduction step.

2. Precipitation of the hexavalent chromium may be achieved directly by the addition of barium salts. While this method is reportedly effective, the sludge (BaCrO_4) is highly toxic which poses a solid waste hazard.

In Patterson and Minear (76), it is indicated that the reduction of hexavalent to trivalent chromium is not always 100% complete. The efficiency will depend upon the time allowed for reduction, the pH of the reaction mixture, the concentration, and type of reducing agent employed. They noted that an initial hexavalent concentration of 140 mg/l can be reduced to a total of 0.7 to 1.0 mg/l as hexavalent chromium, using sodium bisulfite as a reducing agent. As the use of sodium bisulfite can cause odors and corrosion, it is often replaced by sulfur dioxide. Patterson and Minear reported that the use of sulfur dioxide at an IBM plant achieved total removal of as much as 1,300 mg/l of hexavalent chromium. The pH of the waste was decreased to 2 with a total detention time of 90 minutes. Other reports indicated that the use of sulfur dioxide is much more efficient in the reduction hexavalent chromium than the bisulfite (76).

In discussing the precipitation of the trivalent form of chromium, it was indicated that the most effective pH range is from 8.5 to 9.5. This is the point of minimum solubility of the chromic hydroxide sludge formed by the precipitation of trivalent chromium (76). The most common

alkali used is calcium hydroxide or other forms of lime.

At the previously mentioned IBM plant, a final effluent concentration of 0.06 mg/l as total chromium was obtained. It was also noted that a coagulant aid (Separan NP-10) was used to improve the precipitation and sedimentation characteristics of the chromic hydroxide.

In several of the plants discussed by Patterson and Minear, it was shown that filtration of the final effluent following sedimentation improved the overall removal of chromium. For one waste, sand filtration reduced the initial chromium concentration of 1.3-4.6 mg/l to a final concentration of 0.3-1.3 mg/l (as total chromium). Most of this chromium was reported to exist as the soluble hexavalent form rather than the trivalent chromium.

The efficiency of the reduction, neutralization, and precipitation of chromium, reported in various works investigated, are summarized in Table VI-4.

TABLE VI-4
THE REMOVAL OF CHROMIUM BY
REDUCTION, NEUTRALIZATION, AND PRECIPITATION

<u>Source</u>	<u>Concentration, mg/l</u>		<u>Reference</u>
	<u>Initial as Cr⁺⁶</u>	<u>Effluent, as Total</u>	
Electroplating	10	0.6	(17)
Electroplating	140	1.0	(76)
IBM Plant	1,300	0.06	(76)

A modification of the standard reduction precipitation process known as the Lancy Process has been reported by Lund (61). Lancy's batch or continuous treatment system follows the parameters of the standard reduction precipitation process. The one basic difference is in automation. A pH meter and an ORP controller are utilized to modify the quantities of the chemicals entering the reaction tank. The Lancy integrated system is an extension of the normal process. In the integrated system, a chemical process solution (lime) is used to remove the dragout film and droplets containing the harmful chemical compound prior to recycling. The treatment solution is then recirculated between various wash tank stations and a reservoir where the metal hydroxides are precipitated. Lund reports that effluent qualities from the Lancy batch treatment or continuous flow through system are 0.1 mg/l chromium, and 0.01 mg/l chromium for the integrated treatment system. Mr. Ivan Whittman, of Lancy Laboratories, has indicated to this author that the integrated system has been successfully implemented in plants with design flows ranging from 25 gallons per minute (gpm) to greater than 500 gpm design flows. McDonough and Stewart (64) reported that the Lancy integrated treatment system used by the S. K. Williams Co. of Wauwatosa, Wisconsin, was capable of achieving a total chromium concentration of zero during several years of operation. Other parameters of interest, obtained by the S. K. Williams Company, are a final effluent with a pH of 6.5 to 9.5, cyanide concentration of none, copper less than 0.50 mg/l, nickel less than 1.0 mg/l, iron less than 0.50 mg/l, and settleable solids less than 10 mg/l. (Editorial Note: The 13th edition of Standard Methods (1) does include a method

whereby settleable solids may be reported in terms of mg/l. This apparently is what has been used here.)

Ion Exchange

The 1968 Battelle Report (16) indicated effective chromium removal by ion exchange and evaporation in concentrated waste streams. Similarly, Patterson and Minear's review on the treatment of hexavalent and trivalent chromium indicates that cation exchange can be applied to remove trivalent chromium, and an anion exchange may be employed for the removal of hexavalent chromium (76). Upon exhaustion of an anion exchange column, it may be regenerated with sodium hydroxide to elute sodium chromate. The sodium chromate may then be passed through a cation exchange column to recover purified chromic acid. If recovery of the chromic acid is not desired, the concentrated regeneration waste of the exchange column may be treated by the reduction-neutralization-precipitation method. Patterson and Minear, like the Battelle Report, indicated that the ion exchange process will not only produce reusable water, but may prove to be economically feasible where the waste is highly concentrated, and/or where the cost of water is high.

One of the reports reviewed by Patterson and Minear indicated that ion exchange was both economically and technically feasible for wastes containing chromate ion concentrations up to 200 mg/l, and that chromate concentrations greater than 500 mg/l were suitable for evaporative recovery.

There are two possible alternatives in the treatment technology for trivalent chromium by ion exchange. First, passing concentrated chromic acid baths through a cationic resin removes metallic contaminants

such as iron, aluminum, and trivalent chromium from the chromic acid, thus allowing reuse of the chromic acid solution. Second, dilute rinse waters can be passed through mixed bed resins to remove both the cationic trivalent and anionic hexavalent forms, allowing for the complete reuse and recycle of the rinse water.

In the testimony of Weston (97) before the Illinois Pollution Control Board it was stated that an effluent of 0.03 mg/l is currently obtainable by the use of ion exchange for hexavalent chromium waste. A report by Driver (30), indicates that as little as 1 mg/l of chromium is now being discharged in the cooling waters used by City Service Company, Buttle Rubber Plant at Lake Charles, Louisiana. This plant previously had discharged significant amounts of chromium in their cooling water. By the use of ion exchange, this particular City Service plant is currently recovering the chromate from the rinse water. The chromium is recycled to the cooling towers for further use.

Miscellaneous

Another process reported by Patterson and Minear is that of evaporative recovery. One of the references cited indicated that a plating waste rinse water with only a few mg/l of chromic acid could be concentrated to over 900 mg/l by evaporative recovery (76). Patterson and Minear also indicated that the evaporative recovery was suitable for waste containing over 500 mg/l of chromate.

Other methods researched and reported by Battelle in 1971 (17) for electroplating wastes are summarized in Table VI-5.

The final treatment method investigated for this report was that of biological processes. A report by Stanley consultants (91) and a

TABLE VI-5

POTENTIAL METHODS FOR CHROMIUM REMOVAL

<u>Form</u>	<u>Concentration, mg/l</u>		<u>Method</u>
	<u>Initial</u>	<u>Effluent</u>	
Cr^{+6}	100	10	Ion Flootation
$\text{K}_2\text{Cr}_2\text{O}_7$	100	0-10	Carbon Adsorption, pH 2-3, 4.0 GPM/ft ²
$\text{K}_2\text{Cr}_2\text{O}_7$	1000	0-10	"
CrO_3	1000	0-5	Carbon Adsorption, pH 2-3, 5.0 GPM/ft ²
CrO_3	100	0-4	"
Cr^{+6}	10-100	0.04-0.70	Liquid-Liquid Extraction

1965 PHS study (5) on the interaction of heavy metals indicate a maximum reliable potential of approximately 50% removal of various trace metals. The report by Stanley on tannery wastes indicated that aerobic lagoons were capable of reducing initial total chromium concentration from 11 to 9 mg/l. Activated sludge was found capable of reducing an initial chromium concentration of 60 mg/l to 4 mg/l (91). The PHS study (5) investigated the effects of chromium, copper, zinc, and nickel in four full scale treatment plants receiving combined municipal-industrial wastes. This study indicated that chromium intake levels varying from 0.8 to 3.6 mg/l would be reduced to 0.2 and 2.5 mg/l respectively. The PHS study indicated that hexavalent chromium concentrations up to 0.5 mg/l could be almost completely removed. Concentrations of 2 mg/l in the raw waste will show at least some small quantity of chromium in the effluent. Concentrations of 5 mg/l and higher were found to pass through the biological system.

In summary, it is apparent that chromium can be removed efficiently to a level of 1 mg/l by currently available and utilized methods. With proper control the levels may be reduced to 0.01 mg/l or less. It has also been shown that ion exchange is currently functional even on large volumes of chromium bearing wastes such as cooling water. While the City Service report indicated a chromium breakthrough point of 1 mg/l, it is believed that adequate control of such an operation could reduce this break point level to much lower levels. The testimony of Weston (48) indicated that the more commonly practiced procedures of alkaline reduction, chemical precipitation, and sedimentation are capable of providing an effluent of 0.06 to 4 mg/l for trivalent chromium, and 0.7 to 1 mg/l for hexavalent chromium.

Cost of Treatment

The literature review by Patterson and Minear (76) and the testimony of Weston (97) provide a reasonable idea of the relative capital and operational costs of treating hexavalent and trivalent chromium by the various methods. Table VI-6 summarizes the capital cost data provided in the two references.

Similarly, the operating costs of treating both hexavalent and trivalent chromium as shown in the report by Patterson and Minear are summarized in Table VI-7.

In summary, it is apparent that chromium is no more expensive to remove from wastewaters than many of the other elements and trace metals. In fact, with a cost of about \$1.00 per thousand gallons for reduction and precipitation of chromium, it may be cheaper in some areas than the cost of the water supply, making it beneficial to institute recycling.

SUMMARY AND RECOMMENDATIONS

The following generalizations can be made on the basis of the information discussed above.

1. Chromium exists only at very low levels in nature.
2. Industrial sources are capable of contributing up to 4.17 kg/l if untreated.
3. Man reportedly can consume up to 3.5 mg/l of chromium through his drinking water without known detrimental effects.
4. Animals and wildlife can consume up to 5.0 mg/l in their drinking water without known detrimental effects.

TABLE VI-6

CAPITAL COST FOR CHROMIUM TREATMENT

<u>Form</u>	<u>Method</u>	<u>Flow</u>	<u>Capital Cost</u>	<u>Reference</u>
Hex	Reduction & Precipitation	1 MGD	\$ 200,000	(97)
Hex	Reduction & Precipitation	10 MGD	700,000	(97)
Hex	Ion Exchange	100 gpm	40,000	(76)
Hex	Ion Exchange	1 MGD	300,000	(97)
Hex	Ion Exchange	10 MGD	3,000,000	(97)
Hex	Ion Exchange	50 MGD	4,600,000	(97)
Tri	Precipitation	0.2 MGD	224,000	(76)

TABLE VI-7
OPERATION COST - CHROMIUM REMOVAL (76)

<u>Form</u>	<u>Method</u>	<u>Flow, gpm</u>	<u>Conc. mg/l</u>	<u>\$/1000 Gal.</u>
Hex	Reduction & Precipitation	100	120	< 1.00
Hex	Reduction & Precipitation	70	50	1.00
Hex	Ion Exchange	-	50	1.00
Hex	Ion Exchange	100	50-100	0.68
Hex	Evaporation	0.5-2	-	10.00
Hex	Evaporation	2.0-5	-	5.00
Hex	Evaporation	5.0-10	-	2.50
Tri	Precipitation (Lime Cost)	-	2000	2.50
Tri	Precipitation (Lime Cost)	-	1000	1.25
Tri	Precipitation	0.2 MGD	-	0.80
Tri	Ion Exchange	-	-	0.16-0.24
Hex	Reduction & Precipitation	73	2300	\$33.19/Day
Hex	Ion Exchange	73	2300	\$12.44/Day Net.

5. Plants subjected to chromium concentrations below 3.4 mg/l showed no toxic effects.
6. The threshold of toxicity to fish is about 5 mg/l of chromium for continuous exposure. However, ranges of 10 to 50 mg/l are tolerable for short periods of exposure (days).
7. The lower forms of aquatic life have a limiting toxicity of 0.050 mg/l or less under continuous exposure. Under short periods of exposure (up to one hour), levels of 5.0 mgm/l are tolerable.
8. Both algae and fish appear to be capable of concentrating chromium, while it is reported that other life forms rapidly expel chromium ingested by the oral route.
9. Current treatment methods are capable of obtaining an average total chromium concentration of 0.06 mg/l or less. However, even processes such as ion exchange have breakthrough concentrations of 1.0 mg/l.
10. The costs of construction and operation of chromium treatment facilities are comparable with the costs of treating other metals.

It was apparent in reviewing the material cited, that one of the major causes for residual total chromium found in effluents is the incomplete reduction of hexavalent chromium to the trivalent form, which prohibits complete precipitation. However, the batch-flow through system discussed by Lund (61) indicates that with proper monitoring and instrumentation the standard reduction precipitation process is fully capable of reaching a total chromium level in the effluent of 0.1 mg/l. Other reports showed that filtration may also be needed to more fully control

the total system. It is, therefore, felt that with proper controls in instrumentation, a final effluent concentration of 0.1 mg/l as total chromium is currently achievable.

As chromium in both the hexavalent and trivalent forms has been shown to be toxic, especially to the lower forms of aquatic life, it is recommended that a uniform effluent limit of 0.1 mg/l be established for total chromium. As individual cases are reviewed, one should be cognizant that processes such as the Lancy Integrated Process are currently in full scale operation yielding effluents of 0.01 mg/l or less as total chromium.

It is admitted that the basis for these recommendations is a limited amount of material, particularly with respect to health hazards. It is recommended that further studies be done in this area, especially to confirm the potential concentration effect of chromium within fish and other aquatic life.

CHAPTER VII-COPPER

Copper is found naturally in the aquatic environment in the form of copper salts, inorganic or organic (soluble forms) complexes or precipitates. Table VII-1 shows the concentration of copper in nature and industrial-domestic uses of copper and its salts. Most mining of copper oxide ores is done in the states of Arizona, Michigan, Montana, Nevada, New Mexico and Utah. (48) Copper smelting and plating is done throughout the country, while copper and brass manufacturing takes place in the northeastern quarter of the nation. The major sources of copper as described by Patterson and Minear (76) include metal processing, pickle and plating bath waste, brass and copper metal working waste, jewelry manufacturing, alkaline Benberg rayon process, and acid mine drainage. Copper and its salts are also used in the electrical and plumbing fields where conductivity or corrosion resistance is important, in dye, printing, tanning pigment, pyrotechnic and photographic processes, and in human and veterinary medical preparations (66).

A review of the literature indicates that the concentration of copper in discharges from various industrial processes ranges to a high of 44,000 mg/l. A summary of various concentrations of copper found in wastewaters has been compiled in Table VII-2.

Copper is also known for complexing, especially with cyanide. This is discussed in greater detail in the chapter on cyanide and its removal. A tabulation of copper concentrations found in complex cyanide plating waste is given in Table VII-3 taken from the work of Nemerow (72).

TABLE VII-1

NATURAL SOURCES OF COPPER

<u>Source</u>	<u>Concentration mg/l</u>	<u>Reference</u>
Surface Water	up to 0.05	(66)
Ground Water	12 (Av.)	(66)
Sea Water	0.03 (Av.)	(83)

INDUSTRIAL & OTHER USES OF COPPER AND ITS SALTS (66)

Metallic Copper:	Cooking utensils, electrical industry, pipes, roofing, and other uses where conductivity or corrosion resistance are important.
Copper Chloride: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Electroplating of aluminum, manufacturing of indelible inks, mordant in dyes and printing fabrics.
Copper Nitrate: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	Pyrotechnics, textile dying and printing, photography, insecticides and electroplating.
Copper Sulfate: CuSO_4 & $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	Most common salt of copper. Extensive use for tanning, dyeing, electroplating, process engraving, pigment manufacturing. <u>Human medicine</u> as fungicide, bacteriocide, astringent, and irritant. <u>Veterinary medicine</u> as emetic, anthihelminthic, and treatment of anemia.

TABLE VII-2

CONCENTRATIONS OF COPPER IN PROCESS WASTEWATERS

<u>Process</u>	<u>Copper Concentration</u> <u>mg/l</u>	<u>Reference</u>
APPLIANCE MANUFACTURING		
Spent Acids	0.6 - 11.0	(76)
Alkaline Wastes	0 - 1.0	(76)
AUTOMOBILE HEATER		
Production	24 - 33 (28 Ave)	(76)
BRASS INDUSTRY		
Brass Dip	2 - 6	(76)
Brass Mill Rinse	4.4 - 8.5	(76)
Tube Mill	74	(76)
Rod & Wire Mill	888	(76)
Rolling Mill	34	(76)
Bichromate Pickle		
Tube Mill	13.1	(76)
Rod & Wire Mill	27.4	(76)
Rolling Mill	12.2	(76)
Copper Rinse	13 - 74	(76)
Brass Mill Rinse	4.5	(76)
Brass & Copper Wire Mill	75 - 174	(96)
Pickle Rinse Waters	70 @ 0.5 MGD	(48)
	800 @ 0.02 MGD	(48)
Pickle Bath Dump	10,000	(48)
Pickling Bath Waste	4,000 - 23,000	(72)
Bright Dip Waste	7,000 - 44,000	(72)
BUSINESS MACHINE CORP.		
Plating Wastes	2.8 - 7.8 (4.5 Ave)	(71)
Pickling Wastes	0.4 - 2.2 (1.0 Ave)	(71)
COPPER MILLS		
Mill Rinse	19 - 74	(76)
Plating Rinse Water	5.2 - 41	(76)
Tube Mill Waste	70 (Ave)	(76)
Wire Mill Waste	800 (Ave)	(76)
PLATING & METAL PROCESSING		
Metal Processing	204 - 370	(76)
Plating Wash	20 - 120	
Plating Wash	0 - 7.9	(76)
Rinse Waters	up to 100 (20 Ave)	(76)
4 Plating Operations	6.4 - 88	(76)
Electroplating Waste	0.2 - 10.0	(14)
Cyanide-Copper Waste	18	(16)
Plating Waste	6 - 300	(72)
SILVER PLATING WASTES		
Silver Waste	3 - 900 (12 Ave)	(71)
Acid Waste	30 - 590 (135 Ave)	(71)
Alkaline Waste	3.2 - 19 (6.1 Ave)	(71)

TABLE VII-3

COMPLEXED COPPER-CYANIDE PLATING WASTES (72)

<u>Plating Bath</u> <u>Cu Conc. (mg/l)</u>	<u>Rinse water</u>	<u>Copper concentration (mg/l)</u>
	<u>@ Dragout rate</u> <u>of 0.5 gph</u>	<u>@ Dragout rate of 2.5 gph</u>
51,500	107	535
12,400	2.8	14
30,000	62	310
21,000	44	220

ENVIRONMENTAL EFFECTS OF COPPER

While small concentrations of copper are beneficial and actually necessary for man and animals, higher concentrations of copper create taste and odor problems and are detrimental to various industrial uses of water, plant life, stock and wildlife, fish and other aquatic life.

Effect on Man

A review of the PHS Drinking Water Standards (94) indicates that copper is essential and beneficial to man. Man has a daily requirement of 2.0-3.0 mg/l for adults and approximately 0.1-2.0 mg/l for preschool children (66,94). It was reported, however, that a concentration of 1-5 mg/l of copper will impart an unpalatable taste in the water. A "small" dose of copper may be non-toxic, while a "large" dosage may produce emesis, and prolonged oral administration may result in liver damage. On the basis of the above, the Public Health Service recommended a desirable level of 1.0 mg/l of copper for domestic water supplies.

A review of McKee and Wolf indicates that copper has a definite physiological function in the circulatory system of man. It is not known to be a cumulative poison but is normally excreted through the urine at approximately 1.0 mg/day with excess amounts being excreted through the feces. It is a necessary factor in the utilization of iron by blood-forming organs.

McKee and Wolf (66) report that "doses of 60-100 mg taken by mouth cause symptoms of gastroenteritis, with nausea and intestinal

irritation, but doses of 10-30 mg have not caused poisoning even when continued for many days." These dosages may be those referred to above as "small" and "large" in the PHS Drinking Water Standards. Table VII-4 shows threshold levels for copper in drinking, agricultural and industrial water supplies

McKee and Wolf also reported that the limiting factor of copper in domestic water supplies is its taste. The threshold concentration is in the range of 1-2.0 mg/l while a level of 5-7.5 mg/l copper makes the water completely undrinkable. This latter point is also discussed by Schneider (83). McKee and Wolf also noted that a concentration of 1 mg/l copper has been found to react with soap producing insoluble green curds. It has also been known to produce blue-green staining on porcelain fixtures.

Effect on Irrigation Water and Plant Life

McKee and Wolf report that minute quantities of copper are beneficial and essential for plant growth. However, concentrations in the range of 0.17-7.20 mg/l have been found to be toxic to sugar beets and barley grown in nutrient solution. Similarly a 20 mg/l concentration is toxic to tomatoes, 0.1 mg/l to orange and mandarin seedlings, and 0.5 mg/l or higher to flax. Copper concentrations as low as 0.1 mg/l may be toxic to plants grown in nutrient solutions (6). A tolerance limit of 0.2 mg/l copper is recommended for water irrigated sands which are very low in organic matter, for all other types of soil a safe limit of up to 5 mg/l is suggested. Table VII-5 summarizes the toxic concentrations of copper to plants.

TABLE VII-4

THRESHOLD LEVELS FOR COPPER IN
POTABLE, AGRICULTURAL AND INDUSTRIAL WATER SUPPLIES

<u>Type</u>	<u>Threshold Level mg/l</u>	<u>References</u>
Drinking Water	1	(66)
General Ind. Water Supplies	5	(66)
Textile Water Supplies	0.5	(6)
Beverages* (ready-to-drink and carbonated)	2 - 7	(66)
Irrigation	0.1	(66)
Water Irrigated Sand Soils	0.2	(6)
Other Soil	5	(6)'
Fresh Waters	0.02	(66)
Marine Waters	0.05	(66)

* British Ministry of Agriculture

TABLE VII-5

TOXIC
CONCENTRATION OF COPPER TO PLANTS (66)

<u>Species</u>	<u>Concentration mg/l</u>
Sugar beets	0.17 - 7.20
Barley - Tomatoes	2.0
Oranges and mandarin seedlings	0.1
Flax	0.5

Effect on Stock and Wildlife

The Green Book reports that concentrations of iron and copper in milk, as low as 0.1 mg/l, have been found to contribute to the development of oxidized flavors. However, a concentration of 1.0 mg/l copper was recommended for stock watering (6). On a similar note, McKee and Wolf reported that small amounts of copper are beneficial for the hemoglobin count and growth in rats. Copper is beneficial to the growth of suckling pigs and is believed necessary to prevent scouring and wasting diseases in cattle and sheep.

In general it would appear that copper at a concentration of approximately 1 mg/l is not detrimental to animal wildlife, however, higher concentrations may be.

Effect on Fish and Other Aquatic Life

The effect of copper on fish and aquatic life varies not only with respect to various species, but also with respect to water quality. Table VII-6 summarizes the toxic and synergistic effects of copper with respect to various water quality parameters.

As summarized in Table VII-7, it is apparent that there is a broad range of copper toxicity for various aquatic species (both marine and fresh). Most forms of fresh water fish are capable of withstanding a copper concentration of 0.10 mg/l or greater. Other forms of fresh water aquatic life have substantially greater sensitivities to copper down to approximately 0.002 mg/l. Toxicity to marine life, on the other hand, generally falls within a range of 0.05-0.1 mg/l. It has been reported that copper is less toxic in river water than in lab tests. In addition to being highly toxic to

many forms of aquatic life, copper is concentrated by fish and aquatic life. A summary of this data is shown in Table VII-8.

While one species of algae has been shown in Table VII-8 to have a relatively high concentration factor for copper, copper in the form of copper sulfate has long been utilized for the control of algae in farm ponds, reservoirs, etc. Table VII-9 shows that various species of algae have a comparatively high sensitivity to copper sulfates.

TABLE VII-6
SUMMARY OF SYNERGISTIC EFFECTS
AND COPPER

<u>Parameter</u>	<u>Effect</u>	<u>Reference</u>
Hard Water	toxicity decreased to range of 0.1-1.0 mg/1 Cu.	(66,83)
Soft Water	Cu. toxicity increased to 0.015-3.0 mg/1 range	(66,83)
Zinc @ 8 mg/1	alone killed fish as did copper @ 0.2 mg/1. Zinc @ 1.0 mg/1 & copper @ 0.025 mg/1 also killed fish	(6,15,83)
Chlorine	toxicity of Cu. increases	(66)
Cadmium	toxicity of Cu. increases	(66)
Sodium nitrite & Sodium nitrate	toxicity of Cu. was decreased	(66)
Copper	toxicity of cyanide decreased	(66)
Alkalinity	toxicity of Cu. decreased	(6,66)
Acidity	toxicity of Cu. increases	(66)
Temperature	toxicity of copper sulfate decreased 2.5% for each °C below 15 °C.	(6,66)
Mercury	toxicity of Cu. increases	(6)

TABLE VII-7

TOXIC OR HARMFUL COPPER
CONCENTRATIONS FOR FISH & OTHER AQUATIC LIFE

<u>Species</u>	<u>Concentration</u> mg/l	<u>Reference</u>
Barnacles	10-30 in 2 hours	(6,66)
<u>Mytilus edulis</u>	0.55 in 12 hours	(6,66)
Oysters	0.1 - 0.5	(6)
Soft Clam (<u>Mya arenaria</u>)	0.5 in 3 days	(6)
Giant Kelp (<u>Macrocystis</u> <u>pyrifera</u>)	0.1 in 2-5 days	(6,66)
Red tide organism (<u>Gymnodinium breve</u>)	0.05	(6)
Generally: bacteria & Microorganisms	0.1 - 0.5	(66)
Oyster Larvae	0.1 - 0.5	(66)
Young eels	0-13 for 50 hrs. as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	(66)
Blue gill sunfish (softwater)	1.25 96 hr. TLm	(66)
Rainbow Trout (Lake Huron)	5.0 in 10 hrs. as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	(66)
Sea Lamprey	5.0 in 12 hrs. as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	(66)
<u>Daphnia magna</u> , young	0.027 as CuCl	(66)
<u>Cyclops vernalis</u>	2.7	(in Lake Erie water @ 20-25°C)
<u>Mesocyclops leuckarti</u>	1.9	
<u>Diaptomas oregonensis</u>	0.0024	
<u>Hemacheilus barbatulus</u>	0.20 in 24 hrs.	(15)
<u>Nereis sp.</u> (warm)	0.1 (threshold)	(15)

TABLE VII-7 (con't)

TOXIC OR HARMFUL COPPER
CONCENTRATIONS FOR FISH & OTHER AQUATIC LIFE

<u>Species</u>	<u>Concentration</u> <u>mg/l</u>	<u>Reference</u>
<u>Carcinas maenas</u> (shore crab)	1-2 (threshold)	(15)
<u>Leander squilla</u> (prawn)	0.5 (threshold)	(15)
Crayfish, young	0.125 - 0.6	(15)
<u>Salmo gairdnerii</u>	0.4 - 0.5	(15)

<u>FISH</u>	<u>MAXIMUM CONCENTRATION</u> <u>tolerated as CuSO₄</u>	
Perch	0.5	(66)
Black bass and bluegills	0.8	(66)
Sunfish	1 - 35	(66)
Black bass	2.00	(66)

An additional effect of copper in surface waters, as reported by McKee and Wolf is its interference with BOD determinations and the self-purification process of streams. A concentration as low as 0.01-0.5 mg/l will interfere with BOD and self-purification rates (66). Other investigators reviewed by McKee and Wolf, however, indicated that a concentration of 0.4 mg/l did not interfere with self-purification and that a copper concentration of 8.4-35 mg/l might be needed to cause a 50% reduction in BOD₅. In this case it appears that the water quality may have affected the results of the reported investigations.

TREATMENT TECHNOLOGY-COPPER REMOVAL

Precipitation

One of the oldest and most common methods of treatment of copper bearing wastewater is precipitation of copper hydroxide at alkaline pH conditions. Copper hydroxide has a minimum solubility within the pH range of 9.0-10.3. It is also reported to have a solubility of 0.01 mg/l at a pH of 10 (76). The theoretical level is seldom obtained due to poor settling, incomplete reactions, and the influence of other ions within the solution. Generally, lime is utilized to maintain proper pH conditions. Table VII-10 shows the efficiency of this and other processes, with and without filtration.

TABLE VII-8
CONCENTRATION OF COPPER IN FISH & AQUATIC LIFE

<u>Species</u>	<u>C. F.</u>	<u>Reference</u>
Plankton	1,000-5,000	(6)
Algae (<u>Ochromonas</u>)	1,840-3,040	(66)
<u>Sphaerotilus</u>	3,890	(66)
Marine bacteria	990	(66)
Marine invertebrates, soft parts	5,000	(66)
Fresh water fish	50	(66)

TABLE VII-9

TOXICITY OF COPPER SULFATE TO ALGAESpeciesBLUE-GREEN ALGAEToxicityReferenceCylindrospermum2.0-4.0 mg/l Toxic
for 28 days

(15)

AnabaenaAnacystisCalotrixNostocOscillatoriaPlectonemaGREEN ALGAEArthrodesmusChlorellaClosteriumOocystisGREEN ALGAEScenedesmusStigeocloniumZygnemaGREEN FLAGELLATE AND YELLOW ALGAEChlamydomonasPandorinaTribonemaGomphonemaNaviculaNitzschiaAnabaena

0.09 Conc. mg/l

(66)

Beggiatoa

5.0

Chara

0.2-5.0

Cladophora

1.0

Cladotrix

0.2

Conferva

0.4

Nauicula

0.7

Oscillatoria

0.1-0.4

Scenedesmus

5.0-10.0

Spirogyra

0.05-0.3

Ulothrix

0.2

Volvox

0.25

TABLE VII-10

COPPER TREATMENT EFFICIENCIES

<u>Process</u>	<u>CONCENTRATION mg/1</u>		<u>Ref.</u>
	<u>Initial</u>	<u>Final</u>	
Lime Neutralization and settling	33	less than 1.0	(76)
	204-385	0.5 (ave.)	(76)
	unknown	0.2-2.5	(76)
	unknown	0-1.2 (0.15-.19 ave)	(76)
	10-20	1-2	(76)
	general	0.2-2.5	(97)
Line Neutralization settling & Filtration	previous		
	eff 0.2-2.5	0.2-0.5	(76)
	general	0.5	(97)
Cyanide destruction w/sodium hypochlorite	14-18	0.005-0.5 (Lab scale)	(76)
Coag. w/ferric chloride w/filtration of eff	30	0.16-0.3 (full scale)	(76)
Lancy Batch Treat	electroplating	1.5-2.0	(61)
Lancy Integrated	electroplating	0.15	(61)
Lancy Integrated	electroplating	less than 0.5	(64)
Carbon adsorption of copper cyanide complex	98	less than 1.0	(14)
Process change - Velco Brass & Copper Co.	75-124	0.25-0.35	(96)
Process Modification	40	0.9	(76)
Recovery	unknown	none	(48)
Ion Exchange	1.02	0.03	(76)
Electrolytic Recovery	26	0.0 in 11 days	(76)

Copper-Cyanide Wastes

A new method involving complexed copper cyanide wastewaters utilizes the destruction of cyanide by sodium hypochlorite followed by a pH adjustment and coagulation-precipitation with ferric chloride and lime, and subsequent filtration. Table VII-10 shows the processes efficiency.

Lancy Process

The Lancy Integrated System theoretically is capable of achieving an effluent of 0.15 mg/l. Table VII-10 shows process efficiency of the Lancy System.

In practice, McDonough and Steward (64) reported an effluent copper concentration of less than 0.50 mg/l with the Lancy integrated system. Lund (61) describes the Lancy system which utilizes counter-current rinsing with a chemical solution (lime) that is then recycled after sedimentation.

Carbon Adsorption

Battelle (14) reported complex cyanide-chromium removal from electroplating waste by carbon adsorption. Their report indicated that carbon adsorption of complexed cyanide from electroplating waste was most effective with nickel and copper complexes and at a pH of 10. The cost of removing cyanide by complexing with nickel or copper by carbon adsorption and recovery, after previous contact with cadmium or zinc, was in the range of 20-40¢ per pound of cyanide treated.

Recovery Processes

Copper can be economically recovered from the wastewaters under certain situations. One of the methods which may be utilized as a

recovery step is process modification. According to Patterson and Minear (76) the use of counter current rinsing for one company allowed direct return of their rinse flow to their plating bath as evaporative makeup water. The counter current rinsing for this plant reduced their rinse water flow volume from 480 gph to only 16 gph. This scheme reduced their total copper discharge from 40-0.9 mg/l. The Velco Brass and Copper Company, of Kenilworth, New Jersey (96) has reduced its copper effluent by converting a former sulfuric-chromic acid and ammonium bifluoride-chromic acid pickle to a sulfuric acid, 2-5% hydrogen peroxide pickle (with stabilizing agents). The result has been a reduction in copper in the discharge from 175-124 mg/l to 0.25-0.85 mg/l. Velco (96) reports that by the use of a neutralizing agent chemical rinse following a sulfuric acid-hydrogen peroxide pickle dip, the copper content of the rinse water can be maintained at 0.1 mg/l. At present, the cost of their pickling treatment and recovery process is \$156.00 per operating day (or \$194.00 per operating day including amortization costs). This compares to their previous cost of \$195.00 per operating day, which does not include cost of treatment. Their current treatment recovery cost is only \$46.72 per day or \$.62 per ton of copper wire produced.

Table VII-10 shows the efficiency of other recovery processes including evaporative recovery, ion exchange and electrolytic recovery. Evaporative recovery has been practiced for over 20 years (76). Patterson and Minear indicate, however, that some form of pre-concentration may be needed for this process to be economical.

Ion exchange, according to Patterson and Minear, may be an economical means of removing copper from dilute wastewaters. One of the articles reviewed by them indicated that ion exchange was successfully used from a wastewater containing only 1.02 mg/l copper, at a flow rate of approximately 0.80 gallons per square foot per minute.

Gurnham (48) reports that the Inspiration Consolidated Copper Company of Arizona utilizes electrolytic recovery for their copper sulfate waste to completely eliminate the discharge of copper in their wastewaters. He also reported that the rate of recovery of copper from this facility is about 40,000 tons per year. A pre-concentration step may be necessary for this type of operation (76).

A review of Table VII-7 indicates that while some processes such as ion exchange and electrolytic recovery may be capable of reducing the copper concentration to the range of 0.030 mg/l, destruction processes are currently capable of maintaining effluent levels of 1.0 mg/l. Proper pH control followed by good clarification for removal is needed to reach a lower concentration.

A review of the capital and operating and maintenance cost in Tables VII-11 and 12 would indicate that the operation of a plant utilizing lime neutralization and sedimentation might be more economical if filters are utilized. Further confirmation of this data is necessary prior to using this as a general assumption. It is apparent, however, in reviewing the capital and operating costs that both figures are in line with the cost of removing other metals from wastewaters.

SUMMARY AND RECOMMENDATIONS

After a review of the above discussions and referenced data, the following can be stated.

1. A concentration above 0.05 mg/l in surface waters and above 0.03 mg/l in sea water is considered to be from man-made industrial sources. Industrial waste discharges of copper have been reported to vary anywhere from trace levels up to as high as 44,000 mg/l.
2. Copper is an essential element in both man and animals. While copper at rather high concentrations may be toxic to man and animals it will produce an unpleasant taste to the point of being completely unpalatable long before it has a toxic effect. The 1962 Drinking Water Standard of 1.0 mg/l, appears to be appropriate for human beings.
3. Industrial water supplies may utilize waters containing copper up to 5 mg/l. However, the textile industry is reported to have problems with waters containing as little as 0.5 mg/l.
4. Water containing as much as 5 mg/l copper used for plant irrigation normally does not create problems. However, for sandy soils very low in organic matter, copper may be damaging to plants at a concentration of 0.1 mg/l.
5. The water supply for stock and wildlife has been shown to be beneficial if it contains some copper. However, it is recommended that it not exceed a concentration of 1.0 mg/l.

6. Fresh water fish have been shown to tolerate a concentration as high as 0.14 mg/l. Other fresh water organisms, however, have a toxicity to copper reportedly as low as 0.002 mg/l. Marine aquatic life has a general toxicity range starting at 0.05 mg/l. Various forms of aquatic life including fish and lower forms are known to have concentration factors ranging from 50-5000 C.F. The toxicity of copper is known to increase in the presence of zinc, chlorine, cadmium, and mercury in acid waters and at temperatures above 15°C. Conversely, the toxicity of copper decreases as water hardness increases, calcium concentration, and alkalinity increase, and as the concentrations of other previously mentioned metals decrease. It has also been found to decrease in the presence of sodium nitrate and sodium nitrite and also when the temperature is below 15°C.
7. Copper sulfate is known to be toxic to algae and is used for their control. Effective concentrations range from 0.07 to 10 mg/l.
8. Current achievable treatment is capable of maintaining a maximum effluent level of 1.0 mg/l. Various recovery processes are currently capable of reducing copper down to the 0.03 mg/l range on an average. The cost of both initial installation and operation of treatment facilities is well within the range of treating other metals.

On the basis of the above summary, it is recommended that a uniform effluent limit of 1.0 mg/l be adopted for all wastewater discharges of copper. It is further recommended where copper is of particular concern to the preservation of fish and aquatic life and

where an industrial discharge will not receive dilution by other discharges within the same industry or by rapid mixing or use of a diffuser in the stream, that the industry remove copper to the best obtainable level that is economically possible. On the basis of the literature reviewed for this report the value of copper should offset some of the economic problems of more complete treatment.

TABLE VII-11

CAPITAL COST FOR COPPER REMOVAL

<u>Process</u>	<u>Flow</u>	<u>Cost</u>	<u>Cost/ 1000 Gal.</u>	<u>Reference</u>
Lime Neutralization and settling			\$9,200	(76)
"	1 MGD	\$ 100,000	100	(97)
"	10 MGD	600,000	60	(97)
"	50 MGD	2,600,000	52	(97)
Lime Neutralization Settle & Filter	1.5-2.0	800,000	400-530	(76)
"	1 MGD	300,000	300	(97)
"	10 MGD	1,300,000	130	(97)
"	50 MGD	4,600,000	92	(97)

TABLE VII-12

OPERATION MAINTENANCE COST FOR COPPER TREATMENT (76)

<u>Process</u>	<u>Cost/1000 Gal.</u>
Lime Neutralization and sludge dewatering	\$3.50 (1951)
Lime Neutralization and settling	3.59 (1957)
Assumed "	1.62 Rinse waters only
	2.85 Total
Lime Neutralization settling & filtration	5-9¢ for 1 MGD 11-20¢ for 10 MGD
Recovery Value:	
of copper waste	\$0.60-\$3.00 @ 100-500 mg/l
of brass waste	\$0.20-\$1.20 @ 40-250 mg/l

CHAPTER VIII-CYANIDE

Cyanide is found in the wastes of several industries (14,16, 48,61,66,67,72). These include the extraction of ore, gold mining, photographic processing, coke plants and blast furnaces, manufacture of synthetics, electroplating and metal finishing, and pickle liquor waste, as well as other chemical industries. The major source of cyanide in industrial wastewaters is probably the waste from coke plants, non-ferrous plating baths and plating rinse waters. Various concentrations reported in the literature have been summarized in Table VIII-1.

From this table it is apparent that the concentrations of cyanides in plating baths may be expected to vary from 20,000-100,000 mg/l. The concentration of cyanides found in plating rinse waters is highly dependent upon the rate of drag-out. Concentrations are reported from 10-1500 mg/l. Nemerow (72) indicated cyanide concentrations of various plating baths and rinse waters as functions of the complexing metal and two different drag-out rates. This data has been summarized in Table VIII-2.

In addition to hydrogen cyanide and cyanide salts, cyanide may also appear in discharges as the sodium or potassium salts of cyanate, thiocyanate, ferro and ferric cyanides and also as cyanogen chloride (66). Although concentrations are customarily expressed in terms of mg/l of cyanide ion, the actual form present is a function of pH. Because hydrogen cyanide (HCN) is a weakly dissociated acid, it will be present mainly in the undissociated form at a pH less than 8. In Figure VIII-1 the relative proportions of CN^- and HCN are shown as a function of pH. Below a pH value of 7 less than one percent of the total is present as CN^- .

Above a pH value of 10, 87 percent is present as the cyanide ion (66). This relationship is important because HCN is a more toxic entity than the ion. Therefore, even for a given concentration, toxicity will be critically dependent on pH.

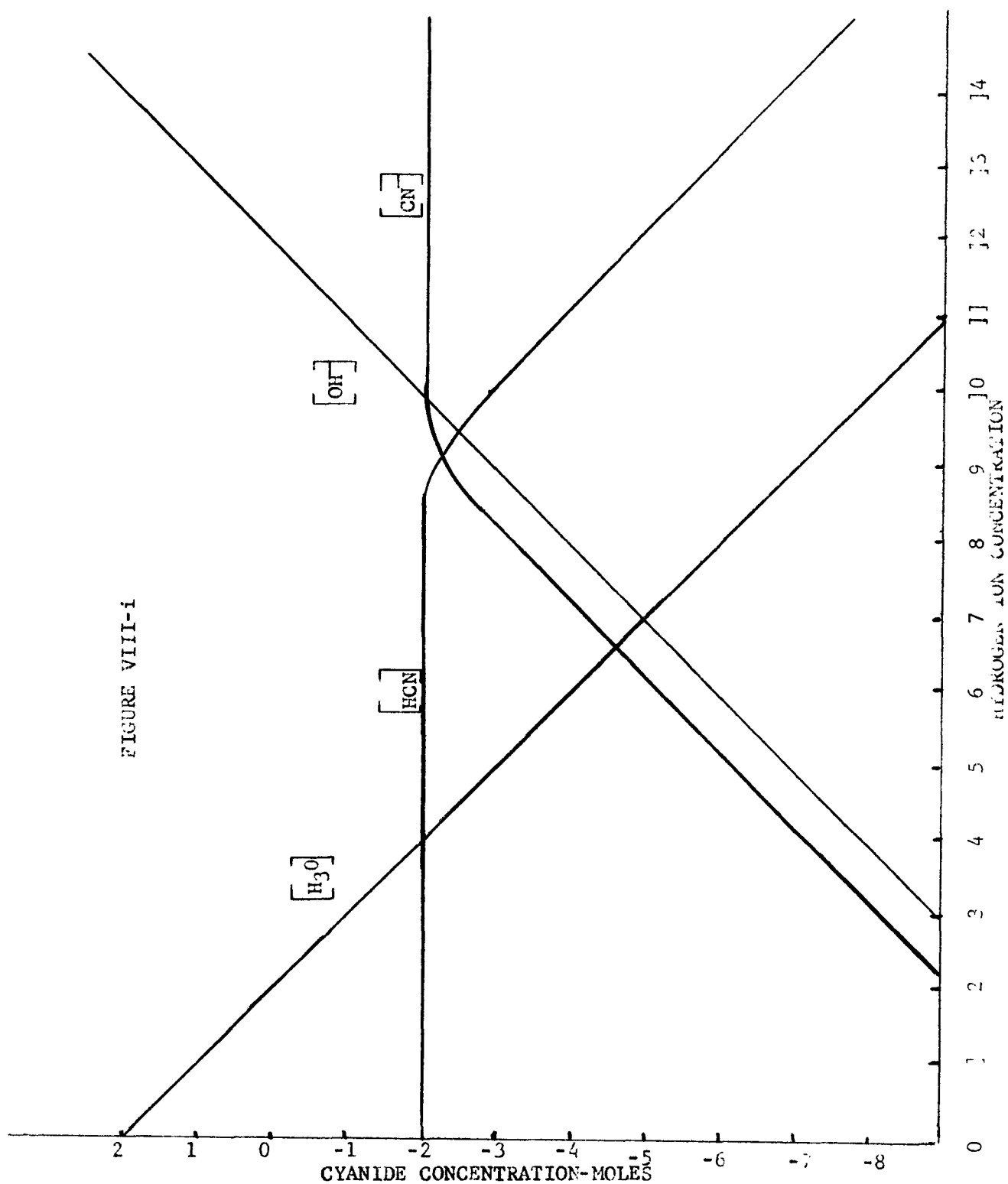
TABLE VIII-1
CONCENTRATIONS OF CYANIDE IN INDUSTRIAL WASTE WATERS

<u>Source</u>	<u>Concentrations, mg/l</u>	<u>Reference</u>
Plating Baths	48,000-100,000	(76)
	21,800- 57,000	(72)
Plating Rinse Waste	10- 700	(76)
	39- 1,500	(16)
	28- 72	(14)
Coke Plant Crude Liquor to Ammonia Still	20- 100	(48)
From Ammonia Still	10- 100	(48)

TABLE VIII-2
COMPLEXED CYANIDE PLATING WASTE
CYANIDE CONCENTRATIONS, MG/L (72)

<u>Plating Bath</u>	<u>(Rinse Drag-Out @)</u>	
	<u>0.5 gph</u>	<u>2.5 gph</u>
28,000 w/Cu	58	290
57,700 w/Cd	120	600
48,900 w/Zn	102	510
47,500 w/Cu & Zn	99	495
21,800 w/Ag	45	225

FIGURE VIII-1



The relative toxicities of a nickel-cyanide complex are such that a pH drop from 7.8 to 7.5 increases the toxicity tenfold and a drop from 8.0 to 6.5 increases the toxicity a thousand fold (6). Adjustment to the optimum pH is also an important facet of the treatment of cyanide as will be discussed later. Direct sunlight on effluents containing the otherwise less toxic ferric and ferro cyanides is also of great importance (16).

ENVIRONMENTAL EFFECTS OF CYANIDE

Effects on Man

The toxicity of cyanide in man is well documented but at relatively high concentrations. It is acknowledged in the 1962 Drinking Water Standards (94) that the 0.2 mg/l CN standard for rejection of a water supply is based on the treatability of cyanide and a safety factor of 100 rather than its toxicity to man. Other recognized standards of 0.01 to 0.2 mg/l are based on fish toxicity rather than toxicity to man (94).

The toxic effects of cyanide on man are summarized in Table VIII-3. McKee and Wolf (66) indicate the average fatal dose of hydrogen cyanide for man is 0.7 to 3.5 mg/kg of body weight. A fatal dose for a 165 lb. man would then be 52-260 mg of HCN.

The maximum safe intake level of cyanide is believed to be about 18 mg/day, part of which may come from natural and industrial exposures (66). An odor threshold of 0.001 mg/l may make water unpalatable before toxic effects are important.

McKee and Wolf (66) also report that the body normally ingests small amounts of cyanide e.g., by consumption of members of the cabbage

family. Small portions of ingested cyanide will be exhaled and the remainder will be rapidly converted by the liver to the relatively non-toxic sulfur compound, thiocyanate which is eliminated irregularly and slowly in the urine. Cyanide, therefore, is a non-cumulative toxin and small doses can be disposed of continuously by the body's natural detoxifying mechanisms.

TABLE VIII-3

ORAL TOXICITY OF CYANIDE FOR MAN

<u>Dose</u>	<u>Response</u>	<u>Reference</u>
0.001	Odor threshold	(66)
2.9 - 4.7 mg/day	Non-injurious	(94)
10 mg single dose	Non-injurious	(94)
<18 mg/day total intake	Maximum safe ingestion	(66)
19 mg/day in water	Calculated from threshold limit in air as safe	(94)
50-60 mg single dose	Fatal	(94)

Effect on Domestic and Wild Animals

With reference to stock and wildlife, McKee and Wolf indicate that hydrogen cyanide and sodium cyanide have been found to be toxic to animals. A hydrogen cyanide concentration of 103 mg/l has been found to be fatal to cows and ducks. Otherwise toxic and lethal dosages of hydrogen cyanide and sodium cyanide are summarized in Table VIII-4. McKee and Wolf report that for sheep the toxic dose of hydrogen cyanide is 1.05 mg/kg of body weight, while the toxic concentration of sodium cyanide is 4.15 mg/kg of body weight.

TABLE VIII-4

TOXIC EFFECT OF CYANIDE ON DOMESTIC ANIMALS (66)

<u>Animal</u>	<u>Dose of HCN</u>
Cow	0.39 - 0.92 grams
Sheep	0.04 - 0.10 grams
Horse	0.39 grams
Dog	0.03 - 0.04 grams

TABLE VIII-5

TOXIC EFFECTS OF CYANIDE ON FISH AND OTHER AQUATIC ORGANISMS
(from McKee & Wolf) (66)

<u>Organism</u>	<u>CN⁻ Conc. (mg/l)</u>	<u>Time of Exposure</u>	<u>Effect</u>
Trout	.02	27 days	survived
Blue gills	.4	96 hrs.	survived
Bullheads	.5	96 hrs.	survived
Brook trout	0.05	120-126 hrs.	lethal
Rainbow trout	0.07	74 hrs.	overturned
Fish	0.1	1 day	overturned
Rainbow trout	0.1-0.2	1-2 days	MLD
Bluegill sunfish	0.12-0.18	96 hrs. TL _m	--
Trout	.126	170 min.	overturned
Trout	.15	4.8-6.4 min.	overturned
Bluegill sunfish	.18	24 hr. TL _m	--
Rainbow Trout	.2	11 min	LD-50
Fish	.2	150 min.	lethal
Adult chub	.33	2.5 hr.	lethal
Trout	.42	4 min.	overturned
Adult Chub	.50	141 min.	MLD
Trout	1.0	20 min.	lethal
Carp	10.0	1.5 hrs.	MLD
<u>Daphnia magna</u>	.34	48 hrs.	lethal
<u>Cricotopus bicinctus</u>	3.2m	--	survived
<u>Mayorella palestinesis</u>	130	--	lethal

The literature reviewed did not contain any mention of the potential effect of toxicity of cyanide on plant life.

Effect on Fish and Aquatic Organisms

The major impact of cyanide on the aquatic environment is its toxicity to fish and other forms of aquatic life. It is again noted that the effect of pH is a significant factor. McKee and Wolf report that an innocuous concentration of cyanide at a pH of 8 may become detrimental if the pH is lowered to 6 or less. They further report "In natural streams, cyanides deteriorate or are decomposed by bacterial action, so that excessive concentrations may be expected to diminish in time." (66) McKee and Wolf also indicated that from 90 to 95 percent of the cyanides in waters have been found to be removed by percolation of wastewaters through soil columns. Greater removal was obtained in soils rich in organic matter.

The toxicity to fish and other aquatic organisms is summarized in Table VIII-5. The Report of the Committee on Water Quality Criteria indicates that the toxicity of cyanide to diatoms was found to vary very little with respect to temperature (6). McKee and Wolf on the other hand indicate that the toxicity of cyanide to fish has been found to increase at elevated temperatures. They report that a rise of 10°C produced a 2 to 3 fold increase in the toxicity of cyanide. Other factors which have an effect on the toxicity of cyanide, as reported by McKee and Wolf, include dissolved oxygen and the presence of certain metals. McKee and Wolf and the "Green Book" (6,66) indicate that a low dissolved oxygen level may increase the toxicity of cyanides.

Trout were exposed at 17°C to a concentration of 0.105 mg/l of cyanide. This level was found to be toxic in 8 hours at 95 percent oxygen saturation, in 5 hours at 73 percent saturation, and only 10 minutes at 45 percent saturation. With respect to the presence of metals, nickel may complex with the cyanide decreasing its toxicity, especially at higher pH values. Zinc and cadmium on the other hand, have been found to increase toxicity. Iron cyanide complexes ($\text{Fe}(\text{CN})_6^{-3,-4}$) are normally less toxic than simple cyanides (1,66). However, McKee and Wolf have reported that under exposure to direct sunlight the previously assumed harmless concentration of 2000 mg/l (under diffuse light) of potassium ferric cyanide or potassium ferrocyanide become toxic at concentrations of 0.5 to 2.0 mg/l. A potassium ferrocyanide concentration of 2.0 mg/l under direct sunlight resulted in a cyanide concentration of 0.36 to 0.48 mg/l which killed fish in 0.5 to 1.5 hours.

A general recommendation of 0.025 mg/l has been proposed by the Aquatic Life Advisory Committee of the Ohio River Valley Sanitation Commission, according to McKee and Wolf, as the limit for being unsafe to fish and aquatic life. They further indicated that proper chlorination under neutral or alkaline conditions is capable of reducing cyanide to a level far below the recommended limit. The acute oral toxicity of cyanogen chloride, which is the product of chlorinating hydrogen cyanide, would be 1/20 that of the hydrogen cyanide alone.

TREATMENT TECHNOLOGY - CYANIDE REMOVAL

The 1968 report the Battelle Memorial Institute (16) discussed the following five conventional methods for cyanide removal from plating waste:

- (1) Oxidation by chlorine gas - complete removal
- (2) Oxidation by hypochlorites - complete removal
- (3) Conversion to cyanate by chlorine gas followed by precipitation and clarification
- (4) Conversion to cyanate by hypochloride
- (5) Conversion to Ferrocyanide by ferrous sulfate - effluent obtained, 5-10 mg/l

They also reported seven newer methods which were being investigated at that time for cyanide removal. These include:

- (1) Complex formation with polysulfides to form sulfocyanates
- (2) Destruction by potassium permanganate
- (3) Oxidation to cyanate by ozone
- (4) Oxidation to cyanate by hydrogen peroxide
- (5) Complexation by nickel salts to highly stable nickel cyanide
- (6) Biological oxidation
- (7) Irradiation, dialysis, reverse osmosis, and electrolytic reduction.

In the 1968 report, Battelle also reported that ion exchange and evaporation have proven feasible for detoxification and recovery of cyanide in more concentrated waste streams. They indicated that the cost of chromium and cyanide removal is highly dependent upon the method selected, the waste volume, the concentration, the degree of recovery and the

value of that recovered, whether it is a batch or continuous operation, and the chemical cost.

According to the recent investigation by Patterson and Minear (76), the three most frequently employed practices for cyanide removal are destruction of cyanide by chlorination, electrolytic decomposition, and ozonation. Table VIII-6 summarizes some typical treatment plant characteristics.

TABLE VIII-6
SUMMARY OF TREATMENT EFFECTS ON CYANIDE

<u>Method of Treatment</u>	<u>Flow</u>	<u>[CN⁻] mg/l</u>		<u>Ref.</u>
		<u>Influent</u>	<u>Effluent</u>	
Chlorination	2500-3000 gals/hr	-	0.1	(76)
Chlorination	2000 gals/mo	32.5	0.0	(76)
Chlorination + Sulfuric Acid Hydrolysis	-	700	0.0	(76)
Electrolytic Decomposition	-	45,000 - 100,000	0.1-0.4	(76)
Ozonation	500 gals/min	25.0	0.0	(76)
Lancy Integrated System	-	-	0.02	(61)

Chlorination

Destruction of cyanide by chlorination may be accomplished by either the direct addition of chlorine gas or by the addition of sodium hypochlorite, thus saving on hydroxide. The selection of the method is one of economics. Chlorine gas is about half as expensive as hypochlorite treatment. However, it is also much more dangerous to handle and the equipment costs are higher.

The destruction of cyanides by chlorination may be carried out in either batch or continuous operations. In the batch operation, sufficient amounts of sodium hydroxide are added to the waste to raise the pH to approximately 10.5. Chlorine is then added at a constant rate with the simultaneous addition of more sodium hydroxide to maintain the pH above 10.5. This oxidizes the cyanide to the cyanate which is less toxic. Continuation of the addition of chlorine will completely oxidize the cyanide to the harmless forms of nitrogen and carbon dioxide. To accomplish this, chlorination is continued without the further addition of sodium hydroxide.

This may also be done by acid hydrolysis. Acid hydrolysis however, must take place at a pH of 2 to 3 which usually necessitates the addition of sulfuric acid and then subsequent neutralization of the acidic waste prior to discharge. This method for complete destruction of cyanide has both advantages and disadvantages. The main disadvantage is that back neutralization increases the total dissolved solids level of the effluent. The main advantage of this process is that cyanate will be destroyed within about 5 minutes contact time.

Complete destruction of cyanide may also be obtained as mentioned by continuation of chlorination alone. The rate of the reaction, however, is relatively slow (up to 24 hours) if the pH remains greater than 10. However, if the pH of the waste is reduced to between 8 and 8.5, the cyanate oxidation can be completed within about 1 hour. One problem encountered in the total oxidation of the cyanate by chlorine alone is that an excess amount of chlorine must be added to prevent liberation of the highly toxic cyanogen chloride gas.

This same process may be carried out on a automated continuous system. The feed mechanisms for adding chlorine and sodium hydroxide are often controlled by pH meter and an oxidation-reduction potential recorder-controller.

As reported by Gurnham (48) the theoretical requirements for the destruction of 1 pound of cyanide are 2.7 pounds of chlorine and 3.1 pounds of sodium hydroxide for the first step of the reaction. The total theoretical chemical requirement is 6.8 pounds of chlorine and 3.7 pounds of sodium hydroxide per pound of cyanide. However, it has been found in practice that approximately 8 pounds of chlorine are required per pound of cyanide destroyed.

As reported by Patterson and Minear (76) several manufacturers have developed small package treatment systems for the destruction of cyanide by chlorination. They indicated that the capacity of these units range from 800 gallons of waste per hour containing a maximum of 450/mg/l of cyanide, to units capable of handling 1,800 gallons per hour with a maximum cyanide content of 350 mg/l. The cost of a unit with the capacity of 800 gallons per hour was reported by Patterson and Minear to be \$15,000 for the complete unit. Patterson and Minear further reported that larger cyanide destruction units require individually tailored treatment systems. They reported that one unit utilizing a 2 step process has been constructed to handle 1.5 MGD.

Patterson and Minear also described the efficiency of these units. One unit, treating from 2,500 to 3,000 gallons per hour of cyanide waste, achieved a final effluent of 0.1 mg/l. Similarly, an IBM plant utilizing alkaline chlorination followed by acid hydrolysis, reduced a

700 mg/l cyanide concentration to 0 mg/l cyanide plus cyanate.

Another plant described by Patterson and Minear was a General Electric Metal Plating operation in Erie, Pennsylvania. They had a waste containing an average cyanide content of 32.5 mg/l. It was treated on a batch basis at the rate of 2,000 gallons per month, and obtained a final concentration of cyanide in the effluent of 0.0 mg/l as cyanide.

Electrolytic Decomposition

Patterson & Minear reported that waste containing high concentrations of cyanide are most effectively treated by electrolytic decomposition. The concentrated cyanide waste is subjected to electrolysis at a temperature of approximately 200°F for several days. When the system is first started, the cyanide will be completely broken down to carbon dioxide and ammonia with cyanate as an intermediate. However, as the process continues, the waste electrolyte becomes less capable of conducting electricity and the reaction may not be completed. It is further stated that the residual cyanate which may be formed will then require chlorination for further destruction. They reported that this system, with detention of 1 to 18 days, is capable of reducing initial cyanide concentrations ranging from 45,000-100,00 mg/l to final cyanide concentrations of 0.1 to 0.4 mg/l.

One of the problems which has been encountered with the electrolytic destruction process, as reported by Patterson and Minear, has been the presence of sulfate in the waste. In removing cyanide concentrations of 695 to 750 mg/l, heavy scaling at the anode prevented further electrolysis.

Ozonation

More recent literature, as reported by Patterson and Minear, indicates that ozonation might offer the cheapest method of destroying cyanide. They reported that cyanide complexed with zinc, nickel, and copper was easily destroyed. However, a cobalt-cyanide complex was found to be resistant to treatment by ozonation. Patterson and Minear indicated that the Boeing Airplane Metal Working plant in Wichita, Kansas, has reported complete destruction of cyanide from a 500 gallon per minute waste stream initially containing 25 mg/l cyanide.

Miscellaneous

As reported in Lund (61), the patented process for treating electroplating waste known as the Lancy system is also capable of obtaining low cyanide concentrations from plating waste. He states that a batch treatment is capable of obtaining a 0.5 mg/l effluent while the integrated system theoretically is capable of obtaining an effluent of 0.02 mg/l of total cyanide. In a report of a full scale operation utilizing the Lancy integrated system, McDonough and Stewart (69) have reported a total effluent cyanide concentration of "none" after several years of operation at an electroplating facility in Wisconsin.

A 1971 report by the Battelle Memorial Institute (14), discussed investigations of several new processes which they have investigated for removal of complexed cyanide. They reported that carbon absorption of complexed cyanide from electroplating waste was most effective with nickel and copper complexes at a pH of 10. Other methods investigated and reported by Battelle included flotation, liquid-liquid extraction, centrifugation followed by extraction, and carbon absorption with recovery.

Their work was aimed at the recovery of the heavy metals associated with the cyanide, and the final effluent concentrations of cyanide obtained are substantially higher than those reported by other methods.

Cost of Treatment

The cost of treating cyanide wastewaters by the various methods has been summarized in Tables VIII-7 and VIII-8 below, Table VIII-7 gives the capital cost and Table VIII-8 the operating and maintenance costs. From these tables, it is apparent that the cost of treating cyanide bearing wastewaters is dependent not only on the process which is utilized, but also on the volume of waste treated, and the concentration of cyanide in the wastewaters. Additional cost data other than that summarized in these tables is shown in the report by Patterson and Minear (76) and in the last chapter of this report.

On the basis of the cost data by Weston (97), as shown in Table VIII-7 the total destruction of cyanide by chlorination under alkaline conditions is comparable with the cost of removing metals from industrial wastewaters.

In remarks before the State of Illinois Pollution Control Board regarding the establishment of effluent criteria, Currie (27) stated that several industrial witnesses, representing firms with cyanide problems, endorsed the proposed Illinois Pollution Control Board limit of 0.025 mg/l for total cyanide. He further reported that while the work of Patterson and Minear and the testimony by Weston indicated that chlorination, among other methods, is currently capable of achieving cyanide effluent levels of zero, the great bulk of their evidence supported the

TABLE VIII-7

CAPITAL COST OF CYANIDE TREATMENT

<u>Process</u>	<u>Flow</u>	<u>Initial Conc. mg/l</u>	<u>Capital Cost (year)</u>	<u>Cost/Gal</u>	<u>Reference</u>
Chlorine destruction	800 GPM	-	\$ 15,000 (1969)	\$0.78-2.34 [*]	(76)
Chlorine destruction	-	450	159,337 (1952)	5.00	(76)
Chlorine destruction	1 MGD	-	200,000 (1970)	\$2.00	(97)
Electrolytic decomposition	5-10 GPM	20	20,000 (1968)		(76)
Ozone decomposition	500 GPM	25	70,000 (1958)		(76)

* Costs shown were calculated @ 24 and 8 hr/day, respectively, for this packaged plant cost

TABLE VIII-8

OPERATION & MAINTENANCE COST FOR CYANIDE TREATMENT (76)

<u>Process</u>	<u>Cost/1000 Gallons</u>
Chlorine destruction	\$ 1.22 (1952 operation cost) 7.67 (1952 including depreciation)
Electrolytic decomposition	\$53.29 (@ 75,000 mg/l) 26.90 Net after copper is recovered
Ozone cost	14¢-15¢ per pound
Chlorine cost	73¢ per pound

maximum effluent concentration of 0.025 mg/l. Such an effluent limit will give some leeway for minor operational upsets versus a 0.0 mg/l effluent limit.

On the basis of the above discussions, the following conclusions are drawn:

- (1) The major sources of cyanide from industries are electroplating and metal finishing, coke plants and blast furnace waste from the steel industry. Concentrations of cyanide from industrial waste may be expected to vary from 10 to as high as 100,000 mg/l. The higher concentrations are from plating bath waste of the electroplating and metal finishing industry. Improved plant housekeeping and the reduction of rinse water drag-out from plating solutions can substantially reduce the concentration of cyanide in the wastewater.
- (2) The toxicity of a cyanide waste is a function of its pH. However, at the pH of most natural waterways most of the cyanide will be present as undissociated HCN, the more toxic form. Due to its natural detoxification mechanisms, the human body can safely ingest up to approximately 18 mg/day of cyanide.
- (3) Cyanide is reported to have an order threshold of 0.001 mg/l.
- (4) The human body reportedly exhales some of the cyanide ingested and the liver converts most of the remainder to the less toxic form of thiocyanate which it then expels through the urine.
- (5) Fish appear to be the organisms most sensitive to cyanide. The cyanide concentrations should not exceed 0.025 mg/l for the preservation of fish life.
- (6) Wastewater treatment technology, as currently practiced, is achieving a final effluent level of 0.0 mg/l of cyanide by at

at least three methods.

- (7) The cost of achieving these levels is within the range of the equivalent cost of removing trace metals from the wastewater.

On the basis of the above conclusions and discussions, it is recommended that a uniform effluent limit be established at 0.025 mg/l for cyanide. It is felt that such a limit is immediately achievable. It is one which will allow for minor operational difficulties, and it is within economic reason. This limit is recommended on the basis of the preservation of fish life. It is also recognized that if chlorination is utilized for the destruction of cyanides then adequate controls will be needed to meet the criteria which is set forth under a separate chapter on maximum total chlorine residuals.

CHAPTER IX-FECAL COLIFORM

As defined in the Drinking Water Standard (94), fecal coliforms are considered an indicator of recent fecal pollution. The fecal coliform group consists of Escherichia coli. E. coli are characteristically found in both human and animal intestines. As such, they are an indicator of the presence of disease producing organisms.

The sanitary significance of fecal coliforms has been aptly discussed in the work of Geldreich (41) and in other literature (1,6, 66,94). Therefore, no general discussion will be presented in this report.

As the most immediate effect of fecal coliforms in surface waters is on recreational use, the recommendation of this report is for the preservation of this use.

With respect to the treatability of wastes containing fecal coliform, substantial reductions will be obtained by biological, chemical and physical treatment. Assurance of low levels is normally achieved by some form of disinfection.

RECOMMENDATION

To preserve the recreational utilization of surface waters, it is recommended that during the months of May through October all discharges not contain more than 400 fecal coliform bacteria per 100 ml sample at any time. This level is set to assist the maintenance of stream standards of 200/100 ml for contact recreational use.

It is recommended that during the remainder of the year, November through April, that discharges not contain more than 2000/100 ml fecal coliform. This level is set to assist maintenance of stream

standards of 1000/100 ml for non-contact recreational use.

Lower levels are not recommended at this time for the following reasons:

- (1) Fecal coliform are found in surface waters due to natural, urban, and agricultural runoff. Therefore, municipal and industrial discharges are not the only contribution and in some cases not the major contributor.
- (2) The chapter on chlorine shows that excessive amounts of residual free and/or combined chlorine are not beneficial.

Our objective, therefore, is to remove the disease producing organisms through more complete biological, chemical, and physical treatment rather than relying upon disinfection by chlorination.

CHAPTER X-FLUORIDE

Fluorine, the most reactive non-metal, is never found free in nature, but occurs as the univalent anion, fluoride, in sedimentary rocks as fluorite or fluorspar (calcium fluoride), and in igneous rocks as cryolite (sodium aluminum fluoride).

Major industrial fluoride discharges are from electroplating, insecticides, steel and aluminum manufacture, glass and ceramics manufacture and fertilizer wastes (76). Disinfection of brewery apparatus, wood and mucilage preservation and fertilizer manufacture contribute additional fluoride. (61,66,76).

Fluoride as HF is now scrubbed from stack gases as a result of tighter air pollution control laws. Fluoride effluent discharges occur from stack effluent scrubbing in phosphoric acid production, steel mills, and chemical plants among other industries (6). Fluoride is added to drinking water and therefrom eventually discharged in domestic wastewater.

Concentrations of fluoride found in industrial discharges, vary from a low of trace levels to 107-145 mg/l for aluminum reduction plants to a high of 1000-3000 mg/l for glass manufacture (76).

ENVIRONMENTAL EFFECTS OF FLUORIDE

A low concentration of fluoride is beneficial to man and animals and possibly even fish. Beyond the fine line denoting benefit, fluoride can be damaging, toxic or, in high enough concentrations even lethal.

Effect on Man

Concentrations of the fluoride ion between 0.8 and 1.5 mg/l have been shown to be beneficial in reducing tooth decay (1,66). Concentrations of up to 5 mg/l are reported not to produce any harmful effects other than occasional mottling (66). A comparison of mortality rates has failed to show any increase in nephritis, heart disease or cancer to be associated with low fluoride levels. Sodium fluoride does have a slight salty taste, but less so than sodium chloride (66).

Higher concentrations of fluoride are reported to be detrimental to man. The concentrations and effects are summarized in Table X-1.

Fluoride also affects industrial uses of domestic water. It is reported that 1 mg/l fluoride in water used for wet milling corn can be concentrated to 6 mg/l in steep water, and 5 mg/l in corn syrup. Malt syrup made with similar water may contain up to 8 mg/l fluoride. Fluoride concentrations from 1-5 mg/l also seem to stimulate yeast activity in the fermentation of malt (66).

Effect on Plants

Fluoride uptake from water is restricted by a combination of elements in soil, a soil pH above that required for uptake, and by plant root discrimination against fluoride. Concentrations up to 10 mg/l in irrigation water have been found to cause no direct damage to various plants. Concentrations of 100 mg/l and more have caused plant damage, however (66). Some of the reported research is summarized in Table X-2.

Effect on Domestic Animals and Wildlife

The toxic threshold for animals is reported to be 1.0 mg/l (66). The effects on animals are analogous to those on man, ie., beneficial in fighting tooth decay but damaging at higher concentrations. Table X-3 gives some typical dose response relationships for a number of species.

Wolf and McKee also reported that for cows consuming water with 500/mg/l fluorides, their milk only contained 0.5 mg/l

TABLE X-1

EFFECTS OF EXCESSIVE FLUORIDE IN DRINKING WATER (1,66)

<u>Concentration, mg/l</u>	<u>Effects</u>
0.8 - 1.5	Threshold for mottling of teeth
1.7 - 1.8	50% of children have mottled teeth
1.0 - 2.0	Mild to moderate mottling
2.0	Dental mottling and weakening of teeth structure
3 to 6	Severe dental mottling
4.4 - 12	Chronic fluorosis and skeletal system damage
6.0	Tooth enamel pitted and chipped
8 - 20	Bone changes expected
11.8	Chronic fluorine intoxication in adults
20 (mg/day)	Crippling fluorosis after 20 years
115	Sub - lethal in drinking water
180	Toxic to man in drinking water
2000	Lethal dose in drinking water

TABLE X-2

FLUORIDE EFFECTS ON PLANTS (66)

<u>Species</u>	<u>Conc of F⁻, mg/l</u>	<u>Effect</u>
Peach, tomato, buckwheat	10	No injury
Peach and buckwheat	100	Severely injured in three days
Sprouting of beans	100 - 150	Inhibited
Buckwheat	180	Did not injure at pH 5.5
Peach, tomato and buckwheat	200	Killed in a short time
Buckwheat and peach	360	Injurious even at pH 6.5
Large bean plants	1000	Stunted growth

TABLE X-3

FLUORIDE EFFECTS IN DRINKING WATER OF ANIMALS (66)

<u>Species</u>	<u>Conc. of F⁻, mg/l</u>	<u>Effect</u>
Cattle	1.0 mg/l	Harmless
Sheep	1.0 mg/l	Fluoride poisoning
Mice	1.4 - 4.5 mg/l	Teeth mottling
Cattle	0.4 mg/kg	No mottling
Cattle, Rats	1. mg/kg	Mottling of teeth
Cattle	3 mg/kg	Bone damage and death
Hogs	6 - 16 mg/l	Severe mottling
Cattle	18 mg/l	Increasing fluorosis
Young Cattle	25 - 100 mg/l	Teeth lesions
Hamsters	50 mg/l	Dental fluorosis in 10 weeks
Sheep	60 mg/day	Affected teeth and bones
Sheep	120 mg/day	Threshold for general health
Rabbits	200 mg/kgm	Lethal

Effect on Fish and Aquatic Life

Fluorides, like many other elements, are most damaging at lower concentrations on fish life. Wolf and McKee reported direct toxic effects of fluoride ions toward fish life. They also noted a relationship between fluorides and fish teeth condition. Whether it is beneficial or detrimental was not indicated, however. The levels toxic to fish are summarized in Table X-4. The fluoride concentration toxic in soft water was found to be approximately 75% of that toxic in hard water in a study reported in the Water Quality Data Book, Volume III (15). Salmo gairdnerii exhibited a 21 day LD₅₀ of 8.5 mg/l fluoride (15).

A 1966 study postulated that rainbow trout are more sensitive to fluoride ions at higher temperatures. The LC₅₀ were given as follows: 5.9-7.5 @ 45°F and 2.6-6.0 @ 55°F. (15).

Other forms of aquatic life, including lobsters, Daphnia, protozoa and rotifers among others, are apparently less sensitive to fluoride than are fish. The toxic levels ranged from greater than 4.5 mg/l for lobsters to 270 mg/l for Daphnia, and up to 1000 mg/l for protozoa and rotifers (66).

TREATMENT TECHNOLOGY - FLUORIDE REMOVAL

Excessive concentrations of natural fluoride ions have been removed successfully for many years in the water treatment industry. The three most common methods of reducing low (less than 10 mg/l) concentrations of fluoride to the 1.0 mg/l range are:

TABLE X-4
EFFECTS OF FLUORIDE ON FISH (15,66)

<u>Species</u>	<u>Conc. of F⁻, mg/l</u>	<u>Effect</u>
Eggs	1.5	Slowed and poorer hatching
Trout	2.3 - 7.3	TL _m at 18°C in soft water
"	2.6 - 6.0	TL _m at 13°C in soft water
"	2.7 - 4.7	TL _m
"	5.9 - 7.5	TL _m at 7.5°C in soft water
Minnows	7.7	Unharmed in one hour
Unspecified	64	10 day TL _m
Carp	75 - 91	TL _m
Goldfish	100	Survived over 4 days
"	120	Killed in 4 days
Rainbow Trout	358	Toxic in soft water
Mosquito Fish	419	96 hr TL _m in turbid water
Tinga vulgaris	678	lethal
Goldfish	1000	Killed in 12-29 hrs. in soft water
"	1000	Killed in 60-102 hrs. in hard water

- (1) Coprecipitation, magnesium in lime - soda softening
- (2) Coagulation with alum and lime in low magnesium hardness waters
- (3) Adsorption on activated alumina (76).

For industrial wastes having fluoride concentrations up to 3000 mg/l, Patterson and Minear (76) report that lime coagulation at a pH of 11 is normally used. The calcium fluoride precipitate has a theoretical maximum solubility of about 8 mg/l at a pH of 11, but is noted for its slow formation. As a result long detention periods are required. Addition of excess lime followed by settling, recarbonation, and resettling are often needed to obtain a 10-20 mg/l effluent with a pH suitable for discharge (61,76).

Other technically feasible treatments include fluoride removal on synthetic and natural (processed bone and bone char) hydroxy apatite, and ion exchange on natural and synthetic zeolites. While both Weston (97) and Patterson and Minear report obtainable effluent levels of 0.5-1.5 mg/l with hydroxy apatite, Patterson and Minear report that this method has been abandoned in most plants due to the excessive cost.

Similarly, while an effective strong cation exchange resin has been developed for fluoride removal, overall treatment and chemical costs are reported as excessive (76).

The effectiveness of the various treatment processes for fluoride removal are shown in Table X-5. In general, the capital costs for lime treatment, alum coagulation and magnesium softening will follow general water treatment costs. Weston reports the capital costs for an alum

TABLE X-5

EFFECTIVENESS OF FLUORIDE REMOVAL (76,97)

<u>Process</u>	<u>Fluoride Concentration, mg/l</u>		Reported Application
	<u>Initial</u>	<u>Final</u>	
Lime Addition	1000 - 3000	20	Industrial
Lime Addition	1000 - 3000	7 - 8 *	Industrial
Lime Addition	500 - 1000	20 - 40	Industrial
Lime Addition	- - -	10	Industrial
Alum Coagulation	3.6	0.6 - 1.5	Municipal
Alum Coagulation		1	Industrial
Hydroxy apatite Beds			
Synthetic	12 - 13	0.5 - 0.7	Municipal
Synthetic	10	1.6	Municipal
Bone char	6.5	1.5	Municipal
Bone char	9 - 12	0.6	Municipal
Unspecified	- - -	0.5 - 1.5	Industrial
Alumina Contact Beds	8	1	Municipal
Alumina Contact Beds	20 - 40	2 - 3	Industrial
Alumina Contact Beds	9	1.3	Industrial
Magnesium softening	3 - 4	0.8 - 0.12	Municipal

coagulation plant yielding a final fluoride effluent of 1.0 mg/l as \$100,000 for 1 MGD, \$600,000 for 10 MGD, and \$2,600,000 for 50 MGD.

SUMMARY AND RECOMMENDATIONS

- (1) Fluoride is found naturally in sedimentary and igneous rock formations. These contribute to natural fluoride ion concentrations found in surface waters of those areas.
- (2) Fluoride ions are added to surface waters by a number of industrial discharges. The use of water scrubbing due to air pollution controls of gaseous discharges of fluoride has added more industries to the list of aqueous fluoride dischargers.
- (3) Fluoride ions at a concentration of 0.8-1.5 mg/l in water are beneficial to man, some industries, and animals.
- (4) Fluoride concentrations above 2.0 mg/l may be detrimental to man, while fluoride concentrations above 10 mg/l in water are definitely damaging to man, industrial uses and plant life, and presumably to animals.
- (5) Fluoride concentrations above 1.5 mg/l are damaging to fish eggs and fluoride concentrations above 2.3 mg/l are toxic to trout and other species of fish.
- (6) High levels of fluoride ion in industrial wastes can be reduced from 3000 mg/l to 10-20 mg/l by lime coagulation and precipitation.
- (7) Industrial wastes bearing less than 40 mg/l fluoride can be treated by one of the more economical processes to a final effluent level of 0.5-1.5 mg/l. Other technically feasible treatment methods exist but are reported to be

less economical.

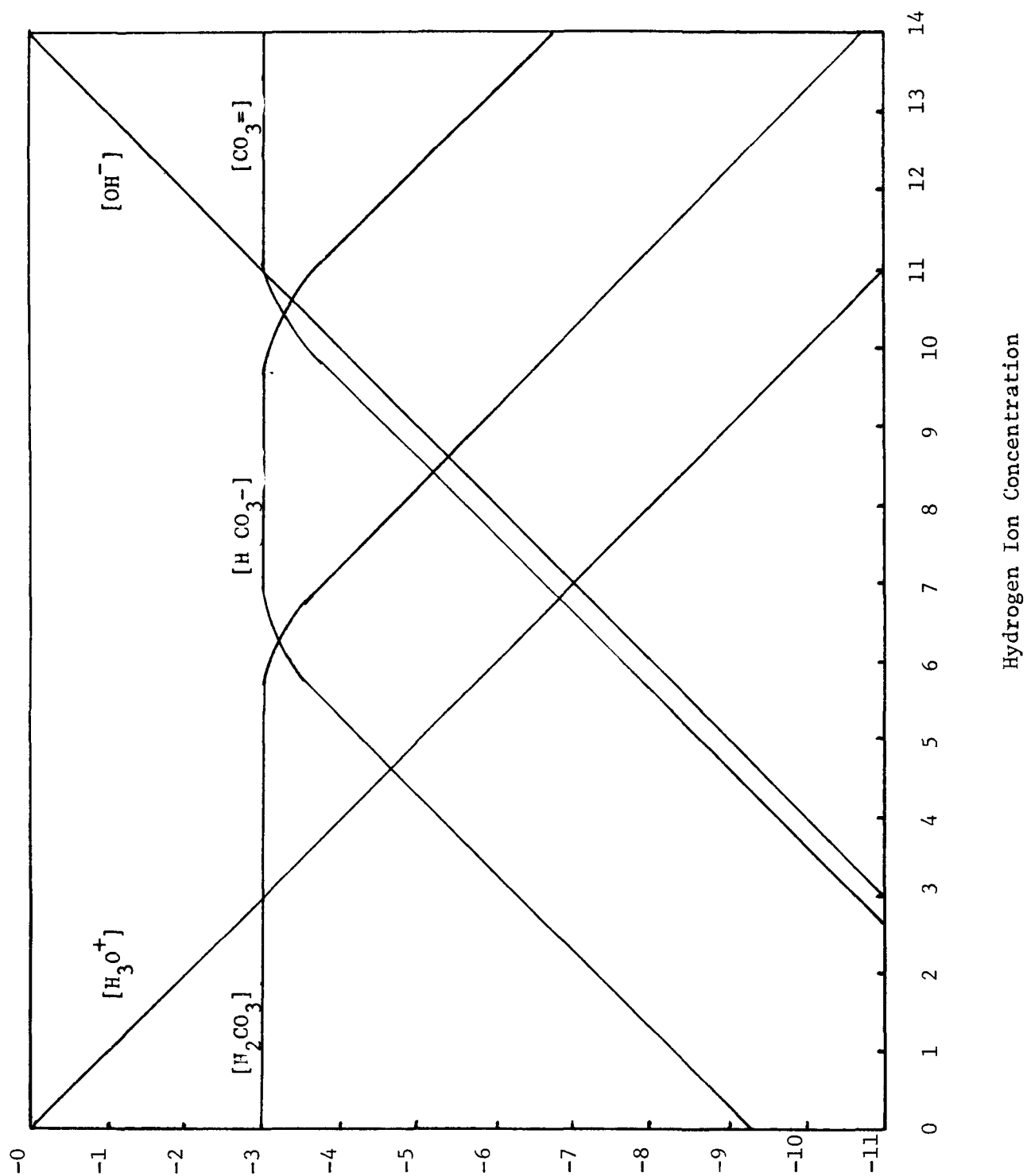
On the basis of the present information, a uniform effluent criteria is difficult to justify at this time. It is recommended, however, that an effluent level of 1.5 mg/l be adopted for fluoride where justified on the basis of water use. It is recognized that two stage treatment will be necessary for industries with wastes containing high levels of fluoride to maintain a 10 mg/l effluent. Attainment of 1.5 mg/l level will not damage the use of water for man, animal, plants, industry uses, fish or other aquatic life.

CHAPTER XI-HYDROGEN ION - ACIDITY - ALKALINITY

Acidity and alkalinity are quantitative measures of the respective abilities of a water to neutralize strong bases and strong acids to an arbitrarily designated pH or indicator endpoint. The pH is an expression of the intensity of the acid or alkaline condition of a solution. It is defined as the negative of the logarithm (base 10) of the hydrogen ion activity.

The most commonly chosen titration endpoints are the methyl orange (pH of 4.5) and phenolphthalein (pH of 8.2-8.4) although in special cases a potentiometric titration may be performed to a pH of particular interest (1). The method of determining a particular acidity or alkalinity is to titrate with .02N NaOH or .02N H₂SO₄ respectively. Table XI-1 lists the various parameters obtained by the titrations. For unpolluted natural waters relatively simple relationships exist between the parameters of Table XI-1 and the concentrations of hydroxide, bicarbonate, carbonate and hydrogen ion. The relationships are handled by Sawyer and McCarty (81).

By the classifications in Table XI-1, the methyl orange acidity consists chiefly of mineral acids, and some neutralization of weak organic and inorganic acids. Phenolphthalein acidity is attributed to the bulk of the weak acids in solution, especially carbon dioxide and bicarbonate in addition to the methyl orange acidity. Similarly, the phenolphthalein alkalinity may be taken as the neutralization of free hydroxyl ions and some weak bases. The methyl orange alkalinity will be the sum of the phenolphthalein alkalinity and the major portion of



LOG CONCENTRATION DIAGRAM FOR CARBONATE

FIGURE XI-1

the alkalinity due to weak organic and weak inorganic bases.

TABLE XI-1

<u>Parameters</u>	<u>Manner Obtained</u>
Methyl-orange acidity (mineral)	Titration to methyl orange end-point with 0.02N NaOH
Phenolphthalein acidity (total)	Titration to phenolphthalein end-point with 0.02N NaOH
Methyl orange alkalinity (total)	Titration to methyl orange end-point with 0.02N H_2SO_4
Phenolphthalein alkalinity (Hydroxyl plus one-half carbonate)	Titration to phenolphthalein end-point with 0.02N H_2SO_4

In clean natural waters simple sum and difference relationships between hydroxyl, bicarbonate, carbonate and hydrogen ion can be written to express the various free and total acidities and alkalinities (81). Their relationships to pH are illustrated in Figure XI-1. In polluted waters and in domestic and industrial wastes these relationships no longer hold. These discharges will contain large amounts of non-carbonate acidities and alkalinities, including weak organic acids (e.g. acetic, propionic and humic) and their salts, weak inorganic acids and their salts (borates, phosphates), ammonia, and hydrated heavy metals (Fe^{++} , Al^{+++}). In these cases the acidity and alkalinity indicate how we may expect a particular water to react to acid or alkaline influences, but tell us little of the chemical composition of the solution involved.

Both acidity and alkalinity are expressed as mg/l of CaCO_3 , implying that the acidity would be neutralized by this amount of CaCO_3 or that the alkalinity is equivalent to this amount of CaCO_3 .

Effects of Hydrogen Ion-Acidity-Alkalinity

The literature more than adequately supports the need to maintain pH levels in surface waters between about 6.0-9.0 for the production and well-being of aquatic organisms. Due to the interdependence of pH, acidity and alkalinity, it is desirable to maintain a minimum buffering capacity. In particular, the pH of primary contact recreation water should be between 6.5 and 8.3 (6). When the pH is outside this range the buffering capacity (i.e., balance between acidity and alkalinity) becomes more important. A brief computation of pH requirements is shown in Table XI-2.

Within the pH range of 6-8, toxicities are attributable to the specific anions or cations involved. The synergistic effects for specific ions at various pH concentrations are treated in the individual chapters.

RECOMMENDATIONS

The pH of all discharges shall not be less than 6.0 nor more than 9.0. An exception to this ruling will be permitted if the receiving water has a natural pH outside of this range. In this case, the pH of the discharge shall not be less than that of the receiving water, when the natural pH is less than 6.0 nor greater than that of the receiving water when the normal pH is higher than 9.0.

It is further recommended that in the interest of maintaining a minimal carbonate-bicarbonate buffering capacity, no discharge shall

contain less than 20 mg/l of alkalinity as CaCO_3 .

TABLE XI-2

DESIRABLE pH RANGES (6,66)

<u>REMARKS</u>	<u>pH RANGE</u>
MAN	
Drinking Water	6.0 - 8.5
Primary Contact Recreation	6.5 - 8.3
ANIMALS	
Farmstead Water Supplies	5.5 - 9.0
INDUSTRIAL PROCESSES	
Brewing	6.5 - 7.0
Confectionary	7.0 minimum
Food Canning and Freezing	7.5 minimum
Laundering	6.0 - 6.8
Oil-well Flooding	7.0 minimum
Rayon Manufacturing	7.8 - 8.3
Steel Making	6.8 - 7.0
Tannery Operations	6.0 - 8.0
PLANT LIFE	
Irrigation water, Permissible	4.5 - 9.0
Irrigation water, Desirable	5.5 - 8.5
Aquatic Plants	7.0 - 9.2
Plankton Production, Optimum	7.5 - 8.4
FISH, MARINE, AND ESTUARY ORGANISMS	
Most Resistant Species	4.0 -10.1
Trout, Tolerance Range	4.1 - 9.5
Trout, Toxic Limit	4.8 - 8.7
Perch, Toxic Limit	4.6 - 9.5
Most Fresh Water Fish, Tolerance	6.5 - 8.4
Optimum for Fish Eggs	6.0 - 7.2
Marine and Estuary Organisms	Ambient \pm 0.1
Marine and Estuary Limits	6.7 - 8.5
Shellfish	7.0 - 9.0

CHAPTER XII-IRON

Iron is found in both the ferric (Fe^{+3}) and in the ferrous (Fe^{+2}) forms in the environment. The form in which iron is found depends upon the pH, dissolved oxygen concentration and complex forming agents present in the water. At a pH of approximately 7.8, and in the presence of oxygen, the soluble ferrous iron will be oxidized to ferric iron which will then be readily hydrolyzed to form an insoluble precipitate, ferric hydroxide. Table XII-1 shows some naturally occurring concentrations of iron.

There are several industrial sources of iron which are of significance. Table XII-2 summarizes concentrations from primary sources of iron-bearing industrial wastewater. Steel mill pickle liquor is the largest source of high concentrations of iron. Acid mine drainage, while not yielding as high a concentration as waste pickle liquor, may add substantially greater volumes of iron to surface waters. Other industrial wastewaters containing significant iron concentrations are the chemical, dyeing, ceramic, ink, printing, metallurgical, cannery, tannery and textile industries. Paint pigments contain iron salts and iron salts are wasted after use as coagulants in water and wastewater treatment processes.

TABLE XII-1
CONCENTRATION OF IRON IN NATURE

<u>Source</u>	<u>Conc. (mg/l as Fe)</u>	<u>Reference</u>
Surface water in U. S.	0.0-0.4	(99)
98 U. S. Rivers	0.02-3.0	(99)
Dissolved mineral matter	0.01-0.950	(99)
Weathering of rock, acid waters, etc.	0.001-1.67	(99)
Surface waters in coal mining area	3-1520	(72)

TABLE XII-2

INDUSTRIAL SOURCES & CONCENTRATIONS OF IRON

<u>Industry</u>	<u>Concentration</u>	<u>Reference</u>
<u>Steel Mills</u>	mg/l (form)	
Waste pickle liquor	70,000 (Total Fe)	(76)
Waste (Continuous) Liquor	130,000-160,000 (FeSO_4)	(48)
Waste (Batch) Liquor	150,000-220,000 (FeSO_4)	(48,72)
Pickle bath rinse	200-5,000 (Total Fe)	(76)
Pickle bath rinse	300-4,500 (FeSO_4)	(72)
HCl pickle liquor	210 (Fe^{++})	(3)
<u>Mine Drainage</u>		
Ferrous iron	36	(76)
Total iron	0.2-22,360,126-157	(72,76,99)
West Virginia	3-1,520	(72)
<u>Motor Vehicle Assembly</u>		
Body assembly	4	(76)
Vehicle assembly	3	(76)
<u>Metal Processing</u>		
Appliance manufacture	0.09-1.9	(76)
Automobile heating controls	1.5-31	(76)
Appliances:		
Mixed waste	0.2-20	(76)
Spent acids	25-60	(76)
Alkaline waste	Trace	(76)
Chrome plating	40	(76)
Plating waste	3.58 (Fe^{++})	(14)
Brass pickle liquor	100-210 (Total)	(72)
Brass bright dip waste	30-360 (Total)	(72)
Metal Plating	1.2-21	(72)

ENVIRONMENTAL EFFECTS OF IRON

The concentration of iron in waters is significant to man, industry, stock, wildlife, fish and aquatic life.

Effect on Man

Current limits for iron in domestic water supplies are based on taste considerations rather than toxicity (94). As little as 0.1 mg/l may impart an unpalatable taste depending upon the form in which it is found (66). Aesthetically, iron is known to stain laundry at a concentration of only 0.3 mg/l (94).

The Drinking Water Standards states that the iron permitted in public water supplies (after control to prevent objectionable taste or laundry staining) "...constitutes only a small fraction of the amount normally consumed and is not likely to have any toxicological significance." The normal daily nutritional requirement for man is 1-2 mg. Man's normal diet contains from 7-35 mg per day.

Effect on Industrial Water Supplies

Table XII-3 shows that more stringent iron requirements have been set for several industries than for domestic water supplies.

Effect on Irrigation, Stock and Wildlife Watering

The presence of iron in irrigation waters is reported to be of little importance. Iron is an essential constituent in the diet of animals. If the iron concentration is too high, however, cows may not consume enough water, which adversely affects their milk production (66).

TABLE XII-3
IRON TOLERANCES FOR INDUSTRIAL USE

<u>Industry</u>	<u>CONCENTRATION, mg/l</u>		<u>Water Quality Criteria (6)</u>
	<u>Camp (24)</u>	<u>McKee & Wolf(66)</u>	
Air Conditioning	0.5*	-	-
Cooling Water	0.5*	0.5	0.5-14
Baking	0.2*	0.2	-
Breweries	0.1*	0.1-1.0	-
Boiler Feed	-	-	0.01-1.0
Canneries	0.2*	-	-
Carbonated Beverages	0.2	0.1-0.2	0.3
Chemical & Allied Industries			0.1
Confectionery	0.2*	0.1-0.2	-
Distilling	0.1*	-	-
Electroplating	-	trace	-
Food, General	0.2*	0.2	0.2
Ice	0.2*	0.2	-
Laundry	0.2*	0.2-1.0	-
Oil Well Flooding	-	0.1	1.0
Petroleum	-	-	1.0
Photographic Processing	-	0.1	-
Plastics, Clear	0.2*	-	-
Pulp & Paper			
Ground Wood	1.0*	0.3	1.0-0.3
Kraft Pulp	0.2*	0.2-1.0	0.1-1.0
Soda & Sulfit	0.1*	0.1	-
Highgrade Papers	0.1*	0.1	-
Rayon (Viscose)			
Pulp Production	0.005*	-	-
Manufacture	0.0	0.0-0.05	-
Tanning	0.2*	0.1-2.0	0.1-50
Textiles			
General	0.25	0.1-1.0	0.1-0.3
Dyeing	0.25*	-	0.1
Wool Scouring	1.0*	-	0.1
Cotton Bandage	0.2*	-	-

*Applies to iron and manganese individually or to their sum.

Effect on Fish and Other Aquatic Life

Iron can have a major impact on fish and other aquatic life. The toxicity of iron to fish is dependent upon the pH and the buffering capacity of the water. Very little iron normally remains in solution in buffered water, or a water with a pH above 8. As a result iron hydroxides are deposited on the gills of fish, which is believed to irritate and block their respiratory channels. In addition, the heavy ferric hydroxide precipitate is believed to smother fish eggs on the stream bottoms. At a lower pH and in unbuffered waters, iron may have a direct toxic effect on fish and other aquatic life (66).

Table XII-4 reveals that iron may be toxic and interfere with fish life at concentrations as low as 0.2 mg/l in unbuffered, low pH waters over extended periods. Table XII-5, however, shows that well buffered waters with higher pH (high hardness) may support fish life at iron concentrations as high as 10-50 mg/l for exposure times ranging from 1 hour to 96 hours. Most fish are capable of surviving longer periods of exposure at an iron concentration of 0.7-1.0 mg/l, provided that the water is well buffered and has a pH near neutrality (66).

An iron concentration exceeding 0.2 mg/l has been found to create problems due to the growth of the iron bacteria Crenothrix, Gallionella, and others. These iron bacteria utilize iron as a source of energy and store it in their microbial protoplasm (66). It is also apparent from the works of McKee & Wolf that fish and other aquatic life are capable of concentrating iron. Investigations utilizing radioactive iron Fe-59 have been reported to have concentration factors ranging from 720 to 200,000. The concentration factors reported by McKee & Wolf are

summarized in Table XII-6.

TABLE XII-4

TOXIC OR HARMFUL CONCENTRATIONS (mg/l) OF IRON FOR FISH LIFE (66)

<u>Form of Iron</u>	<u>Concentration</u> <u>mg/l</u>	<u>Species of Fish</u>	<u>Type of</u> <u>Water</u>	<u>Time of</u> <u>Exposure</u>
Iron	0.2	three types of fish	-	-
Iron	0.9	carp	pH 5.5 or less	-
Iron	1-2	pike, tench,	pH 5.0-6.7	-
FeCl ₃	0.6	goldfish	tap	-
Iron	10	rainbow trout		5 min.
FeCl ₃	1.2	stickleback	tap	6 days
FeCl ₃	4.35	goldfish	tap	3 days
Fe ₂ O ₃	2.0	trout, salmon, roach	-	-
FeK (SO ₄) ₂	14	young eels	-	-
Fe ₂ (SO ₄) ₃	0.716	shiners, carp,	distilled	12-24 hrs.
FeCl ₂	13	young eels		50 hrs.
FeSO ₄	2.9	shiners, suckers, carp	distilled	4-24 hrs.
Iron	1.28	fish	distilled	24 hrs.

TABLE XII-5
IRON CONCENTRATIONS FOUND NOT HARMFUL
TO FISH LIFE (66)

<u>Form of Iron</u>	<u>Concentration</u> <u>mg/l</u>	<u>Species of Fish</u>	<u>Type of</u> <u>Water</u>	<u>Time of</u> <u>Exposure</u>
Iron	0.7	good fish fauna	supported in 95% waters	-
FeCl ₃	1.0	sticklebacks	taps	10 days
FeCl ₃	5.0	young eels	-	50 hrs.
Fe ₂ (SO ₄) ₃	5.0	rainbow trout, bluegill sunfish, sea lamprey	Lake Huron	24 hrs.
FeCl ₂	10	goldfish	hard water	96 hrs.
FeSO ₄	5	carp, shiners, suckers	-	24 hrs.
FeSO ₄	17.1	minnows	-	1 hr.
FeSO ₄	50	bass, bluegills	-	7 days
FeSO ₄	50	trout	-	24 hrs.

TABLE XII-6
CONCENTRATION FACTORS FOR RADIOACTIVE IRON (Fe-59)
IN FISH & AQUATIC LIFE (66)

<u>Organism</u>	<u>C.F.</u>
Phytoplankton	200,000
Invertebrates, skeleton	100,000
Filamentous algae	100,000
Insect larva	100,000
Algae, non-calcareous	20,000
Invertebrates, soft parts	10,000
Fish	10,000
Flagellate, <u>Rhodomanas</u>	7,500
Flagellate, <u>Chlamydomonas</u>	6,000
Diatom, <u>Nitzschia</u>	5,533
Vertebrates, skeleton	5,000
Diatom, <u>Navicula</u> conf.	4,220
Alga, <u>Ochromonas</u>	1,550-4,480
Vertebrates, soft parts	1,000
Flagellate, <u>Platymonas</u>	720-1,030

Treatment Technology for Iron Removal

The primary method for iron removal is the conversion of ferrous iron to the ferric state, followed by precipitation of ferric hydroxide at a pH of approximately 7.8, where the solubility of ferric hydroxide is at a minimum. This method of iron removal has been used for many years in treatment of municipal water supplies. As reported by Patterson and Minear (76), waters with a high concentration of iron are usually found to have a high concentration of carbon dioxide. In the removal of carbon dioxide by aeration, the ferrous iron is converted to ferric iron. Lime is frequently utilized to maintain the pH at the desired level for maximum precipitation of the ferric hydroxide.

Fair, Geyer and Okun (37), and Patterson and Minear (76) note that insoluble iron oxide frequently exists in suspension as a fine colloidal dispersion which resists sedimentation due to its small particle size, when precipitated at a pH of 9. A very low specific gravity makes it difficult to remove by sedimentation without prolonged detention times or filtration. A summary of iron removal efficiencies currently obtained in various industries is given in Table XII-7. While greater than 1 mg/l total iron remained in the effluents noted in Table XII-7 for sedimentation only, a filtration step held other effluents to less than 0.5 mg/l.

It is also worth noting that some companies are capable of recovering byproducts from waste sulfuric acid pickle liquor. Byproducts recovered by some companies include copperas with ferrous sulfate; copperas with sulfuric acid; ferrous sulfate with sulfuric acid; ferric sulfate with sulfuric acid; ferric iron with sulfuric acid; iron powder; ferric oxide;; ferric oxide with aluminum sulfate. Nemerow also stated that

TABLE XII-7

IRON REMOVAL EFFICIENCY

<u>WASTE</u>	<u>Concentration mg/l</u> <u>Inf.</u>	<u>Eff.</u>	<u>Flow</u>	<u>Method</u>	<u>Reference</u>
Pickle Liquor	210	1-10	100-1450 gpm	Limestone, settling	(76)
Unknown	360	7		Limestone, Prim settling	(76)
Unknown	360	0		Limestone, 24 hr. settling	(76)
Pickle Liquor	210(Fe ⁺²)	0.88(Fe ⁺²)	730 gpm	Limestone, settling	(3)
		3.38 (Total)			
Mine Drainage	145	5	1.27 gpm	Limestone, settling	(99)
	157	1.6	1.58 gpm	Lime settling	(99)
	126	2.3	2.91 gpm	Soda Ash, settling	(99)
Coal Washing w/mine drainage	551	0-1.0	225 gpm	Froth-flotation, lime coagulation, settling	(72)
Metal Finishing		0.50		Lancy, Integrated	(64)
Miscellaneous	1.5	0.05		Chlorine, alum, lime sodium, settle	(76)
"	2.4	0.00		Lime, settling, filter	(76)
"	2.5	0.13		Aeration, filter	(76)
"	5.7	0.13	1.5 MGD	Aeration, filter	(76)

TABLE XII-7 (Cont.)

<u>WASTE</u>	<u>Concentration mg/l</u>		<u>Flow</u>	<u>Method</u>	<u>Reference</u>
	<u>Inf.</u>	<u>Eff.</u>			
Foundry	3760 (SS)	10 (SS)		Settling, lime & alum, settle, 2nd lime & alum, flotation	(72)
Dissolved Iron		0.3		Chemical coagulation, settle, filter	(97)
Dissolved Iron	2.25-4.70	0.3		Walker Process	(76)

regeneration is possible when hydrochloric acid is used as a pickle liquor. The Braw-Knox-Ruthner process is one such recovery method (72).

An additional method of treatment reported in both Nemerow (72) and Patterson and Minear (76) is the use of deep well disposal. However, as this does not reportedly enter surface waters, it is not considered here as a treatment process for setting an effluent criteria.

One other process described by Patterson and Minear (76) is the "Walker Process". The system consists of distributing the wastewater, after restabilization, over graded anthracite coal which accomplishes aeration of the wastewater. The bed surface is reported to contain residual iron hydroxide which acts as a catalyst for the oxidation of the ferrous iron to the ferric form, followed by precipitation of ferric hydroxide. The units need periodic back washing with subsequent solids removal and disposal.

The final method of iron treatment reported in the literature is that of combining waste sulfuric acid pickle liquor with chromate wastewaters from cleaning operations. Combinations of the acid pickle liquor with the chromate waste are utilized to reduce the chromium hexavalent form to the chromium trivalent form. Then both the iron and the chromium are precipitated by lime. Effluents of 0.5 mg/l total soluble iron and 0.05 total chromium have been reported (76).

A summary of the capital costs reported in the literature reviewed for iron removal is summarized in Table XII-8 below.

As indicated from this tabulation, the costs vary substantially according to the process utilized and the capacity of the facility. Similarly, a summary of the operating and maintenance costs for various methods of iron removal and neutralization is given in Table XII-9.

TABLE XII-8

CAPITAL COST FOR IRON REMOVAL

<u>Method</u>	<u>Flow MDG</u>	<u>Capital Cost Million Dollars</u>	<u>\$/1000 Gal</u>	<u>Ref.</u>
Chemical Coagulation Settling & Filtra- tion	1.0	0.3	300	(97)
Settling & Filtra- tion	10.0	1.3	130	(97)
Settling & Filtra- tion	50.0	4.6	92	(97)
Neutralization, coag- ulation,settling (HCl Pickle Liquor)	0.06 0.1	0.1 1.0	1670(8 hr. flow) 10,000	(76) (72)
HCl Pickle Liquor w/Recovery)	0.1	4.0	40,000	(72)
Walker Process	2.7	0.05	18.5	(76)
Total Iron: Foundry Waste by Coagulation & Filtration	7.5	134	0.0178	(76)

TABLE XII-9

OPERATION AND MAINTENANCE COST FOR IRON REMOVAL & NEUTRALIZATION

Method	Flow, MGD	\$/1000 Gal	Acidity, mg/l	¢/mg/l Acid/1000 Gal	Ref.
Neutralization (w/Lime assumed), Equalization, and Sludge Dewatering					
	.5	15	500	3.0	(76)
"	0.5	29	1000	2.9	(76)
"	0.5	108	20000	0.54	(76)
"	1.0	25	500	5.0	(76)
"	1.0	26	1000	2.6	(76)
"	1.0	103	20000	0.51	(76)
"	10.0	12.5	500	2.5	(76)
"	10.0	20	1000	2.0	(76)
"	50.0	11	500	2.2	(76)
"	0.06	0.02	---	---	(76)
W/Limestone	---	20	Steel Mill pickle liquor	---	(76)
Neutralization w/Lime	--	0.032	---	0.0052	(99)
W/Limestone	---	0.0591	---	0.010	(99)
W/Soda Ash	---	0.268	---	0.0486	(99)
Neutralization (\$5-\$10 per 1000 lb. acid)					(72)
Neutralization W/Lime or Limestone	0.1	20	HCl Pickle liquor		(72)
Regeneration of HCl Pickle Liquor	0.1	8800	Gross Cost		(72)
Total Iron: Foundry Waste by Coagula- tion & Filtration	7.5	23.28			(76)

SUMMARY AND RECOMMENDATIONS

- (1) Iron exists in both ferric and ferrous forms in nature. The ferrous iron may be rapidly converted to the ferric state at a pH greater than 7.
- (2) The sources of iron from industrial waste are numerous. Their concentrations range from trace quantities to 220,000 mg/l as ferrous sulfate.
- (3) The effect of iron on man is basically aesthetic. Water with an iron concentration greater than 0.3 mg/l will stain domestic laundry.
- (4) Many industrial uses require water containing less than 0.1 mg/l of iron in order to maintain product quality.
- (5) Iron is directly toxic to fish life through precipitation of ferric hydroxide within the respiratory system of the fish and on the stream bottoms, smothering fish eggs.

The toxic concentration will depend upon the pH and the buffering capacity of the waters. As the water hardness, the buffering capacity and pH decrease, and the toxicity has been found to increase.

The concentration of iron by fish and other aquatic life ranges from 700 to 200,000 times the external aqueous level.

- (6) Present technology is capable of removing dissolved iron from wastewater to concentrations of 1.0 mg/l or less and removing total iron from wastewater to concentrations of 2.0 mg/l.
- (7) Capital costs for facilities needed to remove iron are generally equivalent to or below the cost of secondary treatment facilities. However, the cost may be substantially increased when neutralization is involved for efficient conversion of the ferrous iron to the

ferric state.

- (8) The operating costs for the removal of total iron from foundry wastewater are expensive. However, they are comparable with the operating costs of neutralizing other acid iron-bearing wastewaters.

On the basis of present information, it is recommended that a uniform effluent criteria of 1.0 mg/l be adopted for dissolved iron and 2.0 mg/l be adopted for total iron.

CHAPTER XIII-LEAD

Lead occurs naturally in the environment as a primary metal and in limestone and galena (PbS) deposits, Table XIII-1. The aquatic forms of soluble lead are Pb^{++} or its complexions. At basic pH, hydroxide and carbonate precipitates are readily formed.

Lambou and Lim (56) report that while there are 500 companies in the United States which mine, smelt, and refine lead, 65% of the total output is by seven companies. In addition, 96% of all domestic lead mines are located west of the Mississippi River. The industries' statistics for 1964 through 1968, as reported by Lambou and Lim, indicate that 89% of the lead is mined in Missouri, Idaho, Utah, and Colorado - 47% being mined in Missouri alone. Tables XIII-2 and 3 show the United States lead production from 1964-1968 and lead consumption in 1968 and 1969.

Secondary production from the recovery melting and smelting of scrap lead is done by 200 companies within the United States. However, over 50% of this production is done by the American Smelting and Refinery Company and the National Lead Company. Gurnham (48) has indicated that the secondary lead recovery production is as large in tonnage as is the primary lead production. Its potential, however, from the industrial waste viewpoint, is much greater. He reported that 50 of the largest plants are located on the seacoast and near the Great Lakes. Recovery of lead from storage batteries, for example, has the potential problem of antimony and antimonial lead alloys, the discarding of unwanted waste products by burning, as well as the high toxicity of the lead itself.

Industrial effluent concentrations, commercial uses and common lead alloys are shown in Table XIII-4.

TABLE XIII-1
NATURAL SOURCES OF LEAD

<u>Source</u>	<u>Concentration</u>	<u>Reference</u>
Limestone & Galena Deposits	0.4-0.8 mg/l	(66)
Surface & Ground Water	Trace to 0.04 mg/l, 0.01 avg.	(66)
Sea Water	0.003-0.03 mg/l	(6)

TABLE XIII-2
U. S. LEAD PRODUCTION* (56)

	<u>1964</u>	<u>1965</u>	<u>1966</u>	<u>1967</u>	<u>1968</u>	<u>5 Yr.Avg.</u>
Domestic Ores (recoverable lead content)	286.0	301.1	327.4	316.9	359.2	318.1
Primary Lead (refined)	449.4	418.2	440.7	379.9	467.3	431.1
Antimonial Lead (primary lead content)	8.6	6.6	11.2	9.1	19.5	11.0
Secondary Lead (lead content)	<u>541.6</u>	<u>575.8</u>	<u>572.8</u>	<u>553.8</u>	<u>550.9</u>	<u>559.0</u>
	1285.6	1301.7	1352.1	1259.7	1396.9	1319.2

NOTE: Lower figures for 1967 reflect the results of an industry-wide strike.

* Thousands of tons

ENVIRONMENTAL EFFECTS OF LEAD

A review of the tabulated data indicates that while lead may be present to some extent in our natural environment, the basic impact on the environment is from its utilization in numerous commercial products, particularly in leaded gasoline. Lead may enter the environment in liquid, or solid waste discharged from industrial production or in exhaust from consumption of leaded fuel. It then can be returned to the earth by rain or snow.

McKee and Wolf (66) have reported that lead is foreign to the human body and has no known nutritional value. The total intake of lead must be considered in evaluating its impact on man as it may enter the body through food, air, tobacco smoke, water, and other beverages. While the exact level at which the human body accumulates lead over the amount excreted has not been definitely established, McKee and Wolf report that it is probably between .3 and 1.0 mg/day. Table XIII-5 gives the effect of different lead concentrations on man.

Effect on Man

Lead is a cumulative poison which tends to be concentrated in the bone. McKee and Wolf reported that since the sensitivity to lead differs considerably with individuals, a safe level of lead cannot be definitely stated. "Typical symptoms of advanced lead poisoning are constipation, loss of appetite, anemia, abdominal pain, tenderness, pain, and gradual paralysis in the muscles, especially of the arms. A milder and often undiagnosed form of lead poisoning also occurs in which the only symptoms may be lethargy, moroseness,

TABLE XIII-3

LEAD CONSUMPTION IN THE UNITED STATES BY PRODUCT (56)(Short tons)

<u>Product</u>	<u>1968</u>	<u>1969</u>
Metal Products:		
Ammunition	82,193	79,233
Bearing Metals	18,441	17,406
Brass & Bronze	21,021	21,512
Cable Covering	53,456	54,203
Caulking Lead	49,718	44,857
Casting Metals	8,693	9,918
Collapsible Tubes	9,310	12,484
Foil	6,114	5,881
Pipes, Traps, & Bends	21,098	19,407
Sheet Lead	28,271	25,818
Solder	74,074	72,626
Storage Batteries:		
Battery grids, posts, etc.	250,129	280,386
Battery Oxides	263,574	302,160
Terne Metal	1,427	1,583
Type Metal	<u>27,981</u>	<u>25,660</u>
	915,500	973,134
Pigments:		
White Lead	5,857	6,617
Red Lead and Litharge	86,480	79,898
Pigment Colors	14,163	14,670
Other *	<u>3,234</u>	<u>1,201</u>
	109,734	102,386
Chemicals:		
Gasoline Antiknock Additives	261,897	271,128
Miscellaneous Chemicals	<u>629</u>	<u>602</u>
	262,526	271,736
Miscellaneous Uses:		
Annealing	4,194	4,252
Galvanizing	1,755	1,797
Lead Plating	389	406
Weights and Ballast	<u>16,768</u>	<u>17,368</u>
Total	23,106	23,813
Other, unclassified uses	<u>17,924</u>	<u>18,287</u>
Grand Total**	1,328,790	1,389,358

* Includes lead content of leaded zinc oxide and other pigments.

** Includes lead which went directly from scrap to fabricated products.

TABLE XIII-4

CONCENTRATION OF LEAD IN INDUSTRIAL WASTEWATER (56)

<u>Source</u>	<u>Concentration</u>
Engine Parts Plant	2.0 - 140.0 mg/l
Plating Bath Rinse Water	0- 30 mg/l
Lead Mining Operations	0-.04 mg/l

COMMERCIAL USES OF LEAD (56)

<u>Compound</u>	<u>Major Commercial Uses</u>
1. Lead Metal, Pb:	Found chiefly alloyed with antimony, tin, or copper.
2. Litharge, PbO:	Used especially in storage-battery manufacturing.
3. Red lead, Pb ₃ O ₄ :	Used in paints and storage batteries.
4. Lead dioxide, PbO ₂ :	Used in chemical industry.
5. Lead carbonate, 2PbCO ₃ Pb (OH) ₂ :	White lead, used in paints.
6. Lead sulfate, PbSO ₄ :	A paint pigment.
7. Lead titanate, PbTiO ₃ :	A paint pigment.
8. Lead acetate, Pb(C ₂ H ₃ O ₂) ₂ :	The most common water-soluble compound of lead.
9. Lead arsenate, Pb ₃ (AsO ₂):	A common insecticide.
10. Lead chloride, PbCl:	Probably formed when fluxes are used with heated lead.
11. Lead silicate, PbSiO ₃ :	Present in glasses and vitreous enamels.
12. Lead chromate, PbCrO ₄ :	Used in yellow and green pigments.
13. Lead borate, Pb (BO ₂) ₂ :	Employed in certain plastics.
14. Lead sulfide, PbS:	Occurs naturally as galena.
15. Lead tetraethyl, Pb(C ₂ H ₅) ₄ :	Used in gasoline.

COMMON LEAD ALLOYS (56)

Solder: lead and tin; 50 - 80% lead.

Type metal: lead, tin, antimony; 60 - 90% lead.

85 - three 5 bronze: copper, tin, lead, zinc; 5% lead.

Bearing bronze: copper, lead, zinc; 15 - 20% lead.

constipation, flatulence, and occasional abdominal pains". (66)

Continuous consumption and exposure to low concentrations of lead create a cumulative toxicity of greater significance than exposure to occasional small doses.

TABLE XIII-5

EFFECTS OF LEAD ON MAN (66)

<u>Form</u>	<u>Concentration</u>	<u>Remarks</u>
Lead, Total	0.33 mg/day	Avg. American Intake
"	.01 - 0.03 mg/day	Avg. Am. Intake from water
"	0.1 - 0.6 mg/day	Dangerous over lifetime
"	0.042-1.0 mg/l	Reported Pb poisoning
"	0.01 -0.16 mg/l	Reported non-poisonous
"	0.1 mg/l	Chronic poisoning for hypersensitive persons

The pharmacological and physiological mechanisms of lead poisoning have been reported by Lambou and Lim (56). They reported that the salts of lead are known to precipitate proteins, thereby acting as local astringents. While their acute toxicity is low, they are absorbed over long periods of time to produce cumulative effects. Lambou and Lim also report, "Chronic lead poisoning is especially dangerous because it develops insidiously, and is often not recognized until it is far advanced. The symptoms involve the nutrition, the blood, the nervous and muscular structures, apparently independently.

Eventually there may be degradation of the kidneys and other organs." The physiological mechanisms involved with lead toxicity include a paroxysmal phenomena resembling flocculation and the alteration of the calcium level of the blood.

Lambou and Lim (56) also reported the toxicity of lead compounds to be influenced by the solubility of lead within body fluids, the time of contact with the body fluids, the quantity ingested, inhaled, or absorbed, and the quantity present within the circulatory system at any given time.

The degree of toxicity of various lead compounds, as consumed through oral ingestion, in decreasing order are as follows: lead arsenate, lead carbonate, lead monoxide, and lead sulfate. Other lead compounds of similar but lower degrees of toxicity, again in descending order are metallic lead, lead chromate, red lead, lead dioxide, lead phosphate, and lead sulfide. Lambou and Lim indicated that there is definite evidence, from experiments with both man and animal, that lead has injurious effects on the germ cells of both male and female. The effects may be passed maternally through the fetal blood during gestation. A report of Cantarow and Trumper (1945), reviewed by Lambou and Lim, indicated that it has been repeatedly demonstrated that lead will pass through the placenta into the fetal tissues. This has been reported to increase the incidence of epilepsy, muscular spasms, convulsions, and other nervous disturbances in the child (56).

In conjunction with the effects on humans, Lambou and Lim reported an investigation of persons working in a Japanese storage battery plant with the following two conclusions:

1. The rate of sterility was approximately twice as high among those exposed to industrial lead concentrations.
2. 8.2% of the group had pregnancies ending in premature or stillborn births while the control group, not exposed to the industrial lead poisoning, averaged 0.2%.

The present lead standards based upon physiological effects on humans are shown in Table XIII-6.

Effect on Plants and Animals

Available data on the effects of lead on non-aquatic plants and animals are summarized in Table XIII-7

Lambou and Lim comment that "animals and birds are also subject to chronic lead poisoning, and show practically the same symptoms as man. An interesting effect of lead pollution can be demonstrated in water fowl mortality due to lead poisoning. Twelve million pounds of lead shot are expended annually over the nation's best water fowl habitats. The shot remains there relatively unchanged. Water fowl frequently ingest these shots and die of lead poisoning. Annual mortality has been estimated at roughly one million birds. For aquatic fowl ingestion of lead shot is doubly dangerous because approximately 0.5% of arsenic is added" (56).

Effect on Fish and Aquatic Life

The toxicity of lead to fish and other forms of aquatic life has been well documented by McKee and Wolf. While the toxicity of lead may vary with respect to the lead salt considered, it may definitely be stated that it is very toxic and is concentrated within

the fish flesh. The degree of toxicity has been reported to vary with respect to the total hardness, the calcium ion concentration, the concentration at which it is present in the water, and the level of dissolved oxygen.

TABLE XIII-6

PRESENT LEAD STANDARDS PROMULGATED BASED ON HUMAN EFFECTS (94)

<u>A. Physiologically Safe</u>	<u>Concentration</u>
(1) Lifetime	.05 mg/l
(2) Short period, few weeks	2 - 4 mg/l
<u>B Harmful</u>	
(1) Borderline	2 - 4 mg/l, for 3 mo.
(2) Toxic	8 -10 mg/l, several weeks
(3) Lethal	Unknown, probably 15 mg/l, several weeks

TABLE XIII-7

EFFECTS OF LEAD ON PLANTS AND ANIMALS (66)

<u>Species</u>	<u>Concentration</u>	<u>Remarks</u>
Oats, Potatoes	1.5 - 25 mg/l (lead nitrite)	Growth stimulation
Oats, Potatoes	50 mg/l (lead nitrite)	Detrimental
Sugar beets	51.8 mg/l (lead)	Injurious
Cattle	18 mg/l (soft water)	Lead Poisoning
Farm animals	0.5 mg/l	Maximum safe limit

The toxicity of lead as total lead and as various salts has been summarized in the work of McKee and Wolf, and is shown in Table XIII-8. It is apparent that toxic effects are observed at concentrations as low as 0.01 mg/l.

Lambou and Lim reported the investigations of Pringle et al. on the concentration effect of lead in shellfish. The concentration in the shellfish increases with the concentrations in water on a 1:1 ratio. The depletion rates for lead in oysters increased as the exposure decreased below a level of 0.05 mg/l. Above the level of 0.05 mg/l, the depletion rate remained relatively constant. A summary of investigations of lead concentrations in shellfish from Atlantic coast waters and Pacific coast waters is shown in Table XIII-9.

The work of Lambou and Lim indicates that lead is concentrated in various species of the aquatic environment (56). A compilation of concentration factors for various organisms is summarized in Table XIII-10.

McKee and Wolf reported an investigation of water hardness versus the concentration of lead in solution. It was found that with a total hardness of 14 mg/l (CaCO_3), that precipitation of the lead by calcium carbonate occurred as the lead concentration reached 9 mg/l. When the total hardness was increased to 53 mg/l (as calcium carbonate), the maximum concentration of lead which would remain in solution was approximately 1.6 mg/l. Schneider (83) reported a similar low toxicity for lead in waters containing 50 mg/l hardness as calcium carbonate. High concentrations of calcium carbonate are therefore

TABLE XIII-8

TOXICITY OF LEAD TO AQUATIC LIFE (66)

<u>Species</u>	<u>Form</u>	Concentration, mg/l	<u>Remarks</u>
Aerobic bacteria	Lead, Total	1.0	Toxic
Flagellates	" "	0.5	Toxic
Infusoria	" "	0.5	Toxic
Bacterial Decomposition	" "	0.1 - 0.5	Inhibition
Fish	" "	0.1 - 0.2	Toxic or Lethal
Sticklebacks	" "	0.1 - 0.2	Toxic or Lethal
Trout, 48 hours	" "	0.62	No visible Harm
<u>Daphnia magna</u>	" Chloride	0.01- 1.0	Deleterious
Fresh water fish	" "	0.33	"
Stickleback	" Nitrate	0.16	Death
Minnows, Stickleback & brown trout	" "	0.53	"
<u>Microregma</u>	" "	1.25	Deleterious
<u>Escherichia coli</u>	" "	1.3	"
Bluegill sunfish (<u>Lepomis Macrochirus</u>)	" Tetraethyl	0.20	Min. Safe Conc.

TABLE XIII-9

LEAD IN SHELLFISH FROM ATLANTIC COAST WATERS(MAINE THROUGH NORTH CAROLINA) AND INTHE PACIFIC OYSTER (WASHINGTON) (56)

<u>Species and Location</u>	<u>Lead Concentration in Tissue</u> <u>(mg/kg, wet tissue*)</u>	
	<u>Range</u>	<u>Average</u>
Atlantic Coast (Maine through North Carolina)		
Eastern Oyster	0.10 - 2.30	0.47
Northern Quahog	0.10 - 7.50	0.52
Softshell Clam	0.10 -10.20	0.70
Surf Clam		0.20
Blue Mussell (Narragansett Bay, R. I.)		0.20
Common Rangia (Pongo River, N. C.)		0.20
Channeled Whelk (Narragansett Bay R. I.)		3.20
Pacific Coast (Washington)		
Pacific Oyster		0.20

* Shucked, drained meats were homogenated, lyophilized, wet digested, diluted, and read by atomic absorption.

TABLE XIII-10

CONCENTRATION FACTORS FOR ORGANISMS STUDIED (56)

<u>Organism</u>	<u>Concentration Factor</u>
Phytoplankton	40,000
Mollusk (Whole animals)	4,000
Zooplankton	3,000
Ocean Fish: Hard Tissue	5,400
Soft Tissue	35
Fresh Water Fish: Hard Tissue	1,400
Soft Tissue	15
Clams & Oysters: Soft Tissue	1,050
Channeled Whelk	1,100
Brown Algae	700
Softshell Clam	230*
Northern Quahaug	170*
Eastern Oyster	160*
Common Rangia	70*
Surf Clam	70*
Blue Mussel	70*
Mollusk-Muscle	40
Pacific Oyster	70*

* Assumed dissolved lead concentration of 3 ug/l in seawater.
 Hard Tissue on basis of ash weight of bone.
 Soft Tissue on basis of live weight.

capable of reducing the toxicity of lead by removal of the lead from solution.

McKee and Wolf also reported that investigations by the California Water Pollution Control Research Board indicated that the toxicity of lead on rainbow trout increased with a reduction of the dissolved oxygen. A factor of 1.0, 0.95, 0.85, or 0.71 should be applied to the lethal or toxic concentration of lead as the percent of saturation for dissolved oxygen decreases as follows: 100%, 80%, 60% and 40%.

In summary, it has been shown that lead is toxic at low levels to man, animals, fish, and other aquatic life. As even low concentrations of lead are concentrated within the blood system and bone structure of man, animals, fish, and other aquatic life, it is imperative to control any discharge of lead into the aquatic environment.

TREATMENT TECHNOLOGY

In the previous sections it has been noted that the carbonate and hydroxide forms of lead are relatively insoluble. It has also been shown that a total hardness of 53 mg/l (as calcium carbonate) alone is capable of reducing the soluble lead to a concentration of approximately 1.6 mg/l. Lime precipitation is therefore as one process by which lead may be removed from solution. This is supported by Weston (97) who states that chemical precipitation and sedimentation is currently capable of producing an effluent concentration of 0.1-1.4 mg/l. As described by Patterson and Minear (76), precipitation of lead as lead carbonate or lead hydroxide yields tremendous savings in the overall cost of treatment. Table XIII-11 outlines the treatment

TABLE XIII-11

TREATMENT OF LEAD IN INDUSTRIAL WASTEWATERS

<u>Method</u>	<u>Initial Conc.</u>	<u>Effluent Conc.</u>	<u>Reference</u>
Total Hardness 53 mg/l (CaCO_3)		1.6 mg/l (soluble Pb)	(66)
C.P.S. *		0.1-1.4 mg/l	(97)
"	2.0 - 140 mg/l	Trace	(76)
" (Lime)	0.31 mg/l	0.1- mg/l or less	(76)
"	66.1 mg/l (Pb Tetraethyl)	Trace	(76)
" (FeSO_4) (pH 10.4-10.3	45 mg/l (Inorganic Pb)	1.7 mg/l	(76)
Lancy Batch Process	-	0.5 mg/l	(61)
Lancy Integrated Process	-	0.01 mg/l	(61)
Ion Exchange	.055 mg/l	0.0015 mg/l	(76)
	126.7-140.8 mg/l	0.02-.53 mg/l	(76)

* Chemical Precipitation and Settling.

of lead in industrial wastewater.

Patterson and Minear reported that the cost of removing lead by chemical precipitation is similar to that of removing other metals. The cost of treating lead is shown in Table XIII-12. While direct cost figures were shown in the literature reviewed for ion exchange, it was felt that the net cost would be based on the recovery of the lead. Otherwise the construction and operating cost would be similar to that for hexavalent chromium removal.

In summary, it has been shown that lead is readily treatable by precipitation to a final effluent level of 0.1 mg/l provided that proper controls are available and the plant is efficiently operated. It is recognized that filtration might be required to control the suspended solids which could contain a substantial concentration of lead. It is also apparent that ion exchange, and processes such as the Lancy Integrated System are capable of reaching final effluent levels of 0.01 mg/l or less. The Lancy Integrated System is currently an achievable treatment process for plants with a total discharge in the range of 25-500 gpm. It is difficult, however, to estimate its economic feasibility for larger facilities. It is felt that ion exchange is currently more in the realm of "best available treatment" than "currently applicable treatment." In the utilization of a process such as ion exchange, one must remember that the regeneration brines must ultimately be disposed of.

TABLE XIII-12

COSTS FOR TREATMENT OF LEAD BY PRECIPITATION

<u>Type</u>	<u>Capital</u>	<u>Operations</u>	<u>Reference</u>
Metal Plating Ind.	\$1,108/thousand gal.	\$.80/thousand gal	(76)
Metal Plating Ind.	\$1.62/thousand gal.*	\$.62/thousand gal.	(76)
1 MGD	\$100,000	-	(97)
10 MGD	\$600,000	-	(97)
Precipitation by FeSO ₄	4.2% of Total Treatment of Wastewater		(76)

* Amortized Capital Cost, interest rate and period of amortization were not reported.

SUMMARY AND RECOMMENDATIONS

In general the following statements can be made relative to lead in the environment:

1. Lead occurs naturally in the aquatic environment up to concentrations of 0.8 mg/l with average levels of 0.01 mg/l in surface and ground waters.
2. Lead is cumulative in man, animals, fish and wildlife.
3. A total intake of 0.1 mg/l in water or a total of 0.6 mg/day may cause lead poisoning for hypersensitive persons although man excretes lead to a degree.
4. Fish and aquatic life are capable of concentrating lead from 40-40,000 times the background aquatic levels. Fish and aquatic life are sensitive to lead concentrations in the range of 0.01-0.1 mg/l. Lead toxicity may be reduced in hard waters and/or in the presence of high dissolved oxygen.
5. Lead is currently treatable by available means to an effluent level of 0.1 mg/l for all discharges at a cost comparable to the removal of other trace metals. Current achievable treatment will remove lead from some wastewaters with flows up to 1 MGD at final effluent concentrations of 0.01 mg/l at a reasonable cost. Ion exchange may yield final effluent concentrations as low as 0.0015 mg/l. Implementation of this process on a full scale, however, needs to be proven prior to its adoption as a best available method.

On the basis of the above review, it is recommended that a uniform effluent criteria of 0.10 mg/l be adopted. It is further recommended that an average effluent concentration of 0.01 mg/l of lead be the objective of all wastewater bearing lead up to a flow rate of 1 MGD.

It is recognized that the recommended, presently obtainable effluent level of 0.1 mg/l lead may not protect all of the aquatic life under continued exposure. It has been shown, however, that even the more sensitive aquatic life species are capable of withstanding higher concentrations in the 0.1 mg/l range for short durations. It has further been shown that this level would at least meet the recommendation of McKee and Wolf for maximum levels in the drinking water for man's consumption. It is also noted that this is below the level recommended for short periods of exposure in man's drinking water by the U. S. Public Health Service Drinking Water Standards.

CHAPTER XIV-MANGANESE

Manganese ores are very common and are widely distributed, in both the manganous, Mn^{+2} , and manganic, Mn^{+3} forms. The oxides, carbonates, and hydroxides of manganese are only sparingly soluble in water and, therefore, manganese ions are not found in natural surface waters above 1.0 mg/l (66).

Common industrial uses of manganese are in steel alloy, dry cell battery, glass and ceramics, paints and varnishes, ink and dyes, match and fireworks industries. The manganous form of manganese is generally used in dyeing operations, disinfection, linseed oil driers, electric batteries, dyeing porcelain, glazing, varnishes, and in special fertilizers. The permanganate ion (MnO_4^-) is used as a strong oxidant which is normally reduced to insoluble manganese dioxide (66).

Due to their similar chemical properties, manganese is often found in the presence of iron. Gurnham (48) reports that clarified wastewaters of the iron mining industry after milling, flotation, and agglomeration, contain as much as 27.6 mg/l of manganese. Another similarity between iron and manganese is that manganese oxides are known for creating brown or black stains on porcelain fixtures, laundry items, and fine papers. In contrast to iron, however, Fair, Geyer and Okun (37), report that the manganous form of manganese oxidizes rather slowly to the insoluble manganese dioxide form, while iron is rapidly oxidized from the ferrous to the ferric state. Oxidation of manganese requires approximately 90 minutes at a pH of 9.3 and approximately 60 minutes at a pH of 9.5.

ENVIRONMENTAL EFFECTS OF MANGANESE

Manganese is an essential nutrient for man, animals and plants. In general, manganese is not toxic to aquatic life except in concentrations exceeding 25 mg/l (66). The main objection of high concentrations of manganese in surface waters is aesthetic and economic damage by staining and forming of deposits. The presence of manganese has been found to hinder many industrial water uses.

Effect on Man

The 1962 Drinking Water Standards (94) reports two reasons for limiting the concentration of manganese in drinking water. These are: (1) to prevent aesthetic and economic damage and (2) to avoid any possible physiological effects from excessive intake. A domestic consumer may find a brownish color imparted to laundered goods, and an objectionable taste to beverages such as coffee and tea by waters containing manganese.

With respect to the possible physiologic effects, the Drinking Water Standards reported hepatic cirrhosis in rats treated with very large dosages however, neurological effects of manganese have not been reported to result from oral ingestion by man or animal. McKee and Wolf indicated that slight toxic effects to high concentrations of manganese have been reported (66). For example, manganese may be toxic in a concentration of 0.5-6.0 g/kg body weight when administered to rabbits daily. McKee and Wolf cite a few instances of manganese toxicity to humans near Tokyo and Manchukuo (66). However, they point out that in these isolated circumstances the concentration of manganese

was far higher than the amount that would normally be tolerated aesthetically in drinking water.

The Drinking Water Standards (94) indicate that the average consumer could tolerate concentration of manganese of 0.01-0.02 mg/l for aesthetic reasons. However, a recommended drinking water standard of 0.05 mg/l was set.

McKee and Wolf (66) reported that manganese salts will impart a metallic taste to water at concentrations ranging from 0.5-20 mg/l. They also indicated that manganese in excess of 0.15 mg/l has been found to cause turbidity problems. Manganese has also been known to promote growth of some microorganisms in reservoirs filters, and distribution systems. It will also coat the sand particles in rapid sand filters in water treatment plant, promoting the formation of mudballs and clustered sand particles, reducing the overall efficiency of the filter.

Effect on Industrial Water Supplies

In general, manganese is undesirable in water used for many industries. Table XIV-1 indicates the limit of tolerance of manganese in certain industries.

Effect on Plants

McKee and Wolf (66) reported that manganese is essential for the growth of plants, apparently as an enzyme activator. Manganese has been used to enrich soil which stimulates plant growth (6,66). On the other hand, manganese has also been found to be toxic under some conditions. Manganese toxicities have been reported at a concentration of 0.5 mg/l (6). The toxicity depends upon the various plant species and conditions of nutrient imbalance.

TABLE XIV-1

INDUSTRIAL WATER SUPPLY LIMITS FOR MANGANESE AND IRON, mg/l

<u>Industrial Use</u>	<u>Mn</u>	<u>Mn & Fe</u>	<u>References</u>
Air Conditioning	0.5	0.5	(24,66)
Baking	0.2	0.2	(24,66)
Brewing, Light & Dark	0.1	0.1	(24,66)
Canning	0.2	0.2	(24,66)
Carbonated Beverages	0.2	0.2, 0.1	(24,66)
	0.2	0.2	(24)
Confectionary	0.2	0.2	(45,66)
Cooling Water	0.2	0.2	(66)
	0.5	0.5	(45,66)
Distilleries	0.1	0.1	(24)
Dyeing	0	0	(66)
Food Processing	0.2	0.2	(24,66)
Ice	0.2	0.2	(24,66)
Laundering	0.2	0.2	(66)
Milk Industry	0.03-0.1		(24)
Pulp & Paper	0	0	(24)
Groundwood	0.1-0.5	1.0	(24,66)
Kraft pulp	0.1	0.2	(24,66)
Soda & Sulfite	0.05	0.1	(24,66)
Highgrade paper	0.05	0.1	(24,66)
Fine paper	0.05	0.1	(24)
Kraft paper, Bleached	0.1		(24)
" " Unbleached	0.5		(24)
Photography	0	0	(24)
Plastics (clear)	0.02	0.02	(24,66)
Rayon & Viscose			
Pulp production	0.03	0.05	(24,66)
Manufacturing	0.02	0	(24,66)
Tanning	0.2	0.2	(24,66)
Textiles, General	0.1 -0.25	0.1 -0.25	(24,66)
" Dyeing	0.25	0.25	(24,66)
" Wool Scouring	1.0	1.0	(24,66)
" Bandages	0.2	0.2	(24,66)

McKee and Wolf (66) have also reported that manganese injury has been found to be intensified in the presence of molybdenum, vanadium, and nitrate and diminished in the presence of cobalt, iron, molybdenum, aluminum, a phosphorus deficiency, ammonium and ammonium nitrate. It is believed that nearly all species of plants are capable of tolerating up to 2 mg/l of manganese (6).

Effect on Domestic Animals and Wildlife

Manganese has been found to be an essential nutrient for animals. McKee and Wolf (66) reported that a deficiency in manganese produces ovarian disfunction, testicular degeneration, poor lactation, lack of growth, bone abnormalities, and disturbance of the central nervous system. Manganese may have been partly responsible for the occurrence of infectious anemia in horses at a concentration far above what would be expected in a normal water supply.

Effect on Fish and Other Aquatic Life

McKee and Wolf (66) report that manganese and its salts are generally toxic to fish and aquatic life at a concentration greater than 25 mg/l. Permanganates, are much more toxic to fish than the manganous salts, however. They have been found to kill fish at concentrations of 2.2-4.1 mg/l as manganese. Fortunately, the permanganates are readily reduced to insoluble manganese dioxide under natural water conditions.

The conclusions and recommendations of McKee and Wolf (66) summarizing the limits of manganese in different types of water supplies are given in Table XIV-2.

TABLE XIV-2

RECOMMENDED LIMITS OF MANGANESE IN WATER SUPPLIES (66)

<u>Water Supply</u>	<u>Concentration (mg/l)</u>
Domestic	0.05
Industrial	0.05
Irrigation	0.50
Stock Watering	10.00
Fish & Aquatic Life	1.00

TABLE XIV-3

PROCESSES FOR MANGANESE REMOVAL (76)

<u>Process</u>	<u>Comments</u>
Aeration	Slow and ineffective below pH 9.
Chlorine and Hypochlorite Oxidation	Not particularly effective for organically bound manganese.
Adjustment of pH	Lime soda type treatment gives removal at pH 9.5.
Catalysis	Copper ion enhances air oxidation.
Ion Exchange	Effective for small quantities of iron and manganese. Resins quickly fouled by iron and manganese oxides.
Chlorine Dioxide	Rapidly oxides manganese to the insoluble form, but expensive.
Manganese Dioxide or Potassium Permanganate	Regeneration, green sand and filter process. Economic disadvantage of requiring excess permanganate.
Direct Potassium Permanganate Addition	Requires sand filtration

TREATMENT TECHNOLOGY - MANGANESE REMOVAL

Drinking Water Standards (94) indicate that manganese is difficult to remove to residual concentrations of much less than 0.05 mg/l. Manganese removal has been practiced for many years in the treatment of municipal water supplies and industrial process waters. In general, the technology consists of the removal of the soluble manganous ion as an insoluble precipitate. Since many wastewaters contain both manganese and iron, the methods utilized in iron removal are appropriate for the removal of manganese. The one difference is that a pH of 9-9.5 is needed for removal of manganese while a pH of 7.5-8.5 is needed for the removal of iron (37,66). Patterson and Minear (76) have summarized the effective processes for removal of manganese in Table XIV-3.

As reported in Patterson and Minear (76), chemical oxidants to assist conversion of the manganous ion to insoluble manganese have been used although this has also caused problems with filtration. The formation of manganese flocs with strong oxidants has been found to clog slow sand filters. They indicated that utilization of chlorine, followed by lime coagulation, and rapid sand filtration was effective in the removal of manganese, at an initial concentration as high as 5.7 mg/l. They also reported that for effective oxidation of manganese, a free chlorine residual of 0.5 mg/l was required. The oxidation utilized 1.29 mg of chlorine per mg of manganese oxidized.

The use of ion exchange for iron and manganese removal was also reported by Patterson and Minear (76). They indicated that the

advantages of ion exchange process are: s smaller capital investment than for coagulation filtration, up to 4 times greater flow rates, smaller plant requirements, and simpler operation. A disadvantage of this process is that the brine utilized to regenerate the ion exchange unit creates a major disposal problem since the manganese is found to remain in a soluble form in the brine. An additional drawback is that an absolute anaerobic condition must be maintained in the ion exchange unit to prevent the manganese being oxidized by the air and forming a precipitate which will clog the ion exchange bed.

In summary, it has been reported by both Patterson and Minear (76) and Weston (97) that it is possible to obtain a final effluent concentration of 0.05 mg/l of manganese. Table XIV-4 summarizes the efficiencies of various units. Table XIV-5 indicates the capital costs and Table XIV-6 shows the operation and maintenance costs. The operation and maintenance cost and the capital investment for the removal of manganese is well within the range of the cost for removing other metals.

TABLE XIV-4

TREATMENT EFFICIENCY FOR MANGANESE REMOVAL

<u>Process</u>	<u>Concentration, mg/l</u>		<u>Reference</u>
	<u>Influent</u>	<u>Effluent</u>	
Chlorination and lime coagulation and filtration	5.7	split flow used	(76)
Permanganate oxidation and filtration	1.0	0.05	(76)
Permanganate oxidation plus sodium alginate	0.35	0.02	(76)
Permanganate oxidation and filtration	--	0.05	(97)
Lime coagulation, settling and filtration	--	0.05	(97)
Greensand filter	1.7	0.0	(76)
Ion exchange	1.7(37)*	0.1(0.5)*	(76)
	1.0(53)	0.0(0.3)*	(76)
	1.3(52)*	0.0(0.1)*	(76)

* Iron - mg/l in parenthesis (however, unspecified)

TABLE XIV-5

CAPITAL COST FOR MANGANESE REMOVAL

<u>Process</u>	<u>Flow</u>	<u>Cost</u>	<u>Reference</u>
Chemical coagulation, settle and filter	1.0 MGD	300,000	(97)
	10.0 MGD	1,300,000	(97)
	50.0 MGD	4,600,000	(97)
Chlorination, settle and filter	1.0 MGD	300,000	(97)
	10.0 MGD	1,300,000	(97)
	50.0 MGD	4,600,000	(97)
Aeration, lime coagulation, settle filter and recarbonate	*	75,000	(76)
Greensand filter	*	26,000	(76)

* Treating the same flow and wastes (however, unspecified).

TABLE XIV-6

CHEMICAL COST FOR MANGANESE REMOVAL (76)

<u>Process</u>	<u>Cost/1000 Gallons</u>
Lime coagulation and filtration	2.1¢
Permanganate, only	0.3¢
Greensand, pressure filter	3.5¢ (permanganate regeneration only)

SUMMARY AND RECOMMENDATIONS

- (1) Manganese is normally found with iron in the nature.
- (2) Manganese is found in several industrial wastewaters.
- (3) Manganese is a basic and essential nutrient to man, plant and animal life. Manganese damages plants only at concentrations above 2 mg/l. Manganese at a concentration below 10 mg/l has no adverse effect on animals.
- (4) Manganese is not toxic to fish and aquatic life until the concentration approaches the 1-2 mg/l range in the stream.
- (5) Current technologies are capable of removing manganese to less than 0.05 mg/l with reasonable costs.
- (6) The major problem of manganese in surface waters is aesthetic.

Based on the above summary, it is recommended that a uniform effluent criteria be established at concentration of 0.10 mg/l for manganese.

CHAPTER XV-MERCURY

Mercury was not widely recognized as a water pollutant until 1966 when Irukayama reported on the 1953 mercury pollution incident in Japan. Since that date, mercury has moved to the forefront as one of the most closely watched pollutants being discharged into our nation's waters. The major sources of mercury discharges are summarized in Table XV-1. All of these sources are discussed in a recent publication by Selikoff (85).

Chlor-alkali plants are reported to discharge from 51-85 grams of mercury per ton of chlorine produced. It was also noted that prior to the recognition of mercury as an important pollutant this figure may have been much higher (85).

The use of mercurial catalysts to convert acetylene to acetaldehyde resulted in losses of mercury estimated at 300 kg/yr for one plant in Sweden (85). Discharge concentrations for mercury slimicides utilized in the pulp and paper industries have not been reported in the literature although their usage is extensive.

The agricultural usage of mercury in pesticides has been reported to amount to not less than 2100 metric tons per year. Of this amount, 400 tons per year have been attributed to use within the United States.

TABLE XV-1

MAJOR INDUSTRIAL SOURCES OF MERCURY POLLUTION

Chlor-Alkali Plants

Slimicide Treatment of Distribution Systems

Fungicide Treatment of Seed Grains

Combustion of Fossil Fuels

Disposal of mercurial antiseptics (hospital, laboratories, dental clinics)

Disposal of mercury containing switches, rectifiers and measuring devices (thermometers, barometers fluorescent tubes, mercury lamps, batteries, etc.)

Mercury pigments and impregnating agents

Processing of some raw materials (e.g. coal, carbon, chalk, phosphates, pyrites).

Coals in the United States contain mercury in concentrations from a few parts per billion to several parts per million. Based on an estimated average of one part per million, the annual consumption of 500 million tons of coal per year would contribute 1,000,000 pounds of mercury per year to the environment. This value does not include mercury contributed from the refinement and use of crude oil products which may contain even higher concentrations of mercury (85).

Mercury occurs naturally in the form of the mineral cinnabar, a mercury sulphide, and rarely, as the free element. These forms may be leached or volatilized into the water and air environments, providing a low but constant background (66).

Both air pollution and natural sources of mercury must be considered in evaluating the total exposure of man and animal. Table XV-2 summarizes both the total world consumption of mercury and United States trends (85),

Lambou reports that mercury is usually discharged in one of the five forms listed in Table XV-3 (54). The reactions and inter-conversions these forms may undergo are illustrated in Figure XV-i. Experimental work has confirmed that metallic mercury can be easily oxidized to divalent mercury under the conditions often found at the bottoms of lakes and streams. Under reducing conditions, metallic mercury is stable and remains in the sediment as a reservoir which may be converted years later to the divalent form.

TABLE XV-2

TOTAL WORLD PRODUCTION OF MERCURY AND TRENDS IN THE U. S. (85)

	1968 (a) (tons)	1969 (a) (tons)	Estimated 1974-1975 (b) (tons)
Total world production	9,836	10,885	--
Trends in uses of mercury in U. S.			
Agricultural use	130	102	101
Amalgamation	10	7	9
Catalyst manufacture	73	112	89
Dental (c)	116	116	144
Electrical equipment	746	710	863
Chlor-alkali plants	663	788	869
Laboratory use (b)	75	78	79
Industrial controls (b)	202	265	351
Paints	401	370	407
Paper and pulp	16	21	9
Pharmaceuticals	16	27	25
Other uses (d)	302	368	226
Not accounted for (e)	12	42	
	2863	3006	3172
Sources and export of Mercury in U. S.			
U.S. domestic mines	1097	1090	
Imported	910	1164	
GSA sales to industry (f)	745	117	
GSA transfers to govt. agencies	68	--	
GSA transfers to inter- National redevelopment	91	--	
Redistilled (g)	316	380	
Secondary recovery (h)	402	402	
GSA stock	86	539	
Exported	289	19	

NOTE: These values do not include any mercury held by General Services Administration or Atomic Energy Commission.

- a. U.S.D.I. Bureau of Mines, USGS 1968 1969 (Mercury).
- b. Trends in Usage of Mercury, National Materials Advisory Board, National Research Council, Washington, D.C.
- c. Includes redistilled mercury.
- d. Includes purchases for expansion and new chlor-alkali plants.
- e. Mercury, chiefly from secondary recovery - uses not specified.
- f. General Services Administration
- g. This mercury is from other sources and is given additional purification.
- h. This mercury is recovered from battery scrap, dental amalgams and other reprocessed sources.

TABLE XV-3

THE FORMS OF MERCURY PRESENT IN INDUSTRIAL DISCHARGES

1. Inorganic divalent mercury - Hg^{++}
2. Metallic mercury - Hg^0
3. Phenyl mercury - $\text{C}_6\text{H}_5\text{Hg}^+$
4. Methyl mercury - CH_3Hg^+
5. Alkoxy-alkyl mercury - $\text{CH}_3\text{O}-\text{CH}_2\text{CH}-2\text{Hg}^+$

FIGURE XV-1

POSSIBLE INTERCONVERSIONS OF MERCURY COMPOUNDS
IN NATURAL AQUATIC ENVIRONMENTS (102)

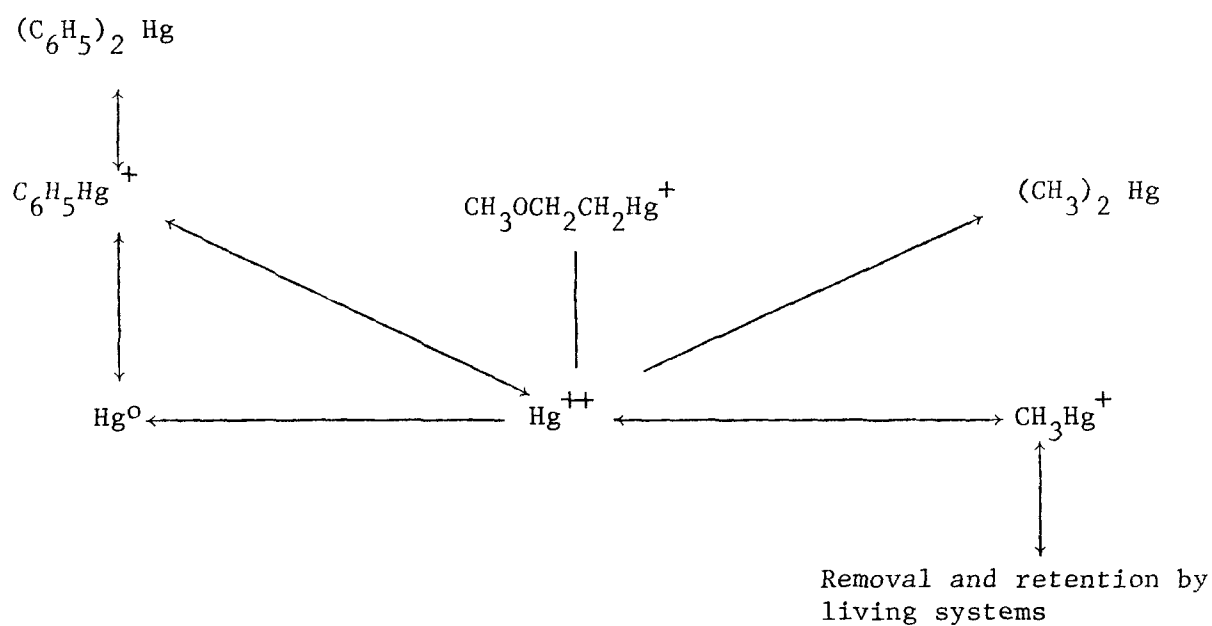


TABLE XV-4

MERCURY RESIDUES IN GRAIN AND FRUIT UNTREATED AND
TREATED WITH PHENYL MERCURY FOLIAM SPRAY (85)

<u>Commodity</u>	<u>Mercury (ppb)</u>	
	<u>Untreated</u>	<u>Treated</u>
Rice	20-100	100-700
Mandarin orange		
Skin	10-50	30-240
Pulp		10-40
Apple		
Skin	10-50	70-310
Pulp	10-50	30-130

TABLE XV-5

MERCURY IN FOODS (85)

<u>Food</u>	<u>Country</u>	<u>Nanograms/gram</u> <u>(range) (pp⁺)</u>
Haddock	United States	17-23
Herring	Baltic states	26-41
Apples	United Kingdom	20-120
Apples	New Zealand	11-135
Pears	Australia	40-260
Tomatoes	United Kingdom	12-110
Potatoes	United Kingdom	5-32
Wheat	Sweden	8-12
Rice	Japan	227-1000
Rice	United Kingdom (imports)	5-15
Carrots	United States	20
White bread	United States	4-8
Whole milk	United States	3-10
Beer	United States	4

Both phenyl and alkoxi-alkyl mercury have been reported to undergo conversion to methyl mercury through inorganic divalent mercury (54).

Divalent mercury has a strong affinity for organic muds and has been shown to be biochemically methylated in the benthic sediments. Two products are possible from this reaction, monomethyl and dimethyl mercury. The monomethyl form is accumulated by aquatic organisms, while the dimethyl form is apparently lost through evaporation to the atmosphere. High pH favors the formation of the dimethyl form. The methylation of mercury is not only rapid but is also reported to be enhanced by anaerobic conditions (85).

In Sweden, regardless of the nature of the mercury pollutant, only methyl mercury has been found in fish, indicating that a methylation of mercury compounds also takes place in the fish itself (54). Jernelov (102) found that the mucus on pike is able to convert inorganic bivalent mercury almost completely into methyl mercury within a short period of 2-4 hours.

Mercury in natural aquatic systems is apparently converted to the methylated form regardless of the form in which it was introduced. In reviewing the impact of mercury on the environment it will be seen that not only is this form the most toxic, but it is also the form most easily retained by living creatures.

ENVIRONMENTAL EFFECTS OF MERCURY

Effect on Man

Prior to 1963, it was reported that adults could safely consume water containing from 4-12 mg of mercury per day and that a fatal

dose of mercury from such water would be about 75-300 mg/day (66). It is now believed that water is not the critical mode of ingestion for man. Exposures of the general populace to toxic concentrations of mercury is likely to result from the consumption of contaminated fish and possibly other food and not directly through water or air. The tragic outbreaks of the so-called Minanata disease in Japan have been attributed to the long term consumption of fish which had concentrated methyl mercury from polluted waterways (85). Such a mechanism is extremely important in nations like Japan where the normal diet of the population contains a high percentage of fish and seafood.

There have been other incidents of mercurial poisoning in Iraq, Pakistan and Guatemala where farmers receiving fungicide treated seed grain ate the seed instead of planting it. Table XV-4 illustrates the variation of mercury content between treated and untreated food stuffs. Table XV-5 gives the mercury residues found in a number of food products from a variety of world markets.

The potential contamination of fish and shellfish is obviously critical in determining the hazards associated with mercury discharges. Recognition of the natural methylation of mercury in the environment and the concomitant biological magnification in successive predators requires setting criteria at the lowest feasible level if we are to maintain the safety of commercial fisheries.

It is difficult to calculate threshold levels for toxic effects on humans due to the intermittent nature of the exposure in the reported cases of chronic mercury poisoning. For acute, single dose

exposures mercuric chloride and all the organomercurials tested fell into the extremely toxic category, (LD_{50} 's are between 5 and 50 mg/kg). The levels of mercury contamination necessary to induce chronic poisoning have not been reported in the literature. This is due to the difficulty of ascertaining the eating habits of the affected individuals and problems inherent in relating mercury concentrations ingested to mercury concentrations in fish caught after the incident. The situation is further complicated by the fact that there can be several weeks delay between the ingestion of the critical amount of mercury and the onset of symptoms. This could result in acute cases being diagnosed as chronic. The symptoms of alkyl mercury poisoning are indicative of damage to brain tissue and are in many cases irreversible.

Prenatal and postnatal exposures are also of importance. Acute and chronic exposures can be readily passed through the placental barriers to the fetus and also to infants through the mother's milk. Studies in both man and animals indicated a concentration of mercury within the fetal blood about 20% higher than that in the mother (54). Silikoff reports that the concentration may be 30% higher in the fetal red blood cells than in the red blood cells of the mother (85).

Children born of mothers exposed to methyl mercury have been found to suffer from symptoms approaching a cerebral palsy like disease. The disease varies in severity from mild to moderate spasticity and ataxia, to severe intellectual retardation, seizures, and evidence of generalized brain damage.

Lambou reports that about 15% of the total body accumulation of methyl mercury is found within the brain cells. It was found that neurological symptoms begin to manifest themselves when the brain cells contain about 0.020 mg/gram (20ppb) of mercury in the wet tissue in the brain.

The threshold mechanism appears to be due to the number of damaged brain cells rather than the methyl mercury threshold. Rapid damage of many brain cells could clinically be reported erroneously as the methyl mercury threshold (54).

The alkyl mercury compounds have also been reported to damage gametes prior to fertilization and to increase the frequency of chromosome breaks in Swedish fishermen whose blood levels of methyl mercury were higher than the general population. These elevated levels were attributed to their high dietary intake of fish (102).

Effect on Mammals and Birds

Reports indicate that many mammals and birds are affected by mercury poisoning through the consumption of contaminated fish. Study of the Minamata incident shows that cats had been dying before humans were noticeably affected. Experimentally, cats have been killed by feeding them fish and shellfish containing 5.7 ppm mercury. Both acute and chronic toxic concentrations of methyl mercuric chloride have been reported for cats and rats. The toxic concentrations for cats have been found to be between 10-50 mg/kg. Most acute cases of poisoning had received a 20 mg/kg oral dose and chronic effects were noted at a concentration of 1 mg/kg per day. Similarly, rats

have been shown to be acutely poisoned at concentrations of 20 mg mercury per 100 grams delivered orally and to show chronic effects of poisoning after oral dosages of 1-2 mg/100 gm/day (85).

The retention time of methyl mercury in the tissues of various species tested varied widely. The experimental half-lives are shown in Table XV-6.

The toxic concentrations of methyl mercury to birds have been found to be about the same as those for laboratory mammals, approximately 12-20 mg/kg. The mercury residue found in the liver and kidney of birds killed experimentally with treated seed ranged from 30-130 ppm for pheasant, 70-115 ppm for jackdaws, and 50-200 ppm for magpies. In pheasants, it was also found that the level in the muscles ranged from 20-45 ppm. Liver and kidney residues of approximately 30 ppm seemed to be associated with the onset of critical symptoms in the subject birds. A normal level would be less than 1 ppm (85).

Toxicity to secondary consumers is also of concern. It was found that goshawks and ferrets died within 2-3 weeks after eating hens which had died from methyl mercury poisoning. It was also found that hawks and owls which had eaten seed-eating prey with concentrations up to 140 ppm had died with levels of 300 ppm. Deaths of secondary consumers can be expected as the result of successive concentration of mercury levels through lower trophic levels (85).

Methyl mercuric chloride has been placed in the acute toxicity ranking of organic chemicals found in fresh water as determined by the LD₅₀ in mammals using oral administration. It ranks number 2

TABLE XV-6

BIOLOGICAL HALF TIMES OF METHYL-MERCURY RESIDUES
IN VARIOUS SPECIES (101)

<u>Species</u>	<u>Approximate Half-Times (days)^a</u>
Mouse	8
Rat	16
Young dogs	20
Squirrel Monkey	65
Man	70
Seal	500
Poultry	25
Molluscs	700
Crab	400
Pike	700
Flounder	1000
Eel	1000

(a) Half-Times is the Time for excretion of 1/2 body burden.

with the concentration of 099 mg/kg, and as number 11 in the range of 100-199 mg/kg. Two other organic mercury compounds have also been listed in the ranking of acute toxicity of potential organic pollutants as determined by the LD₅₀ in mammals using oral administration. They are ranked as number 55th Diethyl mercury at a concentration of 50-99 mg/kg; and, as number 96th ethyl mercuric chloride at a concentration of 200-299 mg/kg (59).

Effects on Fish and Other Aquatic Life

McKee and Wolf report that mercuric ions are considered to be highly toxic to all forms of aquatic life (66). A concentration of mercury within the range of 0.004-0.02 mg/l (as mercury) has been reported to be harmful to fresh water fish. Table XV-7 summarizes the toxic concentrations of the various forms of mercury to various species of fish and aquatic life.

A concentration of 1.0 mg/l of mercury, as mercuric chloride, has been found to reduce the rate of oxygen utilization in BOD tests by 80%. Mercuric chloride has also been shown to increase in toxicity from 0.02-0.2 mg/l for sewage organisms. The mercuric metals which form the most insoluble sulfides have been found to be the most toxic (15). Mercuric compounds were found in a study in Denmark to be concentrated by pike. A mercury content of 0.07 ppb was found to be concentrated within pike as much as 3,000 times (102).

Concentrations of methyl mercuric chloride in waters receiving acetaldehyde plant wastes have been reported at 14.4 mg/l and concentrations of mercury in fish varied from 9-88 mg/kg of dry weight (60).

TABLE XV-7

TOXIC CONCENTRATIONS OF MERCURY ON AQUATIC LIFEAdapted From McKee and Wolf (66)

<u>Form</u>	<u>Conc.,mg/l</u>	<u>Species</u>	<u>Remarks</u>
Mercury Chloride	0.008	Sticklebacks	Injury or kill
(as Hg)	0.01	Sticklebacks	" "
"	0.01	Minnows	" "
"	0.011	Sticklebacks	Threshold
"	0.02	Guppies	Injury or kill
"	0.15	<u>Microregma</u>	Threshold
"	0.2	<u>Escherichia coli</u>	"
"	0.03	<u>Scenedesmus</u>	"
"	0.03	<u>Daphnia magna</u>	"
Mercuric Cyanide	0.02	<u>Daphnia magna</u>	"
(as Hg)			
" "	0.15	<u>Scenedesmus</u>	"
" "	0.20	<u>Escherichia coli</u>	"
" "	0.16	<u>Microregma</u>	"
Mercuric Nitrate	0.015	Isopod	1st Response
(as $\text{Hg}(\text{NO}_3)_2$)			
" "	0.015	Fish (Stickleback)	" "
" "	1.00	Polychaete	" "
Mercurio-Organics	0.02-1.4	Minnows	Fatal
" "	0.02-1.4	Shiners	"
Phenylmercuric acetate	0.01	Young Salmon	Max. Safe Conc.
Mercuric acetate	0.02-0.05	" "	" " "
Phenylmercuric acetate	0.005-0.01	<u>Daphnia pulex</u>	" " "

A temperature effect on mercury toxicity has also been reported by Lambou (54). An investigation of the toxicity of various organic mercury compounds to fingerling channel catfish is summarized in the Table XV-8.

TABLE XV-8

TOXICITY OF ORGANIC MERCURY COMPOUNDS ON
FINGERLING CHANNEL CATFISH (54)

<u>Chemical</u>	<u>Temperature</u> °C	<u>TLm in mg/l</u>			
		24 hrs.	48 hrs.	72 hrs	96 hrs.
Phenylmercuric acetate	19	4.1	3.4*	3.3	3.3
Pyridylmercuric acetate	24	3.8	---	0.49	---
Ceresan M (a)	19	1.8	1.8	1.6	1.6
Lignasan (b)	19	2.0**	2.2	1.7	1.3
Tag 10% solution (c)	20	1.5	0.78	0.60	0.58

* At 45 hours

** At 28 hours

(a) Ethyl mercury p-toluene sulfonanilide, 7.7 percent (total mercury as metallic, 3.2 percent)

(b) Ethylmercuric phosphate, 6.25 percent

(c) Phenylmercuric acetate, 10 percent.

Effect on Plants

It has been reported that a concentration of 0.5 mg/l mercury added as mercuric chloride caused a 50% inactivation of photosynthesis in giant kelp during a four day exposure, and that a concentration of 0.1 mg/l decreased photosynthesis by 15% in one day, with complete inactivation after four days (6). A minimum lethal concentration of mercuric salts has been reported in the range of 0.9-60 mg/l for phytoplankton.

Selikoff reported that the organic compounds of mercury may produce genetic mutations and chromosomal aberrations in certain systems of plants (85).

TREATMENT TECHNOLOGY

A review of current literature in the field of industrial waste treatment (48,61,72) indicates that very little is known or reported on the treatment and control of mercury waste discharges. The report by Lelikoff (85) and more recent works indicate that control of a mercury discharge is feasible at least from the production of chlor-alkali.

Selikoff reported on nine process and housekeeping changes that were able to produce a tenfold decrease in mercury discharges from chlor-alkali plants in Sweden (85). These procedures, current and planned, are listed below.

1. Cooling the hydrogen gas to less than 0° at 2 atm of pressure and returning condensate to decomposer
2. Returning condensate obtained by cooling chlorine gas to the brine solution.

3. Separating waste streams and using epoxy on concrete floors to prevent entrapment of mercury
4. Enlarging and improving sedimentation basins.
5. Filtering wastewater through activated charcoal.
6. Treating wastewater with disulfide and subsequent coagulation, sedimentation and filtration.
7. Treating waste by means of ion exchange, probably after pre-treatment by another method.
8. Improving procedures for reactivating cell anodes.
9. Recirculating all water used in production.

A summary of the improvements made in the mercury discharge from a chlor-alkali plant in Sweden is presented in Table XV-9.

In testimony presented to the Illinois Pollution Control Board, R. F. Weston indicated that total mercury could be reduced by ion exchange to a total effluent level of 0.002-0.005 mg/l (97). He also estimated the capital cost to be \$1.2 million for a 10 MGD treatment facility, or \$120/1000 gallons.

A recent report (9) indicates that mercury may be reduced in the atmosphere at chlor-alkali plants to a level of one ppb or as low as 6 mg/metric ton of chlorine produced. One of the techniques developed by B. P. Chemical Company consists of a process which washes the mercury laden vent gases in hydrogen with a solution of sodium hypochlorite and sodium chloride at a pH of about 9-10.5. It was reported that the chloride ion keeps the mercury in solution as a complex salt. Mercury is then recovered by blending of the

scrubber solution with a brine, which then enters an amalgam cell, or electrolytic or chemical reduction process.

The B. P. Chemical Company process was reported to have an installation cost of approximately \$665,000 for a 60,000 metric ton facility in England. The operating costs were reported not to exceed \$250 per year for the scrubbing chemicals used and an annual maintenance cost of \$7,000 per year.

A second process has been developed by Monsanto Company Enviro-Chemical Division. Their process utilizes the adsorption of mercury onto a specially formulated adsorbent. After complete utilization of the adsorbent, Monsanto Envir-Chem states that the canisters containing the adsorbent may be returned to them for disposal. Reportedly, they have two processes for disposing of the mercury containing adsorbents which do not contribute to environmental pollution.

A review of the report prepared for EPA by General Technology Corp. (42) on the waste of the inorganic chemical alkali and chlorine facilities indicates an average wastewater discharge of 20,000 gallons per ton of chlorine produced in a chlor-alkali plant. This flow factor of 20,000 gallons per ton of chlorine produced can be applied to the data shown above in Selikoff's report. The data then indicate that mercury concentration for the new plant at Stenungsund, 1969, would equal 0.0362 mg/l and technically possible mercury levels by 1970 would range from 0.0070-0.01466 mg/l. This data compares favorably with that of Weston who indicated an achievable level of

0.002-0.005 mg/l.

Mr. Frank Hall of the Enforcement Division of EPA, Headquarters has indicated that an effluent level of 0.1 pounds of mercury per day has successfully been obtained through various legal actions on several chlor-alkali plants in recent years. This maximum effluent criteria of 0.1 pounds per day can not be applied indiscriminately to other types of mercury discharges. However, it has been defined as technically feasible for plants utilizing either the B. P. or Monsanto processes as discussed above (9).

TABLE XV-9

MERCURIAL DISCHARGE FROM CHLOR-ALKALI PLANTS IN SWEDEN (85)

<u>Loss to</u>	<u>Loss of mercury (g/ton of chlorine)</u>		
	<u>Range</u> <u>Aug. 1967</u>	<u>New plant at</u> <u>Stenungsund, 1969</u>	<u>technically</u> <u>possible in 1970</u>
Water	30-40	0.55	0.01-0.1
H ₂ gas	5-10	0.4	0.01
Alkali	1-10	0.8	0.01-0.5
Ventilation	15-25	1.0	0.5
Total	51-85	2.75	0.53-1.11

SUMMARY AND RECOMMENDATIONS

1. The largest single man made source of mercury is the production of chlorine in chlor-alkali plants. There are, however, numerous other industrial and commercial sources of mercury pollution.
2. Mercury is toxic in all forms, but in the aquatic environment it is converted to its most toxic form, methyl mercury. In the form of methyl mercury it may be rapidly absorbed by fish and other forms of aquatic life. Mercury is subject to biological magnification, that is, increasing residue concentrations in the higher trophic levels.
3. The principal danger to man is from the ingestion of mercury contaminated fish and foodstuffs. Such ingestion may cause genetic, nerve, or brain damage and/or death. An additional concentration effect in fetal blood and tissues is noted. Methyl mercury accumulates so well that repeated minute intake during a prolonged period can kill or create permanent disability.
4. The fatal dose of mercury for man could range from 75-300 mg/day.
5. Mercury has been found to be 20% higher in the fetal blood of mammals than in the mother
6. A mercury concentration of 0.5-0.9 mg/l has been reported as the lethal concentration to plant life.
7. Organic mercury may produce genetic mutations and chromosomal aberrations in plants.

8. Secondary poisoning by mercury in birds and mammals if of importance.
9. Harmful concentrations of mercury for fresh water fish have been found to be within the range of 4-20 ug/l
10. Methyl mercury chloride ranks as the second most toxic organic chemical to animal life through injection by the oral route.
11. Chlor-alkali plants are capable of achieving effluent levels below 0.1 lb/day with existing technology, and levels of 0.002-0.005 mg/l are feasible in treated discharges.

It is the public policy of the Environmental Protection Agency as stated by the Administrator, Mr. William Ruckelshaus, that there should be no man-made discharges of mercury. An appropriate interpretation of Mr. Ruckelshaus' statement would mean a non-detectable concentration of mercury.

On the basis of the above conclusions, it is readily apparent that mercury should be maintained at an absolute minimum level. It is recognized that for some industries this may necessitate a change of product, or of materials and/or processes utilized. It is recommended that an interim maximum uniform effluent criterion of 0.005 mg/l be adopted for all discharges. It is further recommended that a maximum total discharge of 0.1 pounds/day be adopted for all chlor-alkali plants.

It cannot be overstressed that our objective is to reach a total non-existent discharge of mercury into the aquatic environment. Therefore, our objective is a non-detectable concentration of mercury in all surface and ground waters. Currently, the limit of detection of mercury by flameless atomic adsorption, as described in W.Q.O. Methods for Chemical Analysis of Water and Wastes, April 1971 is ten nanograms per liter (0.000010 mg/l).

CHAPTER XVI-NICKEL

Natural aquatic concentrations of nickel are found as the divalent nickel ion or its complexes. Nickel is leached from its ores and minerals. Nickel salts are noted for their solubility and characteristic green color. Table XVI-1 gives the concentrations of nickel found in nature.

INDUSTRIAL SOURCES

The primary source of nickel pollution in surface waters is the metal plating and metal finishing industry. The second major source is the manufacture of nickel-copper alloys known as monels. Most monels consist of 63-67% nickel and 30% copper. Other nickel copper alloys known as cupro nickel consist of more than 50% copper (24). Various concentrations found in these industrial wastewaters are summarized in Table XVI-2. Other industrial uses of nickel are in the manufacture of synthetic ink, brown ceramic colors and the dyeing and printing of fabrics.

In discussing the disposal of nickel bearing wastewaters, Nemerow (72), reported that nickel concentrations discharged to municipal sewers should not contain more than 2-5 mg/l nickel. He reported that 2.0 mg/l will be toxic to the bacteria utilized in sludge digestion.

ENVIRONMENTAL EFFECTS OF NICKEL

Effects on Animals and Plants

Tables XVI-3 and XVI-4 summarize the toxic concentration of nickel to certain plants and animals. While the U. S. Public Health

Drinking Water Standards (94) do not have a limit on nickel, Water Quality Criteria Data Book Volume 2 (105) indicates that the Russians have placed a maximum permissible concentration at 0.1 mg/l.

TABLE XVI-1
CONCENTRATION OF NICKEL IN NATURE (6)

<u>Sources*</u>	<u>Concentrations</u>
Seawater	0.0054 mg/l
Marine Plants	Up to 3 mg/l
Marine Animal	0.4025 mg/l
Serpentine Rocks	400-5,000 mg/kg
Natural Soil	5-100 mg/kg

* Nickel sources as their salts.

McKee and Wolf report that while there is no data on the toxicity of nickel to man, it is believed to be low. They did indicate, however, that nickel in the water supply may hinder the growth of the liver in amphibia, reptiles, birds, and mammals (66).

TABLE XVI-2

CONCENTRATION OF NICKEL IN CERTAIN INDUSTRIAL WASTEWATERS

<u>Source</u>	<u>Concentration (mg/l)</u>	<u>Reference</u>
Plating wastewaters	11.3 mg/l avg. 5.0-35 mg/l range*	(72)
Plating and pickling operation	12.6 mg/l avg. 6.0-32 mg/l range**	(72)
Metal finishing waste	30-300 mg/l	(16)
Electroplating waste	5.0-58 mg/l	(14)

* Flow of 100 gpm

** Flow of 50 gpm

TABLE XVI-3

TOXIC CONCENTRATION OF NICKEL TO CERTAIN PLANTS

<u>Plants</u>	<u>Toxic Level</u>	<u>Reference</u>
Flax (water culture)	0.5 mg/l*	(66,6)
Horse beans and corn	any conc.	(66)
Citrus plants	unspecified	(66)
Sugar beets	injurious level	(66)
Tomatoes	15.9-29.4 mg/l**	
Potatoes		
Oats		
Kale		

* with molybdenum, symptoms were reduced

** grown in a nutrient solution sand culture

TABLE XVI-4

TOXIC CONCENTRATIONS OF NICKEL TO CERTAIN ANIMALS

<u>Animals</u>	<u>Conc.</u>	<u>Effect</u>	<u>Reference</u>
Biological Sludge	2.0 mg/l	toxic	(72)
Rats	5.0 mg/l*	increased mortality	(66)
Cats & dogs	(4-12 mg of Ni(Ac) ₂ or NiCl ₂ per kg of body weight) over 200 days	non toxic	(59)

* Nickel in drinking water with a selenium solution (11 mg/l conc.) - Synergism suggested.

Effect on Fish and Other Aquatic Life

One study reviewed by McKee and Wolf indicated that nickel may be more toxic to fish than iron or manganese. However, they also reported that fish were found living in waters polluted with mine effluent containing 13-18 mg/l of nickel. In general, McKee and Wolf report the nickel is less toxic to fish and river crabs than copper, zinc, brass, or iron.

McKee and Wolf reported that nickel readily combines with cyanide to form a nickel cyanide complex which is relatively stable. One Ni-CN complex with a concentration as high as 100 mg/l (as cyanide) was found to be not harmful to fish life if moderately alkaline conditions prevailed. A review of the data presented in the Water Quality Data Book, Volume 3 (42) indicates that nickel, as nickel chloride, is much more toxic to fish and aquatic life in soft water than it is in hard water: 4-5 mg/l nickel chloride is toxic in soft water while 24-42 mg/l is toxic in hard water.

With respect to marine plant life, a nickel concentration of 2.0 mg/l has been found to cause a 50% reduction of photosynthesis in kelp (15). On a similar note, McKee and Wolf report that a concentration of 2.5 mg/l of nickel oxide from nickel sulfate in a water culture has caused plants to wilt and die.

As noted in Table XVI-4, Nemerow (72) indicated that 2.0 mg/l of nickel is toxic to the sludge digestion process. McKee and Wolf report that a nickel concentration of 3.6 mg/l as nickel sulfate

has caused a 50% reduction in the oxygen utilization in synthetic sewage.

In summary, little is known about the toxicity of nickel to man. Nickel's toxicity to plant life has been noted as well as its effect on certain animals and wildlife. The presence of nickel, for example, may have a hindering effect on the growth of the liver but the actual toxic concentration has not been reported. Sticklebacks are known to have a lethal limit of 0.8 mg/l of nickel while other forms of fish and aquatic life appear to have greater resistance to nickel toxicity. In general, it has been found that nickel is more toxic to aquatic life in soft water than in hard water.

TREATMENT TECHNOLOGY - NICKEL REMOVAL

Process modification and good housekeeping to reduce accidental spills and to reduce dragout loss of nickel from plating bath solutions have been recommended by both Nemerow (72) and Patterson and Minear (76). After waste reduction and in plant process changes, an economical treatment system can be utilized for nickel destruction (i.e., precipitation and disposal) or recovery of higher concentrations of nickel, possibly followed by destruction of diluted wastes.

Destructive Treatment

Nickel forms an insoluble precipitate, nickel hydroxide, which is effectively removed at a pH of about 9.5 or above. Nickel hydroxide has a minimum theoretical solubility of 0.01 mg/l at a pH of 10. While the removal of nickel as nickel hydroxide is most effective at a high pH, little efficiency is gained above a pH of 10 (76).

Both Patterson and Minear (76) and Weston (97) report that the addition of lime is effective in raising the pH to the desired level for the precipitation of nickel hydroxide. They indicate that the nickel in most wastewaters can be effectively reduced to a final effluent of less than 1.0 mg/l.

A modification of the normal lime coagulation, precipitation, sedimentation process is the Lancy Process as reported by Lund (43). As mentioned in other reports on electroplating wastes, the Lancy system (integrated process) utilizes a chemical solution (lime) to rinse the dragout plating solution from the material. The chemical solution is allowed to precipitate the metals which are then recycled.

Recovery Processes

Patterson and Minear report that the processes currently used for the recovery of nickel are countercurrent rinsing, direct reuse, ion exchange, evaporative recovery, electrolytic recovery, and reverse osmosis. The more usually employed methods are countercurrent rinsing and direct reuse both of which reduce the total volume of the flow, concentrating the nickel within the waste thereby reducing the cost of nickel recovery. Patterson and Minear reported that nickel bearing wastes ranging in concentrations from 100-900 mg/l have an estimated recovery value of \$.80-\$7.00 per thousand gallons.

Patterson and Minear gave one example where the use of countercurrent flow with multiple rinse tanks allowed for direct reuse of the nickel plating solution dragout and resulted in a final nickel concentration of only 0.9 mg/l in the final rinse (76).

As reported by Patterson and Minear, the other most commonly utilized means of recovery which does not necessitate further treatment, is the use of ion exchange. Their data indicated that the additional cost of ion exchange was rapidly offset by the value of the nickel recovered. However, they did not discuss the treatment or further disposal of the regeneration waste from the ion exchange unit.

The remaining three recovery processes reported by Patterson and Minear, evaporative recovery, electrolytic recovery, and reverse osmosis, all necessitated further nickel removal from the diluted wastewaters following nickel recovery prior to disposal. In general, it would appear that these processes are feasible for recovering high concentrations of nickel. The wastewaters from these facilities with a residual nickel concentration of approximately 20-30 mg/l, can be treated by lime coagulation, precipitation, and sedimentation to a final effluent of less than 1.0 mg/l.

A summary of the various treatment processes and their efficiencies is given in Table XVI-5. The initial installation cost of various methods of treating nickel for either destruction or recovery are summarized in Table XVI-6 and the chemical and operating costs for the treatment units are given in Table XVI-7.

From the standpoint of treatment feasibility and economics, both recovery of concentrated nickel bearing wastes and destruction of lower concentrations of nickel bearing wastes are achievable. Selection of the most appropriate method of destruction and/or recovery naturally needs to be evaluated on an individual basis by

the industry. The value of recycled nickel, however, will be an incentive to reduce the volume of nickel bearing wastewater thereby facilitating nickel recovery and/or destruction.

TABLE XVI-5

REMOVAL EFFICIENCY OF NICKEL FROM INDUSTRIAL WASTEWATERS

<u>Process</u>	<u>Nickel Concentration, mg/l</u>		<u>Reference</u>
	<u>Initial</u>	<u>Final</u>	
<u>Lime coagulation</u>			
	100	1.5 @ ph = 9.9	(76)
with filtration	---	0.1 - 1.9	(97)
with filtration	21	0.09- 1.9	(76)
	35	0.4	(76)
w/Sepron NP-10	39	0.17	(76)
(Plating Waste)	15	0.5	(76)
Lancy Batch	Electroplating	3 - 4	(66)
Lancy Integrated	"	0.5	(66)
Lancy Integrated	"	Less than 1.0 max	(64)
<u>Ion Exchange</u>			
	870	Complete Removal	(76)
	60,000	Reclaimed	(76)
<u>Recovery & Destruction</u>			
Evaporative recovery	High		
Electrolytic recovery,			(76)
& Reverse Osmosis		20 - 30	
followed by Lime			
coagulation	20-30	1.0	

TABLE XVI-6

CAPITAL COST OF NICKEL DESTRUCTION OR RECOVERY UNITS

<u>Process</u>	<u>Flow</u>	<u>Capital Cost</u>	<u>Cost/ 1000 Gal.</u>	<u>Reference</u>
Lime Coagulation	0.45 MGD	187,000	\$1,108 (1966)	(76)
	1.0 MGD	300,000	300 (1971)	(97)
	10.0 MGD	1,300,000	130 (1971)	(97)
	50.0 MGD	4,600,000	92 (1971)	(97)
Evaporation	400 GPH	45,000		
Recovery	50 GPH	5,000- 6,000	6.42 - 7.71	
Reverse Osmosis	500 GPD	10,000-20,000		

TABLE XVI-7

CHEMICAL COST FOR NICKEL REMOVAL OR RECOVERY (76)

<u>Process</u>	<u>Initial Ni conc. (mg/l</u>	<u>Operation Cost</u>	<u>Recovery Value</u>
Lime Coagulation	35	80¢/1000 gal	@ 0.45 MGD
Recovery Value	150 - 900		\$0.80-7.00/1000 gal.
Ion Exchange		52¢/lb. nickel recovered	
Evaporation			
Recovery	--(400 GPH		\$100,000/yr.

SUMMARY AND RECOMMENDATIONS

On the basis of the literature reviewed and the above discussions, the following can be stated:

1. Nickel is found in natural soils at concentrations ranging from 5-100 mg/kg and in serpentine rock at concentrations of 400-5,000 mg/kg.
2. Nickel is present in several industrial wastes, predominately from metal finishing and plating industries.
3. Little is known of its toxicity to man and no limit has been set for nickel in the 1961 Drinking Water Standards. In general, the toxicity of nickel to man is believed to be very low.
4. Nickel is toxic to plants, and naimals. The lowest toxic level reported was (.5 mg/l (water culture) to flax.
5. Nickel may hinder the growth of the liver in animals; the concentration has not been reported in the literature reviewed.
6. Nickel complexes with cyanide, however, it is reported as not toxic to fish life at a concentration of 100 mg/l (as cyanide) in alkaline waters. The lowest toxic concentration to fish has been reported for the stickleback fish at 0.8 mg/l. The toxicity of nickel decreases by a factor of approximately 7-10 in soft water as compared to hard waters.
7. Nickel is economically recovered from concentrated waste streams, sometimes at a profit. Therefore, treatment cost of nickel may be substantially less than that for treating and removing other metals.
8. Nickel is removed from solution by precipitation with lime to a final effluent concentration of less than 1.0 mg/l.

While nickel is substantially less harmful to most forms of life than many of the other trace metals, it is toxic to plants and potentially toxic to animals and fish life. On the basis of the above review it is recommended that a uniform effluent concentration be set at 1.0 mg/l as nickel. Should future studies indicate nickel to be more toxic than is currently reported, it is recommended that the effluent level be adjusted.

CHAPTER XVII-OIL AND GREASE

Oil and grease covers a broad spectrum of substances. In this report we are speaking not only of lubricating oil, vegetable oils and grease but the large group known as hexane extractables.

There are many definitions of what constitutes oils and greases. Patterson and Minear (76) define oil and grease as that material extracted from wastewaters using hexane. Hexane solubles include such materials as waxes, fats, soaps, fatty acids, lubricants, cutting fluids and other light and heavy hydrocarbons. Other substances extracted in hexane include primary petrochemicals such as ethylene and propylene, and such intermediates as xylene, ammonia, methanol, ethanol, butanol, ethyl-benzene and some chlorinated hydrocarbons.

The American Petroleum Institute (API) classifies oil waste as follows: (1) light hydrocarbons including light fuels, (2) heavy hydrocarbons, crude oils and tars, (3) lubricants and cutting fluids, (4) fats and fatty oils originating from food processing (76).

The sources of oils and grease are primarily industrial and are listed in Table XVII-1. The volume of industrial discharges containing oil may vary from small trickles to millions of gallons per day discharged from steel mills, for example. Similarly, the concentrations may vary from minute traces up to 24,400 mg/l reported for seafood stick water.

The presence of oils and greases in water is of great aesthetic concern to man. Oils and their soluble products are also of concern because of their toxicity to fish and other aquatic life.

TABLE XVII-1

INDUSTRIAL WASTEWATER
OIL & GREASE SOURCES AND CONCENTRATIONS
PRIOR TO TREATMENT

<u>Source</u>	<u>Concentration, mg/l</u>		<u>Reference</u>
	<u>Total</u>	<u>Emulsified</u>	
<u>Oil Refinery:</u>	4-13	--	(44)
Refinery, Detergent Alkylate	73	--	(45)
<u>Petro Chemical:</u>	42-8,000	--	(44)
P.C. Sour Water	500	--	(44)
P.C. Mixed Chemicals	547	--	(45)
P.C. Phenols, Cresols	Trace	--	(45)
<u>Steel Mills:</u>	1276	--	(2)
Coolant Water	14,600	3,494	(2)
Cold Rolling	700	200	(76)
Hot Rolling		20	(76)
Cooling Waters		100-5,000	(76)
<u>Meat Packing:</u>	600-2000	(1200 typical)	(48)
Catch Basin effluent	420	--	(48)
Slaughter, cut, cook	2180	--	(48)
Bacon	370	--	(48)
Salami	320	--	(48)
Ham, Pork, Sausage	200	--	(48)
Beef, lard	2350	--	(48)
Vat Wash, etc.	240	--	(48)
Sausage grind & mix	330	--	(48)
Smoked meat	970	--	(48)
<u>Seafood:</u>			
Herring Pump Water	4,500	--	(87)
Stick Water	4,200-24,400	--	(87)
Sardine Rendering	5,700	--	(87)
Salmon Cannery	250	--	(87)
Tuna Processing	287	--	(87)

ENVIRONMENTAL EFFECTS OF OIL AND GREASE

Effects on Man

The basic objection to the presence of oily material centers around one of aesthetics and safety. As noted in McKee and Wolf (66), the immediate impact of oil is: "a) spoiling of beaches, and coastal resorts; b) destruction and injury of seabirds; c) the fouling of boats, fishing gear and quays; d) the risk of fire in harbors and other enclosed areas; and e) damage to marine flora and fauna". Recently, incidents have been reported of oil spills causing not only aesthetic damage but damage to fish and other aquatic life, plus potential damage to the entire area if oil-covered waters become ignited. Some specific problems caused by oil and grease are turbidity, films, iridescence, and increased difficulty in the treatment for potable water. With respect to toxicity, McKee and Wolf reported, "It appears, therefore, that hazards to human health will not arise from drinking oil polluted waters for they will become aesthetically objectionable at concentrations far below the chronic toxicity level."

Effects on Industrial Water Supply

Oil in industrial water supplies becomes important from two aspects. First, serious damage has been reported when boiler feed water contains only a few parts per million of oil. Oil deposits within the boiler tube surfaces may prevent proper heat transfer, and cause overheating and failure of the metal. Second, the taste and odor from oily materials within the water supply have a noxious

effect on products which are prepared for human consumption. Oil in the water used for the manufacture of paper and cement has also been reported to detract from the quality of the product.

Effects on Animal and Birds

Effects on animals and livestock are both scant and inconclusive. However, consumption of oily water may produce some laxative effect (66). Anyone who has ever had any association with an oil spill, will be well aware of the detrimental effects of oil on birds. There are many well documented attempts to save birds from the pitfalls of oil spills. Once a bird comes into physical contact with oil, the oil penetrates the bird's plumage, resulting in the bird losing its natural insulation to cold and, for those birds which normally fly, its ability to take flight. Even with the desperate attempts of many volunteers to save water fowl, the rate of survival is extremely low.

Effects on Plants

McKee and Wolf report that aromatic solvents, of petroleum origin at concentrations up to 300 mg/l have been used to control weeds along irrigation ditches with no detrimental effect on crops subsequently irrigated from the ditches. However, they also report that oil pollution may be partially responsible for the loss of large areas of eel grass along the American and European coasts. They concluded, "Where large areas of eel grass have disappeared there has been a great decrease in mollusks and crustaceans, wild fowl have moved elsewhere, and coastline erosion has often followed."

Effects on Fish

The discharge of oily wastes to receiving waters has its major impact through its effect upon fish life. McKee and Wolf report that free oils or emulsion have been found to adhere to the gills of fish reducing oxygen transfer (See Table XVII-2.) They also note the coating of algae and plankton with oily waste which removes them from the food web. Settled deposits may coat the bottom destroying the benthic organisms and interfering with spawning. Oxygen transfer at the air-water interface is hindered and photosynthesis may be affected by a surface coating of oil. Lastly, McKee and Wolf report a toxic effect of oils directly on fresh water fish at concentrations as low as 0.3 mg/l (6). Toxic reactions to petrochemicals are reported at concentrations from 12-97 mg/l.

To repeat, discharge of oily wastes has been shown to be of significance in the production of tastes and odors in drinking water. It has also been shown of even greater significance to the fish and aquatic life, through direct toxicity, reduction of oxygen transfer, reduction of photosynthesis, and deleterious affect on the food chain balances.

Oils and greases are also a matter of aesthetic concern, accounting for the destruction of beaches and tidal areas. Oils foul boats and fishing gear and cause fire damage and property losses.

TABLE XVII-2
EFFECTS OF OIL AND GREASE

<u>Waste Source</u>	<u>Receptor Affected</u>	<u>Effect</u>	<u>Conc. (mg/l)</u>	<u>Reference</u>
Petroleum	Man	Taste	1.0 - 2.0	(66)
Raw Petroleum	Man	Odor	0.1 - 0.5	(66)
Mineral Oil	Man	Taste	2.5	(66)
Mineral Oil	Man	Odor	5.0	(66)
Gasoline	Man	Taste	0.005	(66)
Gasoline	Man	Odor	0.010	(66)
Aromatic Solvents	Grasses	Weed Control	300	(66)
Crude Oil	Fish	Toxic	0.3	(6)
Petrochemicals	Man	Toxic	12.97	(44,45)

TREATMENT TECHNOLOGY - OIL AND GREASE REMOVAL

A review of current literature on the removal of oils and grease, from various industrial waste sources, indicates the use of several levels of treatment. Primary treatment, consisting basically of gravity separation with skimming, is normally capable of achieving effluent levels of 10-250 mg/l of oils. Secondary treatment, consisting of chemical and physical separation, is capable of achieving effluent levels of 5-150 mg/l. Biological treatment is capable of producing a final effluent level of less than 2 mg/l, provided the waste has been pre-treated by either physical or chemical-physical means and depending upon the characteristics of the oil or grease.

The primary treatment of oil wastes takes advantage of the difference in specific gravity between oils and greases and that of water. The basic principle involves gravity separation in a container of sufficient size to allow the free oils and greases to rise to the surface where they are skimmed off. Three factors which determine the efficiency of gravity separation are: (1) the rate of rise of the oil and grease, (2) the type and concentration of emulsion and (3) the hydraulic loading of the separator. Patterson and Minear (76) reviewed the work of Wallace et.al. who indicated that from 60-70% of the free oil and grease may be removed in a 30-40 minute time span. From this work, it appears that the maximum efficiency by gravity separation would be approximately 75% removal, over a two hour or longer detention time. A 1967 report on the Cost of Clean Water for the Petroleum Industry (7) indicates that the American Petroleum Institute (API) separator is capable of removing from

60-99% of the free floating oil, but it is not applicable to emulsified oil removal.

Similarly, the work of Gloyna and Ford (44,45) reported the efficiency of four common methods for physical removal of oily wastes from the petrochemical industry. These are summarized in Table XVII-3.

While the gravity separation of oils and grease is directed only at the free floating portion, chemical and physical separation is directed at total removal. Oily emulsions may be broken by chemical, physical, or a combination of chemical and physical means. According to Patterson and Minear, chemical methods are most extensively used in the treatment of oily wastewaters. The Cost of Clean Water report (7) noted that chemical and physical treatment of API separator effluent can remove from 60-95% of the floating oil, and from 10-90% of the emulsified oil. It was reported (7) that chemical coagulation and sedimentation are capable of removing 60-95% of the floating oil and 50-90% of the emulsified oil.

In treating combined wastewater consisting of once through cooling water and concentrated coolant waste at a 12:1 ratio, ARMCO (2) found the oil removals listed below using 195 mg/l of alum, 43 mg/l of lime, 32 mg/l clay, and 1 mg/l of a cationic polymer.

TABLE XVII-3

REMOVAL OF OIL FROM PETROCHEMICAL WASTE
BY GRAVITY SEPARATION (44,45)

<u>Process</u>	<u>Oil Concentration, mg/l</u>	
	<u>Influent</u>	<u>Effluent</u>
Circular Clarifiers	7,000-8,000	125
	108	20
	108	50
Impounding	3,200	10-50
Parallel	200-400	10-40
API Separator	220	49
	90-98	40-44
	50-100	20-40
	42	20

<u>Parameter</u>	<u>SRWL*(mg/l)</u>	<u>Effluent</u>	<u>% Removal</u>
Total Oil	1276	76	91
BOD ₅	893	57	93
COD	6320	441	89
Suspended Solids	770	55	93

The report concluded that pH values must be maintained above 6.0 for efficient treatment, and that flow equalization is an absolute must.

Emulsion breaking of fish oils with clay, lime, alum, and ferric chloride has been reported by Soderquist, et.al.(87) to be 75% effective in the removal of BOD. This reference also indicated that chlorination was required prior to sedimentation of the emulsion to control a rather pungent odor condition.

In treating concentrated coolant waste ARMCO (2) reported that cationic polymers were found to be effective in breaking oil emulsions at total oil concentrations of 14,600 mg/l, and emulsified oil of 3,494 mg/l. Emulsions were, however, found to be very sensitive to dosage and temperature. The optimum temperature was found to be between 100 and 150°F. Batch treatment of the concentrated coolant water reduced the total oil level to 730 mg/l, and the emulsified oil concentration to 175 mg/l.

Acidification of oily waste has also been found to be beneficial in breaking oil emulsions. Soderquist, et.al. reported that the acidification of oil fish waste followed by flotation was capable of reducing the fish oil from over 24,000 mg/l to an effluent

* SRWL = Standard Raw Waste Load

concentration of 80 mg/l total.

Other treatment efficiencies reported in the literature for the removal of emulsified and total oil from various effluents are given in Table XVII-4.

TABLE XVII-4
REMOVAL BY CHEMICAL COAGULATION

<u>Chemical</u>	<u>Waste Source</u>	<u>Influent mg/l</u>	<u>Effluent mg/l</u>	<u>Reference</u>
Alum, lime, clay, polymer	Steel mill coolant	1276	76	(2)
Alum, lime, ferric chloride	Fish oils		(75% BOD Removed)	(87)
Lime, alum	Oil refinery		(95% BOD Removed)	(76)
Soda ash, lime polymer	Ball & Roller Bearing Plant	302	28	
Alum, Air flotation	Meat packing	1944	142	(76)

As reported in Patterson and Minear, coagulation with iron salts has been generally effective for de-emulsifying oil waste. However, breaking of emulsions by acidification has generally been found to be more effective since a massive hydroxide sludge will not be formed. In addition, emulsion breaking by the addition of alum and iron salts also adds large quantities of inorganic salts to the effluent, which may create an additional pollution problem by increasing total dissolved solids.

The physical emulsion breaking methods commonly used include heating, centrifugation, filtration, and air flotation. Patterson and Minear report that centrifugation is normally most efficient when applied to oily sludges, rather than to typical dilute oil wastewaters.

Filtration has been found to be effective in treating steel mill waste containing up to 230 mg/l of emulsified oil (76). The removal efficiency of high rate filtration and diatomaceous earth filtration is summarized along with the capital operating cost in Table XVII-5 as reported in Patterson and Minear (76).

The third type of oil and grease removal is the combination of chemical coagulation and/or acidification with air flotation. In a review of Patterson and Minear's work, it is readily apparent that flotation has been used predominately as a method of removing emulsified oils from petroleum and petrochemical industrial wastewaters. The report on the Cost of Clean Water for the petrochemical industry (7) has indicated that air flotation, both with and without chemicals, is a standard procedure for manu refinery and petrochemical industries. Air flotation without chemicals effectively removes 70-95% of the floating oil and 10-40% of the emulsified oil. Flotation with chemicals yields efficiencies of 75-95% and 50-90% for floating and emulsified oils, respectively. In summary of the works reported by Patterson and Minear, Table XVII-6 indicates the improved efficiency of flotation with coagulants, over flotation without them.

While not as widely used as gravity separation and chemical-physical means, biological treatment is also applicable to the removal

of oil and grease from wastewaters. Patterson and Minear report that oil and grease laden waters from food processing plants have been treated biologically. Further works reviewed by Patterson and Minear indicated that an anaerobic lagoon achieved an 84% removal of grease during one 4 day sampling period. The grease in the raw waste ranged from 425-1,270 mg/l while an effluent grease concentration was reported at 69-147 mg/l. Another article also reviewed by Patterson and Minear indicated an 99% reduction of oil from a refinery waste oxidation pond which had initial and final oil concentration of 154 and 18 mg/l respectively.

In a report of the treatment of oily materials by activated sludge, Hydro-science (51) concluded that a system continuously exposed to oily wastes is capable of handling a load of 0.1 lb of hexane extractables per pound of mixed liquor suspended solids (MLSS). This corresponds to an oil concentration of 50 mg/l for MLSS of 2,000 mg/l and 75 mg/l for the MLSS of 3,000 mg/l, etc. Barnhart (of Hydro-science) (13) stated that a well operated activated sludge system is capable of reducing oil and grease from 50-75 mg/l to a 1-2 mg/l effluent. He stressed that good operation and uniform sludge wasting was essential. Filtration of the effluent may be needed to maintain the 1-2 mg/l oil level due to sludge carry over.

Gloyna and Ford (44,45) remarked on the ability of activated sludge to maintain low oil levels in the treatment of petrochemical waste. An activated sludge treatment of refinery, natural gas, liquids, chemical specialties, and sanitary sewage had an effluent oil concentration of 0.5 mg/l. In the treatment of refining process

TABLE XVII-5

FILTRATION OF EMULSIFIED OILY WASTE (76)

<u>Treatment</u>	<u>Effluent^a Oil, mg/l</u>	<u>Capital Cost, \$</u>	<u>Operating Cost, \$/Day</u>
HRF ^b	20	750,000	300
Coagulant & HRF	10	775,000	372
HRF & DE ^c	5	1,000,000	440

^aRaw Waste: 230 mg/l Emulsified Oil @ 3,000 gpm

^bHRF: High rate sand and gravel filter

^cDE: Diatomaceous earth filtration of HRF effluent

TABLE XVII-6

PERCENT REMOVAL OF OIL & GREASE BY
COAGULATION AND AIR FLOTATION
FROM REFINERY WASTE (76)

<u>Floation Alone</u>	<u>Float.W/Coagulants</u>	<u>Dosage</u>
62%	94%	25 mg/l Alum
70%	95%	Polymers & Clay
79%	87%	25 mg/l Alum
70-80%	up to 90%	30-70 mg/l Alum

waste, they reported an oil removal of 75-85% efficiency, with the effluent containing only 1-2 mg/l of oil. Similarly, a final effluent concentration of 1 mg/l was reported in the activated sludge plant treating waste from methylene and acetylene production.

ARMCO (2) reported the cost of breaking the emulsified oils by batch treatment with a cationic polymer at \$2.24-\$7.70 per thousand gallons of waste depending upon the characteristic of the oil treated. They also reported that if the recovered oil was of fuel oil quality, the net cost of oil removal was only 4.8-8.5 cents per gallon of oil recovered. ARMCO also reported the cost of treating the combined once through cooling water with concentrated coolant oily waste. They found that for this combined waste the operation cost ranged from \$0.046-\$0.051 per thousand gallons of waste. The treatment included flocculation and air flotation. Although the recovered oil had no potential as fuel, it was utilized by local municipalities as road oil. Other cost data available in the literature are summarized in Table XVII-7 and XVII-8.

In summary, petroleum refinery wastes are likely to contain much more free oil than emulsified oil. Industrial waste sources such as steel mills, metal finishing, electroplating, food production, tanneries, textiles will contain more emulsified oils. As a result the large producers of refined oils and other petrochemicals are able to achieve a 1-2 mg/l total effluent oil concentration much more readily than are some of the smaller processes which have to handle emulsified oils. One should not infer, however, that low oil

TABLE XVII-7

CAPITAL COSTS FOR REFINERY OILY WASTE TREATMENT (7)

<u>Process</u>	<u>Flow, MGD</u>	<u>Capital Cost, \$</u>	<u>Cost \$/MGD</u>
API Separator	3.0	46,500	15,500
	7.5	105,000	14,000
	15.0	210,000	14,000
Air Flotation	3.0	111,500	37,167
	7.5	222,750	29,700
	15.0	371,250	24,750

ANNUAL MAINTENANCE AND OPERATING COSTS FOR REFINERY
OIL WASTE TREATMENT (7)

<u>Process</u>	<u>Flow, MGD</u>	<u>M & O Cost \$/Yr.</u>	<u>Cost \$/MGD</u>
API Separator	3.0	23,000	7,667
	7.5	36,000	4,800
	15.0	55,000	3,667
Air Flotation	3.0	37,000	12,333
	7.5	74,000	12,333
	15.0	117,750	7,850

TABLE XVII-7 (Con't)

CAPITAL COSTS FOR TREATMENT OF MEAT PROCESSING OILY
WASTES (8)

<u>Process</u>	<u>Flow, MGD</u>	<u>Capital Cost, \$</u>	<u>Cost, \$/MGD</u>
Gravity Separator	0.125	12,000	96,000
	0.54	35,000	64,815
	1.68	250,000	14,881
Air Flotation	0.125	*	
	0.54	60,000	111,111
	1.68	150,000	89,285

* Not Reported

ANNUAL MAINTENANCE AND OPERATING COSTS FOR TREATMENT
OF MEAT PROCESSING OILY WASTES (8)

<u>Process</u>	<u>Flow, MGD</u>	<u>M & O Costs, \$/Yr.</u>	<u>Cost \$/MGD</u>
Gravity Separator	0.125	1,000	8,000
	0.54	10,000	18,519
	1.68	18,000	10,714
Air Flotation	0.125	*	
	0.54	13,000	24,074
	1.68	30,000	11,905

* not reported.

TABLE XVII-8

OPERATING COSTS - WASTE TREATMENT PLANTS
FOR PETROLEUM AND PETROCHEMICAL FACILITIES (44,45)

<u>Industry</u>	<u>Type of Treatment</u>	<u>Daily Operating Costs</u>		<u>No. Plants Reporting</u>	<u>Solids Disposal</u>
		<u>\$/MG</u>	<u>\$/1,000 lb Pollutant</u>		
Refinery	Primary-includes oil separation, coagulation, flotation, and sedimentation	126-160	26-150 (COD)	4	Vacuum Filter Landfill Incineration
	Secondary				Landfill
	Activated Sludge	161	292 (COD)	1	
	Aerated Lagoon	22	9 (COD)	1	-
Chemical	Extended Aeration	28	14 (COD)	1	Holding Ponds
	Primary-all types including oil separation, coagulation, flotation				Landfill
	sedimentation, neutralization, and equalization				Incineration
		11-1,540	3-40 (S.S.)	11	Vacuum Filter Lagoons
	Secondary				
	Aerated Lagoon	31-1,160	6-477 (BOD)	4	Landfill
	Activated Sludge				
	Conventional	1,580	100 (BOD)	1	-
	Extended Aeration	221-276	7-734 (BOD)	5	Landfill, Lagoon
	Contact Stabilization	16-211	23-106 (BOD)	2	Landfill
	Trickling Filter	780-2,050	49-3,750 (BOD)	2	Lagooning
	Facultative Pond	163	39 (BOD)	1	Burning
	Combination				
	Trickling filter and activated sludge	334-378	28-245 (BOD)	2	Landfill

concentrations cannot be achieved in wastewaters containing a large percentage of emulsified oils. From the above data, it is apparent that even some of the worst emulsified oils may be broken down by acidification or coagulation followed by a physical treatment step which would lend them to further reduction by biological treatment.

SUMMARY AND RECOMMENDATIONS

The following conclusions are drawn on the basis of the literature reviewed:

1. Oil and grease are found naturally but only in very low concentrations, and only in marine waters. A large potential exists for adding oil and grease through discharges to surface waters from many industries, and the concentrations range from trace amounts up to 24,4000 mg/l.
2. Large concentrations of emulsified oils are found in steel mills, meatpacking, seafood handling, textile mills and tannery wastes.
3. The major hazard of oily wastes in the aquatic environment is to fish and other aquatic life. Concentrations of 0.4 ml/l (about 0.3 mg/l) of crude oil have been found to be toxic to some fresh water fish. Waters containing oil and/or grease become aesthetically objectionable to man long before they become health hazards. Minute concentrations of oil wastes may conglomerate or precipitate and form oily sludge on the bottoms of receiving waters and smother benthic life. At a later time the sludge may be released to the water environment.

4. Oils and grease may be removed progressively by gravity separation, chemical and physical means and biological treatment. The degree of treatment necessary to reach any given level will depend upon the degree of emulsification and the individual characteristics of the hexane soluble material.
5. Capital costs for oil removal appear to approximate the cost for unit processes of standard design, e.g. clarifiers, oxidation ponds, flocculators, etc. Chemical costs will vary with the waste characteristics.

On the basis of treatment technology it appears that oily waste can be removed to an average effluent concentration of 1-2 mg/l. Varying degrees of emulsification reduce the efficiency and the reliability of chemical and biological processes. It is therefore recommended that a maximum uniform effluent criterion of 10 mg/l be adopted for all wastewaters containing oil and grease.

CHAPTER XVIII-PHENOLS

As noted by Patterson and Minear (76), phenols includes a wide range of organic compounds. According to "Standard Methods", (1) phenolics include phenol, chlorophenols, both ortho-and-meta-substituted, and parasubstituted phenols, in which the substitution is a carboxyl, halogen, methoxy or sulfonic acid group. In terms of effluent quality, the term phenolics includes a general group of similar compounds which have been derived from or include "phenol", the monohydroxy derivative of benzene. Discussion of phenols in this report includes those phenolics which evidence characteristic properties of phenol when in solution. Phenol (known as carbolic acid) is somewhat soluble in water. Most other phenols are insoluble in water. Phenols are colorless, but are easily oxidized and can be colored by oxidation products.

The major industrial sources of phenolic waste are listed in Table XVIII-1, along with typical concentration values. It is evident from Table XVIII-1 that industrial effluent concentration of phenolics can vary from very low concentrations of 17 mg/l to extremely large concentrations of 12,000 mg/l

ENVIRONMENTAL EFFECTS OF PHENOL

Effect on Man

One of the major concerns to man from phenolics in the aquatic environment is the taste and odor problem found in drinking water. When phenolic compounds are present in chlorinated waters a strong medicinal odor is often present. This odor results from the formation of a series of chlorophenols. For example, phenol can combine with

chlorine to form 2 or 4 chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol. These compounds can cause taste and odor problems in drinking at trace concentration (less than 1 mg/l). It was shown by McKee and Wolf (66) that taste and odor threshold concentrations for non-chlorinated phenols can vary from 0.01-60 mg/l with the general threshold value of 1 mg/l, while chlorinated phenols have taste and odor threshold concentrations ranging from 0.002-1.0 mg/l with a general threshold level of 0.002 mg/l. See Table XVIII-2 for threshold value of the different chlorophenols.

Because of the above values, in 1962 USPHS established a drinking water standard of 0.001 mg/l based on taste and odor threshold levels rather than on toxicity. These low threshold concentrations make phenolic compounds undesirable by both domestic and industrial users of water, since the unpalatable taste is passed on to food and beverages.

Man has little to fear from toxicity related problems in drinking water due to the large amounts needed to produce harmful effects. McKee and Wolf (66) report that ingestion of concentrated solutions of phenol will result in severe pain, renal irritation, shock and possible death. A total dose of 1.5 grams is needed to be fatal. It is unlikely that this large quantity could be consumed in drinking water because such concentration are much higher than taste considerations will allow.

Table XVIII-3 lists the characteristics of phenolic waters. The BOD and COD data for many phenolics are presented along with the

TABLE XVIII-1

PHENOL CONCENTRATIONS REPORTED
IN
INDUSTRIAL WASTEWATERS

<u>Source</u>	<u>Concentration, mg/l</u>	<u>Reference</u>
<u>Coke Ovens</u>		
Weak ammonia liquor, without dephenolization	400-12,000	(48,71,76)
Weak ammonia liquor, with dephenolizer	4.5 - 332	(76)
Wash oil still wastes	30 - 150	(48)
Final cooler water	105	(71)
Pure still	72	(71)
Combined waste	6.4	(71)
<u>Oil Refineries</u>		
Sour water	65 - 185	(44,45,76)
General wastewaters	40 - 80	(76)
Detergent alkylate	160	(44,45)
Butadiene, Butyl rubber	17	(44,45)
Post - stripping	80	(76)
General (catalytic cracker)	40 - 50	(76)
Mineral Oil wastewater	100	(76)
Petroleum products	25	(44,45)
<u>Petrochemical</u>		
General petrochemicals	50 - 600	(76)
Mixed organics	10 - 50	(44,45)
Benzene refineries	210	(76)
Nitrogen works	250	(76)
Tar distilling plants	300	(76)

TABLE XVIII-1 (Con't)

PHENOL CONCENTRATIONS REPORTED
IN
INDUSTRIAL WASTEWATERS

<u>Source</u>	<u>Concentration, mg/l</u>	<u>Reference</u>
Synthetic resins, Phenol Formaldehyde, Fatty Acids Glycerol, Phtholic acids, Maleic acids, Pentacrythritol, H. C. solvents	4,500	(44,45)
Aircraft maintenance	200 - 400	(76)
<u>Other</u>		
Rubber reclamation	3 - 10	(76)
Orlon manufacture	100 - 150	(61,76)
Plastics factory	600 - 2,000	(76)
Fiberboard factory	150	(76)
Wood carbonizing	500	(76)
Phenolic resin production	1,600	(71,76)
Stocking factory	6,000	(76)
Nylon		(44,45)
Phenol, Cresols production	280 - 500	(44,45)

theoretical oxygen demand. Taste and odor and human toxicity data are presented where known.

Effect on Fish and Other Aquatic Life

McKee and Wolf report that fish are affected two ways: (1) by direct toxicity, and (2) by tainting of the fish flesh. They point out that there are many difficulties in determining the detrimental effects of phenolic compounds. "The reported lethal concentrations vary widely not only because of the common variables such as species, temperature, time of contact, dissolved oxygen and mineral quality of water but also because of synergistic and antagonistic effects of other substances in the water." It was also reported that a combination of phenolics in a waste is generally more toxic than pure phenol alone.

A review of the literature (15,45,59,66) on the toxicity of phenols indicates that each phenolic has its own lethal limit which has little relation to the time of exposure. There is a wide spectrum of toxic levels and considerable overlapping between the lethal or damaging concentration among species. McKee and Wolf report that the 24, 48, 96 hour TLm concentration for fish is in the range of 10-20 mg/l at 20°C. Generally speaking, the threshold level for fish however, is in the range of 1.0 mg/l. Selected phenolic TLm's are shown in Table XVIII-4.

In conclusion the toxicity of phenol and related compounds toward fish varies with respect to several important parameters. Toxicity increases when the D.O. or hardness of the water decreases, the temperature increases and when there is a combination of the preceding effects.

TABLE XVIII-2

TASTE AND ODOR THRESHOLD
CONCENTRATION AT 25°C (66)

<u>Compound</u>	<u>Geometric Mean Threshold mg/l</u>	
	<u>Taste</u>	<u>Odor</u>
Phenol	1.0	1.0
2-chlorophenol	0.004	0.002
4-chlorophenol	1.0	0.25
2,4-dichlorophenol	0.008	0.002
2,6-dichlorophenol	0.002	0.003
2,4,6-trichlorophenol	1.0	1.0

TABLE XVIII-3

CHARACTERISTICS OF PHENOLIC WASTES (61)

<u>PHENOLIC</u>	<u>BOD</u> <u>lb/lb</u>	<u>COD</u> <u>lb/lb</u>	<u>Theoretical</u> <u>O.D. lb/lb</u>	<u>T&O*</u> <u>mg/l</u>	<u>Toxic**</u> <u>mg/l</u>
Phenol	1.6		2.4	0.15	0.1 - 1.5
Acetophenone				0.17	
Catechol		1.89	1.89		
o-Cresol	1.6	2.4	2.52	0.65	0.5
m-Cresol	1.7	2.3	2.52	0.7	0.5
p-Cresol	1.45		2.52		0.5
p-Cumylphenol		2.6	2.8		
Dibutylphthalate	0.43		2.24		
Methylphenylketone	0.5		2.5		
Morpholine	Nil		2.6		
Naphthalene	0		3.0		
1, 4-Naphthaquinone	0.8		2.1		0.3
2-Naphthol	1.7		2.55		
B-Naphthol	1.8	2.5	2.55	1.3	
Pyridine		0.02	3.03	0.8	1,000
Quinoline				0.7	
Resorcinol	1.15		1.89		
2,4,6-Trinitrophenol		0.92	0.98		
Xylene	0		3.16	2.2	22
1,3,4-Xylenol	1.5		2.62		
1,3,5-Xylenol	0.82		2.62		

* Taste and odor threshold is tentative

* * Toxicity threshold based on fish, species not specified

TABLE XVIII-4
PHENOLIC TOXICITY BIOASSAY RESULTS (44,45)

Compound	TL _m (median Tolerance Limit)			Test Animal	Remarks
	24 Hr (mg/l)	48 Hr (mg/l)	96 Hr (mg/l)		
o-Chlorophenol	21.96	19.12	11.63	Fatheads	Soft Water
	21.52	18.00	14.48	Fatheads	Hard Water
	11.31	10.59	10.00	Bluegill	Soft Water
	14.48	12.37	12.37	Goldfish	Soft Water
	22.17	20.78	20.17	Guppies	Soft Water
o-Chlorophenol Cresol	8.2	8.1		Bluegill	
	24	24	24	Mosquito fish	Small (3.88 cm)
			13.6	Bluegill	Medium (6.09 cm)
o-Cresol			10.9	Bluegill	Large (14.24 cm)
			10.0	Bluegill	Soft Water
	Not found	Not found	12.55	Fatheads	Hard Water
	18.00	13.42	13.42	Fatheads	Soft Water
	22.17	20.78	20.78	Bluegill	Soft Water
o-Nitrophenol	Not found	Not found	23.25	Goldfish	Soft Water
	49.13	25.31	18.85	Guppies	Soft Water
	66.9	46.3		Bluegill	
Phenol	61	51.6			
	22.7	56			
		22.2	0.001	Arctopsycche grandis	
			56	Mosquito fish	
				Bluegill	
			13.5	Bluegill	Small (3.88 cm)
			20.0	Bluegill	Medium (6.09 cm)
			11.5	Bluegill	Large (14.24 cm)
		19	5.7	Bluegill	
Phenol (U.S.P. 100%)	19		34.27	Fatheads	Soft Water
	40.60	40.60	32.00	Fatheads	Hard Water
	38.62	38.62	23.88	Bluegill	Soft Water
	25.85	23.88	44.49	Goldfish	Soft Water
	49.86	49.13			

The second major effect of phenolic waste on fish and other aquatic life is tainting of the flesh. McKee and Wolf report that mixed phenolic substances are the most troublesome. The chlorophenols are known to produce bad taste in fish flesh at concentrations which are far below the lethal or toxic dosages. Mineral oils, carbolated oils, and other light oils which are usually part of the phenolic waste, reportedly have a great bearing on the tainting of fish flesh.

A report by Gloyna & Ford (45) indicates that phenols and other nonchlorinated phenolic compounds have been found to taint fish flesh at concentration of 1.0-10.0 mg/l. However, their report also indicates that chlorinated phenols may taint fish flesh at concentrations as low as 0.005 mg/l.

McKee and Wolf report that phenolic compounds are less toxic toward lower forms of aquatic life (fish food organisms) than they are towards fish. A review of their data indicates that a concentration of 1 mg/l has been found to limit photosynthesis in the Platymonas organism, and threshold effects on several other organisms including Daphnia have been observed at concentrations greater than 1 mg/l. Toxicity of some selected phenolics to Chlorella pyrenoidosa is shown in Table XVIII-5.

In summary McKee & Wolf indicated that the following concentrations of phenol would not interfere with the respective beneficial uses of water:

TABLE XVIII-5

TOXICITY OF SOME SELECTED PHENOLICS (44,45)
TO CHLORELLA PYRENOIDOSA

Organic Chemical	Toxic Conc. (mg/l)*	Ref. (as designated in the work of Gloyna & Ford)
Phenol	1,060	84
Phenol	233	50
Cresol	800	84
Cresol's (ortho,meta,para)	148-171	50
o-Bromophenol	78	50
m,p-Bromophenol	36	50
o-Chlorophenol	96	50
m,p-Chlorophenol	40	50
2,4-Dichlorophenol	21	50
2,4,5-Trichlorophenol	1.5	50
Pentachlorophenol	0.001	50
Xylenols	49-81	50
Nitrophenols	9-14	50
o-Aminophenol	47	50
m,p-Aminophenols	140	50
Hydroquinone	178	50

* Based on 50% Reduction in Chlorophyll Content

- (1) Domestic water supply - 0.001 mg/l
- (2) Irrigation - 50.0 mg/l
- (3) Stock watering - 1000.0 mg/l
- (4) Fish and aquatic life - 0.2 mg/l

TREATMENT TECHNOLOGY-PHENOL REMOVAL

A review of the current literature (45,48,71,76) indicates that methods are available for removing phenolic wastes from a wide range of concentrations to almost any level desirable. For some of the more difficult wastes, however, several steps of treatment may be necessary to reach a given level. The matter of practical economics, rather than technical capability, is the limiting factor and may have some bearing on the so-called currently achievable level. Patterson and Minear (76) indicate that the method of selection for phenolic removal and its efficiency may depend on the overall composition of the wastewater. They report that it is normally necessary to remove both oil and heavy metals prior to removal of phenolics from the wastewater. In general, however, currently available technology is being successfully utilized for efficient phenolic removal.

As shown in Table XVIII-1 the industrial waste loading of phenolics varies from low to extremely high concentrations. As a result, the treatment technology discussed below will be under the categories of recoverable phenolics, biological and other processes for intermediate phenolic removal, and polishing steps.

Recoverable Phenolics

Patterson & Minear report that high concentrations of phenol in a waste stream allow for economical recovery. The phenolic

recovery value reported by Patterson and Minear is 20¢/ton of coal process, for coke plant ammonia liquor, as of 1969. There are currently many methods available for the removal of up to 99% of the phenol from high concentration wastewaters. However, even at this high level of removal, a substantial amount of phenolic compounds remain in the effluent.

In discussing phenolic removal from phenol resins, Nemerow (71) stated that single stage phenol extraction will remove approximately 96% of the phenols and 100% of the formaldehyde present. Other methods discussed by Nemerow include lagooning and thermal incineration. No efficiencies were reported.

Gurnham's (48) review of phenolic waste treatments discussed the use of liquid extraction, vapor-phased dephenolization, and biological treatment. Countercurrent liquid-liquid extraction, on a coke plant's waste, was said to reduce the phenolic content of the crude ammonia liquor from 1500-2000 mg/l to a 10-30 mg/l level. Gurnham also reported that the use of two stage Podbielniak centrifugal extractors on ammonia liquor yielded an efficiency of 99% removal and that with vapor phased dephenolization processes followed by treatment with 10% caustic solution efficiencies of 95-98% removal were obtainable.

Table XVIII-6 gives a summary of currently available phenolic recovery processes from concentrated wastewaters. While the effluent data presented below represents well over 95% removal, in most cases the final effluent concentration still remains substantially high.

TABLE XVIII-6

PHENOLIC RECOVERY FROM
CONCENTRATED WASTES

<u>Process</u>	Phenol Concentration, mg/l		Percent*	
	Influent	Effluent	Removal	Ref.
Benzene-Caustic				
Dephenolization process	3,000	210-240	93	(76)
Counter-Current Podbielniak				
Extractors	2,000	100	95	(48,76)
Single-stage Phenolic				
Extraction	1,600	64	96	(71)
IFAWOL Dephenolization				
Process (Carl Still)	4,000	40	99	(76)
Pulsed Column				
Extractors	2,200	30	98.6	(71)
Steam Evaporation	1,500-2,000*	30-100*	98.5	(48)
Liquid-Liquid Extractors	1,500-2,000*	10- 30*	98.5	(48)
Caustic Recovery	1,500-2,000*	30-100*	99.5	(76)
Keppers Light Oil Extraction	1,500-2,000*	10- 30*		

* Influent load assumed from Table XVIII-1 and Effluent based on referenced percent removal.

Gloyna and Ford (45) have reported that phenols may be removed by solvent extraction with the efficiency depending on the solvent used as shown in Table XVIII-7.

Biological and Other Processes for Intermediate Level Treatment

From an economic standpoint it is expensive to recover phenolics from industrial wastes which contain phenolics in concentrations of less than 500 mg/l. As a result, biological processes including lagoons, oxidation ditches, trickling filters, and activated sludge have been reported for this level of treatment (48,76).

In Gurnham's (48) discussion of phenolic treatment, he reports that activated sludge and trickling filters individually have reduced phenolic waste from 800 mg/l to effluents containing 1 mg/l or less. Certain precautions are recommended for satisfactory operation, such as a wastewater feed of nearly constant composition, a temperature above 70; a pH near neutrality, a storage capacity of 5 or more days, the addition of nutrient phosphorus, and the absence of tars and oils. On a similar note, Patterson and Minear have indicated that the success of biological treatment of phenolic wastes depends on the toxicity of other contaminants in the water to micro-organisms used in the biological process.

While it has been reported that biological processes are amenable to phenolic wastes at concentrations of 5-500 mg/l, Table XVIII-8 from the works of Patterson and Minear indicates that biological processes have been used successfully for concentrations up to twice this value in full scale plants, and up to the 4000 mg/l range on a

TABLE XVIII-7
SOLVENTS USED TO EXTRACT PHENOLS FROM WASTEWATER (45)

<u>Solvent</u>	Phenol Influent (mg/l)	Phenol Effluent (mg/l)	Phenol Removal (%)	<u>Remarks</u>
Aromatics, 75% Paraffins, 25%	200	0.2	99.9%	Solvent Regenerated with Caustic-Lab Study
Aliphatic Esters	4,000	60	98.5	Regenerated by Distillation
Benzene			90-95	Solvent Regenerated by Distillation
Benzene	750	34	95.5	Caustic Regeneration
<u>Light Cycle Oil</u>	300	30	90	Electrostatic Extraction Also Removes Oil from Water At Same Time
<u>Light Oil</u>	3,000	35	98.2-99.5	Centrifugal Extraction, Caustic Regeneration
<u>Straw Oil Distillates</u>			95	Centrifugal Extraction,
Tricresyl Phosphates	3,000	300-150	90-95	Steam or Caustic Regeneration, Very High Extraction Coefficient

TABLE XVIII-8

PERFORMANCE OF BIOLOGICAL SYSTEMS IN THE TREATMENT OF PHENOLIC WASTES (76)

Treatment Process	Source of Industrial Waste	Phenol, mg/l	
		Influent	Effluent
Oxidation Ditch Trickling Filter	Coke oven	990 ave.)	8-5 (ave.)
	Oil refinery	30-40	0.5-0.7
	Oil refinery	9-25	0.6-3.8
	Sourwater and plant sewage	15 (ave.)	1.8 (ave.)
	Aircraft maintenance wastes	8	0.02
Activated Sludge	Coke oven	400-700	10 (app.)
	Coke oven	6.5	0.008
	Coke	9-10	0.9
	Coke oven	890	0.65
	Coke ovens	110-200	0-11
	Coke oven with dephenolization	135	7
	Coke oven without dephenolization	1,400	15

TABLE XVIII-8 (cont.)
PERFORMANCE OF BIOLOGICAL SYSTEMS IN THE TREATMENT OF PHENOLIC WASTES (76)

Treatment Process	Source of Industrial Waste	Phenol, mg/l	
		Influent	Effluent
Activated Sludge	Oil refinery	80	0.5
	Gas liquor	1,200	12
	Gas liquor	200	0.2
	Stocking manufacture	183-455	0.2-1.3
	Oil refinery	40-80	1.0
Activated Sludge plus Dow-Pac Filter	Oil refinery	40-80	0.35
Activated Sludge*	Coke oven	3,350-3,900	0.2-0.8
Aero Accelerator (Activated Sludge)	Coke oven	150	1.0
Nocardia Process	Foundry wastes	3,000	30-150
	Explosives	10,000	24

* Pilot plant - full scale plant in operation with lower loadings consistently produces - 0.1 mg or 99.9% removal, Activated sludge with specially adapted organism culture for phenol removal.

pilot plant scale. The effectiveness of biological treatment on phenolic bearing petroleum wastewaters is summarized in Table XVIII-9.

Other methods which have been utilized for moderate level phenolic waste streams include chemical coagulation, chemical oxidation, and gas stripping followed by incineration. In Patterson & Minear's review on phenolic treatment, it was indicated that coagulation with alum and iron salts has been utilized. It was also found that 10-20 percent of the phenolics starting at an initial concentration of 100-125 mg/l, were removed. One piece of literature reviewed by Patterson and Minear, however, suggested that chlorination plus coagulation with lime would result in almost 100% removal of phenolics, at a cost of \$1.25-\$1.50 per thousand gallons of waste treated.

In Nemerow's (71) discussion of phenolic removal from rubber waste, he stated that chlorination is very effective if sufficient time is given for the reaction. Similarly, Patterson and Minear have reported that extremely high concentrations of chlorine must be added to effect complete removal of phenolics. In addition, it was found that this must be done at a pH of 7 or less, to prevent the formation of toxic chlorophenols.

Patterson & Minear reported on the use of ozone and chlorine dioxide for successful oxidation of phenol. Although ozone was reported as being an efficient treatment process, operating and capital costs are extremely high. It was reported that 1.5-2.5 parts of ozone are required per part of phenol for effective removal, but effluents of down to 0.003 mg/l were obtainable.

Patterson & Minear also reported on the use of hydrocarbon stripping, followed by incineration for the removal of phenol. The cost of this operation will be discussed later in this section.

Polishing Steps in Phenolic Removal

As shown above, biological treatment is generally capable of reducing phenol concentrations down to 1-2 mg/l, or less. While not reported in any of the recent text reviewed for phenolic waste treatment, Patterson and Minear report that Phenol removal is currently achievable to below the 0.1-1.0 mg/l level.

The ozone treatment previously disregarded for higher levels of phenolic waste is much more effective and economical as a polisher process. Another process utilized in polishing is activated carbon. The work of McPhee and Smith, as discussed by Patterson and Minear, indicates that a good grade of activated carbon should have the capacity of removing 0.09 mg phenol for every 20 mg of activated carbon. By utilizing activated carbon, phenolic waste concentrations of 0.020 mg/l can be reduced to a final effluent level of 0.005 mg/l.

On the basis of the above treatment processes, from the recoverable range of phenolic waste, to the intermediate range, to the polishing process, it becomes apparent that a phenolic effluent anywhere from 100 mg/l down to 0.005 mg/l is currently, technically obtainable.

COST OF PHENOLIC TREATMENT

As reported in Patterson & Minear the cost associated with the treatment of phenolic waste appears to be well within the range of equivalent cost for water and wastewater treatment processes. Table XVIII-10 has been prepared from the various data reviewed by Patterson

TABLE XVIII-9

SUMMARY OF BIOLOGICAL TREATMENT
OF PHENOLIC - PETROCHEMICAL
WASTE (44)

<u>Product and/or</u> <u>Process</u>	<u>FLOW</u> <u>MGD</u>	<u>Phenol Conc, mg/l</u>		<u>Treatment</u>
		<u>INF.</u>	<u>EFF.</u>	
Refinery, Natural Gas Liquids, Chemical Specialities, Domestic wst.	4.87		0.05	Activated Sludge
Sour Waters	0.43	65	0.065	TF & AS
Refining Process 83	0.51	33	0.5	Activated Sludge
Petroleum Products	0.27	25	1	A,S.
Synthetic Resins Phenol, Formaldehyde, Organic Acids, H. C. Solvents		4,500	1.5	Two Stage Trickling Filter

and Minear. As noted in Table XVIII-10 the costs for the individual treatment processes and their respective flows have been compared to what has been termed by Weston (97) a typical secondary treatment facility. While the costs for some of the recovery processes appear to be high, one must remember the value of recovered phenol.

As summarized in Table XVIII-11 the recovery value of phenols by the Barrett recovery process has been reported to be in the range of \$400,000 per thousand gallons (76). Patterson and Minear further state that "capital costs decrease from lower removals. Assuming an inflow of 5,000 mg/l and allowing an effluent concentration of 50 mg/l lowers the capital cost of \$150,000 for a 1 MGD plant and \$70,000 for a 0.01 MGD plant. Increasing effluent phenols concentration to 500 mg/l (90% removal) reduces the 0.01 MGD cost to \$60,000. Reduced recovery value is associated with decreased recovery." Phenol recovery from this process offsets any operating costs. A quick estimate of multiple treatment facilities including a recovery step followed by activated sludge, and possibly even a polishing step, would indicate that the total operating costs could be very close to zero. The total capital costs appear well within the realm of the equivalent secondary treatment facility.

Operational costs from the works of Patterson & Minear have also been summarized and shown in Table XVIII-12. These data indicate that the typical operating costs, with the exception of the two chlorination steps, are well below the equivalent costs of removing trace metals.

In conclusion, it is apparent that the technology currently exists to remove phenols to very low residual levels at costs which

TABLE XVIII-10
CAPITAL COSTS FOR PHENOL REMOVAL (76)

<u>Process</u>	<u>Flow, MGD</u>	<u>Cost, \$</u>	<u>Cost \$/1000 Gal.</u>
Incineration		\$10 - 15,000	
Extraction	0.15	500,000	3,340,000
Light Oil Extraction and Electrostatic Field		200,000	
Podbielniak	0.2	500,000	1,000,000
Extractor		600,000	1,200,000
Barrett Recovery	0.01	90,000	9,000,000
Process	0.10	200,000	2,000,000
(5,000 mg/l in	0.17	260,000	1,530,000
5 mg/l out)	0.50	670,000	1,340,000
Activated Sludge	0.11	310,000 (1962)	2,820,000
"	1.92	800,000 (1965)	415,000
Airflotation	6.5	1,000,000	15,400
Holding Basin and Trickling Filter Gas stripped	0.18	25,000	13,900
and combustion	1.1	81,000	7,360
Activated Carbon	1.0	352	352
"	10.0	1,355	135
"	100.0	6,210	62
Typical Secondary Treatment			
By Weston (97)	1.0	1,200,000	1,200,000
	10	4,800,000	480,000
	50	11,000,000	220,000

TABLE XVIII-11
PHENOL RECOVERY BY BARRETT RECOVERY PROCESS (76)

<u>Flow, MGD</u>	<u>Recovery Value</u>	<u>\$/1000 Gal.</u>
0.01	5,500	550,000
0.1	40,000	400,000
0.17	70,000	410,000
0.50	200,000	400,000

TABLE XVIII-12
OPERATIONAL COST OF PHENOLICS REMOVAL (76)

<u>Concentration, mg/l</u>	<u>Final</u>	<u>\$1/000 Gal.</u>	<u>Process</u>
<u>Initial</u>			
7,000		0.015	Incineration
80	0.5	0.22	Activated Sludge
125	34.5	1.83	Permanganate Oxidation
125	0.0	1.25 - 1.50	Lime coagulation & chlorination
5	0.00	1.00 - 1.66	Chlorination
5.6	1.0	00.07 - 0.093	Gas Stripped & Combustion
0.16 - 0.35	0.003	00.0028	Ozone @1000 mg/l
Municipal	0.005	0.153 for 1 MGD Plant	Activated
Secondary	Range	0.068 for 10 "	Carbon
Effluent		0.035 for 100 "	"

are comparable to those of equivalent secondary treatment facilities. It is of particular significance that a two stage process, consisting of a recovery step for initial phenol reduction followed by a biological system, should be capable of achieving a final effluent concentration of less than 1 mg/l. It is also apparent that where needed, technology exists to reduce phenol levels even lower.

SUMMARY AND RECOMMENDATIONS

On the basis of the above, the following conclusions have been drawn:

1. Phenolics include a broad group of organic compounds and are prevalent in many industrial discharges. Industrial waste phenolic sources range in concentration from a few mg/l to 12,000 mg/l.
2. Phenolic compounds are responsible for taste and odor problems and tainting of fish flesh. They can also be toxic to certain fish at low concentrations.
3. A stream criterion of 0.001 mg/l is based upon the threshold odor concentration in domestic water supplies for chlorinated phenolics. A stream criterion of 0.2 mg/l is needed to protect fish life.
4. Current technology is capable of removing phenolics from industrial and municipal discharges to a level of 1 mg/l or less by biological treatment or a combination of recovery steps followed by biological treatment. Polishing steps on biological treatment effluent are capable of producing a final effluent with a phenolic concentration of 0.003-0.005 mg/l.

On the basis of the above statements, it is recommended that a uniform effluent criterion of 1.0 mg/l be adopted for all phenolic waste discharges. This recommendation recognizes that data provided within this report indicates that some biological treatment plants are not currently meeting this condition. However, as has been discussed and documented above, biological treatment processes are capable of reaching much lower levels. It is also recognized that the recommended discharge criterion of 1.0 mg/l could cause some taste and odor problems if a discharge is located immediately (within a 1000: 1 dilution zone) above a domestic water supply intake.

It is further recommended that, where the local situation indicates that the stream water quality criterion of 0.001 mg/l phenolics would be violated by a current industrial or municipal discharge, an effluent level of 0.010 mg/l be adopted. In addition, an average operating condition for a typical process day should be in the range 0.003-0.005 mg/l on the basis of current technology.

It is further recommended that any new industrial discharge, on the basis of current technology alone, should meet an effluent criterion of 0.010 mg/l.



CHAPTER XIX-PHOSPHORUS

Due to the present interest in phosphate as a possible limiting nutrient in algal blooms and concomitant eutrophication problems, sources of phosphorus have been well delineated in the literature. Elemental phosphorus does not occur in nature, but rather is found as phosphates in several minerals and as the soluble, inorganic anion in water. Because of its important role in energy transfer in biochemical cycles, it is also found in a wide variety of organic compounds.

McKee and Wolf (66) state "...it is a constituent of fertile soils, plants, and the protoplasm, nervous tissue and bones of animal life. It is an essential nutrient for plant and animal growth, and like nitrogen, it passes through cycles of decomposition and photosynthesis. It combines directly with oxygen, sulfur, hydrogen, the halides, and many metals."

Naturally occurring inorganic forms of phosphorus are listed in Table XIX-1. Phosphate minerals are formed by the precipitation of ions from super-saturated solution or, in the case of carbonate-apatite, by the active replacement of carbonate with phosphate in previously formed minerals. These minerals represent the natural reservoir of phosphate in the environment.

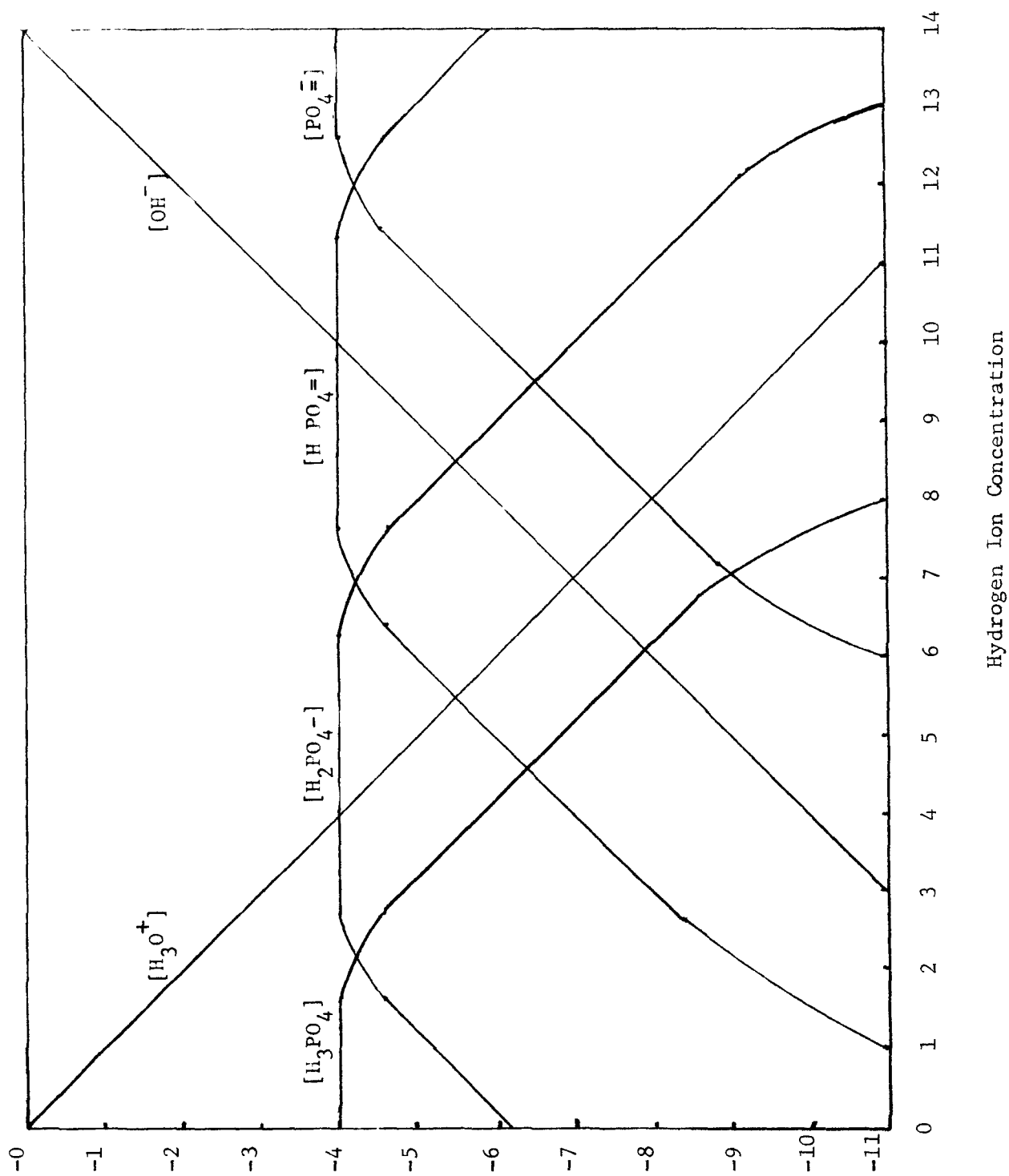
The form of phosphate in solution is controlled by the pH. The log concentration of phosphate versus pH is shown in Figure XIX-i. It can be readily seen that at normal pH levels (6-8) the greatest percentage of the phosphate will be present as H_2PO_4^- or

$\text{HPO}_4^{=}$. This relationship is controlling regardless of the form in which the phosphate is introduced, except for the tripoly and pyrophosphates. In these cases, the kinetics of conversion to orthophosphate are low enough to permit residual concentrations of the compounds. It is the fully dissociated PO_4^{\equiv} form which

TABLE XIX-1

NATURALLY OCCURRING INORGANIC FORMS OF PHOSPHORUS (66,73)

<u>Mineral Forms</u>	<u>Chem-Formula</u>
Fluor-Apatite (Apatite)	$\text{Ca}_5 (\text{PO}_4)_3 \text{F}$
Chlor Apatite	$\text{Ca}_4 (\text{PO}_4)_3 \text{Cl}$
Hydroxy Apatite	$\text{Ca}_5 (\text{PO}_4)_3 \text{OH}$
Carbonate-Apatite (Francoilite)	$\text{Ca}_5 (\text{PO}_4, \text{CO}_3, \text{OH})_3 \text{F}$
 <u>Anion Forms</u>	
Monbasic Phosphate	H_2PO_4^-
Dibasic "	$\text{H PO}_4^{=}$
Tribasic "	PO_4^{\equiv}
Pyrophosphate	P_2O_7
Hexametaphosphate	$(\text{PO}_3)_6$
Tripolyphosphate	P_3O_{10}



LOG CONCENTRATION DIAGRAM DESCRIBING PHOSPHATE EQUILIBRIA

FIGURE XIX - i



is reported to be the most readily available for biological utilization (72,73).

Phosphorus is found in untreated domestic wastewaters at concentrations ranging from 5 to 40 mg/l with typical wastes averaging about 10 mg/l (as P) (19,67). Typical secondary treated municipal effluents contain from 1 to 12 mg/l (as P) (19,26,67). Phosphorus removal in secondary plants depends upon the type of treatment.

Industrial sources of phosphorus are listed in Table XIX-2. Other sources of phosphorus in surface waters include agricultural runoff from feed lots, fertilized acreage and natural organic decayed matter found in general erosion materials.

ENVIRONMENTAL EFFECTS OF PHOSPHORUS

Effects on Man

For many years polyphosphates have been used in low concentrations in boiler waters to reduce corrosion and control scale. At these low concentrations phosphorus is not known to have any physiological significance. Phosphorus compounds are, however, undesirable in high concentrations (450 mg/l) in water used to prepare foods. They have a buffering action on the stomach acids (6). Hexameta-phosphates are converted to phosphoric acid in the low pH environment of the stomach (see Figure XIX-1). High concentrations can cause both vomiting and diarrhea. The safe oral dose is recommended not to exceed 50 mg/l. Other detrimental effects of phosphorus include interference with coagulation and flocculation. As noted in

TABLE XIX-2

SOURCES OF PHOSPHORUS IN WASTEWATERS

Industrial Source

Potato Processing

Fertilizer Manufacture

Metal Finishing Wastes

Flour Processing

Dairy Wastes (P_3O_{10})

Commercial Laundries ($PO_4^{=}$, $(PO_3)_6$)

Slaughterhouse Wastes (P_3O_{10})

Cooling Water ($PO_4^{=}$)

Boiler Blowdown ($H_2PO_4^-$, $PO_4^{=}$)

Petrochemical Plants

Detergent Manufacture ($PO_4^{=}$, P_2O_7)

Textiles ($PO_4^{=}$)

Tanneries ($PO_4^{=}$)

Baking Powder Manufacture ($H_2PO_4^-$)

Medicine (Laxative) ($HPO_4^{=}$)

Photography ($PO_4^{=}$)

Paper Mills ($PO_4^{=}$)

Water Treatment ($PO_4^{=}$, P_2O_7 , P_3O_{10})

Oil Well Drilling (P_2O_7)

the section on surfactants, tripoly- and pyrophosphate concentrations of 0.5 to 1.5 mg/l are known to have interfered with water treatment (66).

Phosphates are also noted for affecting the aroma of beer and its resistance to bacterial action (66).

Effect on Irrigation

Phosphorus is an essential nutrient for plants. Because of this phosphorus has a generally beneficial effect at levels normally found in treated effluents or in surface streams. However, waters having a phosphorus concentration of 60 mg/l can contribute to iron chlorosis in blueberry plants (66).

Effect on Fish and other Aquatic Life

Phosphate is of little importance as a compound directly toxic to fish and aquatic life. Levels necessary to produce a direct toxic effect are several orders of magnitude higher than the levels which would produce severe eutrophication problems. Once phosphorous enters the eco-system, however, it may theoretically exert an oxygen demand of 160 mg per 1 mg of organic phosphorous prior of complete oxidation (6).

Elemental phosphorus is quite toxic. McKee and Wolf report that colloidal phosphorus (as P_4) has a 48-hour TLm of 0.105 mg/l for bluegill sunfish. However, this form represents a relatively minor percentage of normally encountered wastes.

Because phosphate is actively incorporated into the tissues and protoplasm of all living creatures, concentration factors of 4,900-13,600 for algae, 30,000-165,000 for fish and up to 850,000

for spirogyra are routinely found above the background level.
For this reason the release of radio-active phosphorus must
be strictly controlled regardless of form.

TABLE XIX-3

DIRECT TOXIC EFFECT OF PHOSPHORUS

<u>Target Organism</u>	<u>P-Form</u>	<u>Conc. Level</u>	<u>Test</u>	<u>Effect</u>	<u>Ref</u>
Man	PO_4^{\equiv}	450 mgm/l	Used in food prep.	Buffers stomach acid	(6)
Man	$(PO_3)_4$	50 mg/l	Ingestion	Vomiting, diarrhea	(66)
Food Crop (Blueberry)	PO_4^{\equiv}	60 mgm/l	Used as irrigation water	Complexed iron re- sulting in iron chlor- osis	(66)
Bluegill	P_4	Colloidal Dispersion	Immersion	48 hr. TLm= [0.105 mgm/l]	(66)

A more widely recognized effect is the role of phosphorus as a contributing nutrient in algae blooms. Massey and Robinson (63) report that phosphorus is one of 15 elements which may limit growth of algae. Other elements noted in the literature include iron, sodium, nitrogen, carbon, potassium, magnesium, calcium, manganese, silicon (for diatoms), sulfur (as sulfates), and oxygen (6,63).

Of the elements listed, phosphorus and carbon are the two most significant (63).

While nitrogen is significant in discharges, some algae can fix atmospheric nitrogen, making its control as the limiting element highly questionable.

It was not until works by Kuenzel, King, and Kerr and associates were known that carbon was openly considered a limiting element (63). This is an additional reason for the effluent criteria recommended for BOD and SS (see Chapter III of this report).

Phosphates still must be considered one of the possible limiting elements in algal blooms due either to their threshold values or synergistic effects which are neither known or fully understood. As such, it is reported that from 0.009 mg/l to 0.015 mg/l phosphorus can be the limiting concentration (6,63). In addition, it is stated (6) that detention of waters has been found to reduce phosphorus concentrations. It is theorized that this may be due to phosphorous uptake by organisms and/or by precipitation. On the basis of data available in 1967-68 it was recommended (6) that total phosphorus concentrations not exceed 0.10 mg/l in flowing streams or 0.05 mg/l in ponds or reservoirs.

TREATMENT TECHNOLOGY-PHOSPHORUS REMOVAL

Treatment technology for the removal of phosphorus has recently been reported in the literature in substantial volume. The EPA has commissioned the compiling of a "Process Design Manual for Phosphorus Removal" by Black & Veatch, Consulting Engineers (19).

As this manual adequately reviews the current state of the art, the individual mechanisms of the various processes will not be discussed in this report. Rather, the efficiencies and costs of the various methods will be emphasized with respect to achievement levels. In general, the methods which have been reported as effective include the following:

- (1) Coagulation prior to primary clarification, utilizing alum and/or lime, generally known as Phosphate Extraction Process (PEP).
- (2) Utilization of an up-flow clarifier filtration (solids contact) with coagulation either before or after biological treatment and filtration.
- (3) Post biological coagulation with alum and/or lime.
- (4) Moving bed filters with coagulation.
- (5) Activated sludge and other biological processes.
- (6) Biological - Chemical treatment, i.e., the addition of coagulants directly to the activated sludge system.
- (7) Coagulation and precipitation with metallic salts and polyelectrolyte.
- (8) Reverse osmosis.
- (9) Adsorption on activated bentonite.
- (10) Ion exchange.
- (11) Adsorption and uptake by "Activated Algae".

Removal efficiencies reported for the various procedures and capital costs, operation costs and amortized operation costs are summarized in Tables XIX-4 and XIX-5 respectively.

TABLE XIX-4

PHOSPHORUS REMOVAL PROCESSES

<u>Treatment Process</u>	<u>Initial (mg/l)</u>	<u>Final (mg/l)</u>	<u>pH</u>	<u>Ref</u>
Phosphate Extraction: (Primary Clarifier Coagulation)				
W/Lime	13	2	9.5-10	(88)
Followed by Activated Sludge		1		(88)
W/lime	26	15.6	10.5	(89)
Followed by Contact Stabilization		8-13	8.5	(88)
W/Lime after A.S.	40-50	2.5-5	9.5 primary	(82)
W/Lime	10	2(0.3 min)	10.5+	(38)
W/Lime	10	2		(19)
W/Lime	96	3-6	11-12	(26)

SOLIDS CONTACT

Coagulate, settle, filter & activated carbon	10	1.07	9.8	(88)
	10	0.6	11.0	(88)
	9.7	0.5	10.5	(88)

TABLE XIX-4 (cont)

<u>Treatment Process</u>	<u>Initial (mg/l)</u>	<u>Final (mg/l)</u>	<u>pH</u>	<u>Ref</u>
<u>POST BIOLOGICAL COAGULATION</u>				
Amarillo project	40	1.0	10.5	(88)
Nassau County	34.4	6.8		
" " W/Alum	9	1.34	prior to filtration	(88)
	1.0	1.0	after filtration	(88)
		0.9	after carbon column	(88)
Al:P Molar Ratio = 1.5 to 2.1	Domestic	1.6	prior to filtration	(31)
Digester Supernatant				
W/Magnesium ammonia	45-282	2.5		(30)
Citrus plant A. S. W/Lime	2.33	0.46		(53)
		0.16	filtered	(53)
Wash D. C. - 2 stage lime	10.4	0.5		(26)
Filtered Eff.		0.39		(26)
and after carbon				(26)

TABLE XIX-4 (cont)

<u>Treatment Process</u>	<u>Initial (mg/l)</u>	<u>Final (mg/l)</u>	<u>pH</u>	<u>Ref</u>
Lebanon, Ohio - 1 stage lime	8.8			(26)
Filtered eff.		1		(26)
and after carbon		1		(26)
South Tahoe - 2 stage lime	Domestic	0.8	Recarbonated	(88)
<u>MOVING BED FILTER (MBF)</u>		90%	Removal	(88)
Alum & MBF	21.5	2.2		(26)
" "	19.1	0.84		(26)
<u>ACTIVATED SLUDGE</u>	20	6-10		(88)
Full Scale				
Reversed tapered aeration *	10.5	0.9	7.3-7.9	(67)
Pilot plant				
Reversed tapered aeration	15.2	3.0		(67)

* Reversed tapered aeration has higher aeration rates at the effluent end of the basin.

TABLE XIX-4 (cont)

<u>Treatment Process</u>	<u>Initial (mg/l)</u>	<u>Final (mg/l)</u>	<u>pH</u>	<u>Ref</u>
<u>PRIMARY SETTLING</u>				
		5-15%	Removal	(26)
<u>TRICKLING FILTERS</u>				
		20-30%	Removal	(26)
<u>ACTIVATED SLUDGE</u>				
		30-50%	Removal	(26)
<u>BIOLOGICAL-CHEMICAL:</u>				
W/Alum	33	2.0	6.0-6.6	(73)
W/Alum	5	0.005	6.0-6.6	(73)
W/FeCl ₃	24	1.85	7.1	(73)
W/NaAlO ₂	160	36	7.1	(19)
W/Alum	10	1.41	6.75	(19)

TABLE XIX-4 (cont)

<u>Treatment Process</u>	<u>Initial (mg/l)</u>	<u>Final (mg/l)</u>	<u>pH</u>	<u>Ref</u>
Primary Effluent				
Grayling	15.5	2.8		(26)
Mentor	15.7	2.6		(26)
Trickling Filter Eff.				
Lake Odessa		82%	Removal	(26)
Activated Sludge Eff.				
Benton Harbor	7.5	0.6		(26)
Texas City	6.2	0.8		(26)
W/FeCl ₃ & Purifloc	5.2-15.0	0.70		(52)
Nassau County W/Alum	9	0.1-1.0		(19)
Dallas Demo. Plant W/FeCl ₃	(soluble)	(soluble)		
Trickling Filter Eff.	6.5	0.43		(19)
Activated Sludge Eff.	7.0	0.21		(19)

TABLE XIX-4 (cont)

<u>Treatment Process</u>	<u>Initial (mg/l)</u>	<u>Final (mg/l)</u>	<u>pH</u>	<u>Ref</u>
<u>REVERSE OSMOSIS</u>	39	0.4-1.5		
<u>ACTIVATED BENTONITE</u>	19.5	2.7		(86)
<u>ION EXCHANGE</u>		"Essentially Free"	6.0	(88)

TABLE XIX-5

COST OF PHOSPHOROUS REMOVAL

<u>Process</u>	<u>Flow</u>	<u>Capital Cost</u>	<u>Operation Cost \$/1000 Gal.</u>	<u>Amortized Operation Cost ¢/1000</u>	<u>Ref</u>
<u>Phosphate Extraction:</u>					
"	10 MGD			0.25	
"	1 MGD	20,810		0.446	(19)
"	10 MGD	71,740		0.154	(19)
"	100 MGD	697,000		0.149	(19)
"	1 MGD	57,600		3.0	(19)
"	10 MGD	241,000		2.1	(19)
"	100 MGD	926,300		1.7	(19)
<u>Solids Contact & Filtration:</u>			0.055		
<u>Post-Biological, Coagulation</u>					
<u>Filtration:</u>					
1 Stage Lime	10 MGD	375,000		0.04	(88)
Clarification	1 MGD			5.42	(26)
W/Recalcining	10 MGD			3.78	(26)
	100 MGD			3.21	(26)
of Lime	250 MGD			3.11	(26)

TABLE XIX-5 (cont)

<u>Process</u>	<u>Flow</u>	<u>Capital Cost</u>	<u>Operation Cost \$/1000 Gal.</u>	<u>Amortized Operation Cost c/1000</u>	<u>Ref.</u>
South Tahoe	7.5 MGD	5,500,000	(at 95% Removal) (at 80% Removal)	8.6 6.4	(88)
<u>Moving Bed Filter</u>			0.06	7-8.5	(88)
"	1 MGD	280,000		13	(26)
"	1 MGD	264,000		12	(19)
Activated Sludge w/Sludge Elutriation				2.5 to 5.0	(88)
<u>Metallic Salts & Polymers</u>					
	1 MGD		0.024	3.6	(26)
	10 MGD		0.085	14.7	(19)
	100 MGD		0.066	10.0	(19)
<u>Reverse Osmosis</u>				18-25	(88)
<u>Activated Bentonite</u>	10 MGD		0.0003	—	(88)
<u>Ion Exchange</u>	1 MGD	173,000		18.2	(88)
"	10 MGD	1,400,000		17.6	(88)
" w/Prefiltration and Deep Well Injection				24.0	(73)

SUMMARY AND RECOMMENDATIONS

In General the following statements can be made relative to phosphorus and phosphates in the environment.

1. There are both natural and man contributed sources of phosphate in nature. There can be no zero background for phosphorus because it is an essential nutrient of all plant life. In Those areas where the water is devoid of phosphorus little aquatic life will be present.
2. The largest contributors of phosphorus to surface and ground waters are domestic wastewaters and agricultural runoff. Domestic wastewaters contain between 5 and 40 milligrams per liter and average about 10 milligrams per liter. Concentrations of phosphorus in agricultural runoff can be several hundred milligrams per liter.
3. In the normal pH range of most streams (6 to 8) the major ionic forms are dibasic phosphate and monobasic phosphate, that is, H_2PO_4^- and HPO_4^{--} . This is irrespective of the form in which the phosphate was introduced into the water.
4. Phosphate concentrations are of more significance to fish and aquatic life than to man, animals and plants. Fish have demonstrated a 48 hour TLm to 0.105 mg/l of elemental colloidal phosphorus. On the other hand, phosphate concentrations below 50 mg/l do not appear to have any significant effects on man, animal or plants. Some forms of aquatic

life are capable of concentrating phosphorus up to 850,000 times the background concentrations of the aquatic environment.

5. High concentrations of phosphate may interfere with water treatment. Concentrations as low as 0.5 to 1.5 milligrams per liter have been demonstrated to interfere with treatment.
6. The nature of algal blooms is still being investigated and debated. Phosphorus and carbon are widely recognized as being important limiting elements with respect to algae blooms. Concentrations as low as 0.009 milligrams per liter of phosphate have been reported as limiting to algal growth. Other studies indicate somewhat higher concentrations to be the limiting level of phosphate.
7. Current technology can effect a reduction of phosphorus to 1-2 mg/l as phosphorus. The cost of removing phosphorus varies with the process and the size of the plant. Several processes have been shown to be effective.

On the basis of the present information, a uniform effluent criterion is difficult to justify at this time. It is recommended, however, that where stream and impoundment levels are at or above 0.10 or 0.050 milligrams per liter respectively that all municipal and industrial discharges in the zone of influence uniform effluent criterion of 2.0 mg/l as phosphorus.

When the EPA adopts a policy that all municipal discharges, as well as industrial discharges, must meet a uniform effluent criterion for phosphorous, a 2 mg/l (as P) concentration is recommended. Until such a policy is developed, it is prejudicial to levy an effluent criterion on either industry or domestic discharges alone. The phosphorus limitation, like all criteria, must be equally applied to all effluents.

CHAPTER XX-SELENIUM

Selenium is primarily found in soil as elemental selenium, ferric selenite $\text{Fe}_2(\text{SeO}_3)_3$, calcium selenate $\text{Ca}_2(\text{SeO}_4)_3$, and organic selenium compounds. Selenium is often found in association with sulfur. Concentrations as high as 30 mg/kg of selenium have been found in the soils of South Dakota and Wyoming.

Lakin (104) states that, "The selenium content of surface waters is a function of pH of the waters as well as its presence in the drainage system.....Selenium is quantitatively precipitated as a basic ferric selenite at pH 6.3-6.7. At a pH of about 8, selenite may be oxidized to the soluble selenate ion." Table XX-1 shows the naturally occurring forms of selenium in the environment with some indication of the magnitude of their abundance.

Selenium is used industrially in its elemental form and as several salts. Table XX-2 shows the industrial sources of selenium. Selenium may also be expected in trace quantities from municipal sewage containing industrial wastes, as well as directly from industrial waste discharges. A review of the literature has indicated only a few concentrations of selenium which may be found in various wastewaters. A secondary sewage effluent has shown 0.023 mg/l of selenium (104).

TABLE XX-1

NATURAL SOURCES OF SELENIUM IN THE ENVIRONMENT (104)

<u>Sources</u>	<u>Form</u>	<u>Quantity</u>
Crustal Abundance		0.5 ppm
Soil	elemental	
	ferric selenite (pH 4.5-6.5)	
	calcium selenate (pH 7.5-8.5)	0.1-1,200 ppm
	organic	
Sea Water (ave.)		0.00009 mg/l
River Water (ave. of 9)		0.0002 mg/l
Coal		3 ppm
Petroleum		0.2 ppm
Air (U.S.A.)	H ₂ Se (Bacterial Action)	
	Diethyl Selenide Gas	8 million released/yr.
	Se and SeO ₂ particulate from (coal & oil uses)	

TABLE XX-2

INDUSTRIAL SOURCES OF SELENIUM

- 1) paint manufacturing
- 2) dye manufacturing
- 3) glass production
- 4) rectifier and semiconductor manufacturing
- 5) photoelectric cells and other electrical apparatus production
- 6) supplement to sulfur in the rubber industry
- 7) component of alloys
- 8) insecticides manufacturing
- 9) wastewaters from copper ore refineries
- 10) incinerator quench water used to cool fly ash when paper is burned (0.005-0.023 mg/l) [76]
- 11) incinerator residue quench water. (.003 mg/l) [76]

ENVIRONMENTAL EFFECTS OF SELENIUM

Selenium is an essential nutrient to man and other animals in trace quantities but it is detrimental and toxic at higher concentrations. Selenium tends to concentrate in plants and lower forms of aquatic life-possibly without immediate toxic effects. However, when it is ingested by fish, man or animals, it can have toxic effects. Since the concentration of selenium in the soil is relatively difficult to control, it is important to regulate the amount of selenium in all industrial and municipal waste discharges.

Effect on Man

The Drinking Water Standards (94) report that selenium is now recognized as being toxic to both man and animals. They also report that selenium, like arsenic, may have permanent effects. For example, selenium is noted for increasing the incidence of dental caries in man, and is a potential carcinogen. As a result, in 1962 the Drinking Water Standards' criteria for selenium was reduced from its previous value of 0.05 mg/l to 0.01 mg/l. Concentrations in excess of this amount were determined to be grounds for rejection of the water supply. The World Health Organization European Drinking Water Standards (1961) state an excessive limit of 0.05 mg/l. The USSR maximum permissible concentration for drinking water is set at 0.01 mg/l.

McKee and Wolf (66) report, "Proof of human injury by selenium is scanty and definite symptoms of selenium poisoning have not been identified; but it is widely believed that selenium is highly toxic to man." Table XX-3 reviews the effects of selenium on man. McKee & Wolf reported

TABLE XX-3

THE EFFECT OF SELENIUM OF MAN (105)

<u>Selenium Form</u>	<u>Conc. Level</u>	<u>Effect</u>
undefined	2-4 mg/kg	minimum lethal dose
undefine	5-7 mg/1 in food	harmful to liver
	5-7 mg/1 in water	increased suscept- ability to dental caries, Gastro- intestinal distur- bances, icterus
undefined	from seleniferous areas	high rate of dental caries; tendency for increased malocclu- sion and gingivitis

that mild chronic selenium poisoning has been observed in humans living in areas where the selenium concentration of the soil is relatively high. They also reported that selenium, as hydrogen selenide (H_2Se), at a concentration of 0.2 ppm, has caused toxic symptoms as an air pollutant. Nevertheless, it is interesting to note in the McKee and Wolf report that selenium in trace amounts is known to be an essential nutrient for animals including man although very little is known about the mechanisms of its beneficial action.

McKee and Wolf report that selenium salts are rapidly and efficiently absorbed through the gastrointestinal tract, and are largely excreted in the urine. The highest retention of selenium within the human body is found in the liver and kidneys. Selenium appears to act by maintaining the catalytic properties of the enzyme glutathione peroxidase which catalyzes the decomposition of hydrogen peroxide. The intake of selenium through food rather than water appears to be the basic problem for man. The extreme tolerance limit of selenium in foodstuffs is reported at 4.0 mg/kg with a safer limit of 3 mg/kg. The U. S. Food and Drug Administration, however, has placed a "zero" tolerance limit on selenium in fruits and other edible crops for human consumption.

Selenium has been found to be capable of protecting rats against mercury poisoning, a fact which is potentially encouraging to humans since high concentrations of selenium have also been found along with high concentrations of mercury in foods such as tuna fish (100).

Effect on Animal Life

As noted above, the presence of selenium in trace amounts is beneficial to animals. It is reported that a deficiency of selenium in animal diets may result in white muscle disease, while an excess amount

of selenium has been known to cause "blind staggers" and "alkali disease" (6). A concentration of up to 24 mg/kg in the vegetation consumed by livestock will produce the "alkali disease". This involves a lack of vitality, a loss of hair, sterility, lameness, and possibly death from anemia and malnutrition. Table XX-4 reviews the effects of selenium on animal life.

McKee and Wolf reported that any vegetation containing 5.0 mg/kg of selenium has been found to be dangerous to livestock, while fodder has been found to cause selenium poisoning with concentrations as little as 1 mg/kg. They report that the tolerance limit for livestock is about 4 mg/kg in their feed.

Chronic and acute selenium poisoning has been reported to occur naturally among cattle, sheep, horses, pigs, and poultry where the selenium concentrations in the soil were naturally high. While McKee and Wolf report that water containing 0.4-0.5 mg/l of selenium is generally non-toxic to cattle, this concentration of selenium in the water may contribute to selenium poisoning initiated through the feed.

Effect on Plants

It has been reported that plants containing 4 to 5 mg/kg of selenium are considered to induce toxic symptoms in animals (6). They indicated that this level of selenium could result in many crops due to a selenium level of 0.05 mg/l in irrigation waters.

Plants may be affected by selenium due to its presence in the soil as well as its presence in water. Concentrations ranging from 1-6 mg/kg have been found in the top eight inches of soil in many areas (66).

TABLE XX-4

THE EFFECT OF SELENIUM ON ANIMAL LIFE (105)

<u>Species</u>	<u>Selenium Form</u>	<u>Conc. Level</u>	<u>Effect</u>
Rat	Undefined	0.012 mg/kg	Near sub-threshold
Sheep	Undefined	0.4 mg/kg	Stimulated the inhibitory process of brain cortex up to 10-20 days
Livestock	Undefined	----	Anemia, liver damage & icterus
Mouse	$\text{Se}^{+4}(\text{SeO}_3^-)$	3 mg/l for life	Significant increase in growth rate
Rat	$\text{Se}^{+4}(\text{SeO}_3^-)$	3 mg/l for life	Most animals died young
Mouse	$\text{Se}^{+6}(\text{SeO}_4^-)$	3 mg/l for life	Significant decrease in growth rate
Rat	$\text{Se}^{+6}(\text{SeO}_4^-)$	3 mg/l for life	Significant increase in longevity. Increase in serum cholesterol; no effect on serum glucose, blood pressure or on aortic plaques

The ability of plants to concentrate selenium depends on the species, the age of the plant, the season of the year, and the concentration of the soluble selenate ions in the root zone of the plant the pH and electrode potential of the soil. In soils of pH 7.5 to 8.5 selenium exists in the form of the selenate ion which is readily available to plants (104).

McKee and Wolf report that plants under certain circumstances can absorb relatively high concentrations of selenium without apparent damage to the plant itself. For example, a weed (Astragalus) can contain as much as 4,500 mg/kg of selenium. Other plants grown in seleniferous soils have been found to contain as much as 1,610 mg/kg of selenium. Plants reported to have high concentrations of selenium include wheat, up to 63 mg/kg, and onions, up to 17.8 mg/kg. Wheat has been directly damaged by a concentration of 30 mg/kg of sodium selenate in the soil. The presence of chemically similar sulfates have been found to diminish both the uptake of selenium and its toxicity to the plant itself.

Effect on Fish and Other Aquatic Life

While McKee and Wolf report that generally selenium has been found to be toxic to fish and aquatic life in concentrations of 2.0-2.5 mg/l, they also report that concentrations considered to be safe for human beings, over a period of weeks have been found toxic to fish. While no concentration was specified, one would assume that this concentration is in the range of 0.01 to 0.05 mg/l. Barnhart, as cited by Battelles' Columbus Laboratories' report (15), indicated that selenium (possibly acting in synergism with other ions such as uranium or zinc)

TABLE XX-5
EFFECTS OF SELENIUM ON PLANTS (66)

<u>Selenium Concentration (mg/l)</u>	<u>Remarks</u>
0.00 - 0.10	No plant toxicity anticipated.
0.11 - 0.20	The water would be usable, however, long-term accumulations should be carefully monitored.
0.21 - 0.50	Toxic accumulation within plants is probable.
Over 0.50	Water would be unsuitable under any condition for plants.

was believed to be responsible for a fish kill in Colorado. The fish killed included black bullhead, bluegill, channel catfish, large-mouthed bass, rainbow trout, white crappie, and yellow walleye. This work indicated that arsenic was also found in the lake. Samples of the flora and fauna in the lake were found to contain greater than 300 ppm of selenium. The report concluded that it was believed that selenium has been passed up through the food chain to the fish which then accumulated the element to lethal concentrations.

TREATMENT TECHNOLOGY FOR THE REMOVAL OF SELENIUM

As noted by Patterson and Minear (76) very little has been reported in the literature on the levels of selenium in industrial wastewaters or its treatment. A review of the literature (58,76) and personal discussions with Dr. O'Connor (74) indicate that the most logical and efficient means of removal of selenium is by ion exchange. The literature, reviewed by Patterson and Minear, indicated that selenium is most likely to occur in the anionic form in an aqueous solution. Linstedt (58) reported that only 0.9 percent of the selenium was removed by a cation exchange column while a cation and anion exchange column removed 99.7 percent of the selenium concentration. Linstedt, et al. concluded their work by stating that the most effective removal method for selenium, which they had investigated on a bench scale, was the use of a strong acid-weak base ion exchange unit. The removal efficiencies of the processes investigated by Linstedt et al are summarized below in Table XX-6.

TABLE XX-6

BENCH-SCALE REMOVAL OF SELENIUM BY ADVANCED WASTE TREATMENT (58)

<u>Process</u>	<u>% Removal</u>	<u>Concentration mg/l</u>
Initial Feed		Approx. 0.0128
Lime Coagulation & Settling	16.2	0.0107
Cation Exchange	0.9	0.0127
Cation & Anion Exchange	99.7	0.00009
<u>Cumulative Removal by</u>		
Sand Filtration	9.5	0.0116
Activated Carbon	43.2	0.00727
Cation Exchange	44.7	0.00708
Anion Exchange	99.9	0.00001

Similarly Weston (97) recommended to the Illinois Pollution Control Board a combined cation and anion ion exchange unit for the removal of dissolved selenium. However, no cost data or achievable effluent concentrations were provided. Patterson and Minear included within their report two figures showing the chemical and amortization costs of a weak base ion exchange system.

Currie, in his summary, commenting on the adoption of an effluent criteria for selenium for the Illinois Pollution Control Board (27), made the following comment:

Because of the toxicity of selenium, it is desirable to adopt an effluent standard, even in the absence of conclusive evidence as to the removal technology, in order to protect legitimate water uses.

Dodge testified that the very strict 0.01 unit standard was obtainable. Since a somewhat higher level is acceptable for aquatic life, Dodge suggested the standard of 1.0 units, recognizing both that higher control may sometimes be necessary to protect public water supplies and that we may later discover, in a variance proceeding, more information as to the treatability that may result in a re-examination of the standard.

As reported in Patterson and Minear, the work of Linstedt and his co-workers indicated that the common method of lime coagulation, settling, and sand filtration was found to be ineffective in removing selenium from the wastewaters investigated. On the other hand, discussions with Dr. O'Connor (74) indicate that one of the co-authors of the original work, Carl P. Houck, reported that the precipitation of selenium has been effective. According to O'Connor, Houck's article reported the recovery of selenium by its adsorption on a ferric hydroxide sludge at a pH of 8, and by the utilization of ferric alum as a coagulant. Other methods

proposed by O'Connor, which bear investigation for selenium removal include: precipitation with a ferric salt, ion exchange on duplicate matter such as clay, reverse osmosis, and distillation.

It is apparent that little full-scale work on selenium removal has been reported in the literature. On the basis of the bench-scale work, the question remains as to what final effluent level can be obtained at higher initial concentration.

SUMMARY AND RECOMMENDATIONS

1. It is apparent that selenium is both an essential nutrient to man and other animals in trace quantities, and is detrimental and toxic at higher concentrations.
2. Selenium is found naturally in the soil and in water and artificially in industrial and municipal discharges. It is capable of being concentrated in plants and lower forms of aquatic life, possibly without immediate toxic effects. However, upon ingestion and accumulation in fish, man and animals, toxic concentrations are reached. This is a major hazard of selenium toxicity to man.
3. Selenium is also toxic to plants and fish directly, but at higher concentrations.
4. Bench-scale treatment has reduced selenium from an initial concentration of approximately 0.012 mg/l to a final effluent of less than 0.1 ug/l by anionic ion exchange.

5. While effluent levels have not been reported, it appears that selenium may also be removed from wastewaters by coagulation with ammonia hydroxide or ferric alum at a pH of approximately 8. The selenium ion is removed with the ferric hydroxide precipitate.
6. As the concentration of selenium in the soil is difficult to control, especially when it is due to natural causes, it is of extreme importance to control the amount of selenium in all industrial and municipal waste discharges.

It is recommended that a uniform effluent criteria of 0.01 mg/l be adopted at this time. It is further recommended that the investigations and literature review of the treatment technology for the removal of selenium from wastewaters be continued.

CHAPTER XXI-SETTLEABLE SOLIDS

At one time settleable solids were discharged to waters mostly because no treatment was provided. Today, any plant providing primary treatment will remove most of the settleable fractions. More insidious than the deliberate discharges of untreated wastes is the uncontrolled discharge of urban and farm runoff resulting from a myriad of projects. Table XXI-1 is a compilation of the sources of settleable solids.

Settleable solids may be contributed in discharges from both municipal and industrial waste treatment facilities. They include inorganic and organic materials. Inorganic components may include but will not be limited to: sand, silt, and salts from natural runoff and mining operations; gravel washing, dust, and fines from coal washeries; and loose soils, from agricultural land, highway runoff, and construction projects. The organic fraction would normally be expected to include settleable materials such as grease, oils, tars, fats, fibrous material such as you might expect from paper mill, and synthetic plastic production; saw dust, hair, grease, and other various settleable materials from sewers. In addition, any treatment process utilizing clarification and precipitation of metallic hydroxide or carbonate sludges, will also contain settleable solids if not properly clarified.

TABLE XXI-1

SOURCES OF SETTLEABLE SOLIDS

1. Natural Runoff
2. Mining Operation
3. Sand and Ground Quarries
4. Highway and Construction Projects
5. Combined and Storm Sewer Discharges
6. Untreated Industrial Wastes
7. Untreated Municipal Wastes
8. Filter Backwash

Settleable Solids have also been shown to contain high concentrations of trace metals which, if not removed, can be very toxic to the beneficial uses of the water. Various investigations reported in other sections have shown that some of these trace metals once absorbed upon settleable solids, and particulate matter, may at a later date be leached from the solids by changes in water quality and/or by the benthic aquatic life or the biota of the receiving water.

ENVIRONMENTAL EFFECTS OF SETTLEABLE SOLIDS

Effects on Fish and Aquatic Organisms

Settleable solids have adverse effects on fisheries by covering the bottom of streams or receiving water with a blanket of material that destroys both the bottom flora and fauna, and the

strata necessary for the spawning of fish. These deposits may contain organic material which depletes the oxygen supply, creating an anaerobic condition which causes production of hydrogen sulfide, carbon dioxide, methane, and other gases (6).

TREATMENT TECHNOLOGY-SETTLEABLE SOLIDS REMOVAL

It has been well documented that adequate clarification will remove settleable solids from both industrial and municipal waste treatment facilities. The clarification process has also been considered to be a basic primary step of treatment and, therefore, can be considered as a minimum step in treatment well within economic means.

It is recommended that a uniform effluent criteria for settleable solids, as specified in "Standard Methods", not exceed 0.2 ml/l. This criteria will meet the minimum guidelines as established in Water Quality Criteria (6).

CHAPTER XXII - SILVER

Silver is found naturally in its metal state, combined with ores, or as a salt. As an ore, silver appears as Argentite, Ag_2S ; Horn silver, AgCl ; Proustite, Ag_3AsS_3 ; and Pyrargyrite, Ag_3SbS_3 (66). Silver is also reported to be a by-product in the mining of lead, copper and zinc (74). The nitrate salt is the most soluble form followed by the sulfate. The chloride, sulfide, phosphate and arsenate salts are practically insoluble. Table XXII-1 lists some natural and industrial sources of silver.

Table XXII-2 lists industrial uses of silver. Silver has been used as a disinfectant, especially in Europe. While 0.015 mg/l of AgO was reported as effective on some bacteria, it reacts slowly and is expensive (37). Concentrations of 20 mg/l had no effect on some viruses and 1000 mg/l was non toxic to Endameoba histolytica. It was reported as ineffective and hazardous for swimming pool use (24,37).

Nemerow (14) indicated that due to the value of silver most industries will utilize complete recovery processes to remove the silver from the waste prior to discharge to any receiving waters. He cited the examples of one silver plating plant spending \$120,000/year to recover \$60,000 worth of silver by evaporation. Eastman Kodak companies recover 100% silver by the common methods of metallic replacement, electrolysis and chemical precipitation.

ENVIRONMENTAL EFFECTS OF SILVER

As discussed in the Drinking Water Standards (94), the intentional addition of silver to water as a disinfectant is of primary concern. The chief effect on man is cosmetic, consisting of a permanent blue-grey discoloration of the skin, eyes and mucous membranes (argyria). It has been shown that plant and marine life are capable of concentrating silver above the ambient concentrations found

TABLE XXII-1

NATURAL SOURCES OF SILVER

<u>Source</u>	<u>Concentration</u>	<u>Reference</u>
Sea Water	0.0003 mg/l	(66)
Fresh Water, N.E. Basin	0.0019 mg/l (mean)	(59)
Municipal Water Supplies	Up to 0.05 mg/l	(66)

INDUSTRIAL SOURCES OF SILVER

<u>Source</u>	<u>Concentration</u>	<u>Reference</u>
Industrial Waste Water	130 - 564 mg/l	(76)
Silver Plating	51 mg/l(@0.5 gph)*	(14)
Rinse Waters	255 mg/l(@2.5 gph)*	(14)

* Drag-out rates

TABLE XXII-2
USES OF SILVER

<u>Form</u>	<u>Use</u>	<u>Reference</u>
Ag, metallic	Jewelry	(66)
	Silverware	
	Alloys	
	Electroplating	
	Food & Beverage Industry	
AgNO ₃	Photographic Industry	(66)
	Ink Manufacturing	
	Electroplating	
	Coloring of Porcelain	
	Antiseptic	
AgI	Cloud Seeding	(74)
AgO	Disinfectant	(24,37)

in the water (6). Vegetables cooked in silver bearing waters have also been found to concentrate silver (6). Silver is also toxic to fish and aquatic life.

Effect on Man

The chief effect on man is argyria. While the amount of colloidal silver required to produce argyria is not precisely known, the amount of silver from injected Ag-arsphenamine which produces argyria is any amount greater than 1 gram of silver or 8 grams of Ag-arsphenamine. The Drinking Water Standards point out that most common salts of silver may produce argyria when ingested by the mouth or through injection. It was also noted that individuals concurrently receiving bismuth medication have been found to develop argyria more readily.

The Drinking Water Standards state that silver has an affinity for elastic fibers. It is primarily excreted from the body by the liver. Silver within the body is chiefly transported by the blood stream in which it is carried by plasma proteins in the red blood cells. Once silver is fixed in the body tissue, negligible excretions will occur through the urine. Table XXII-3 shows the effects of silver on animals.

On the assumption that all silver ingested is deposited in the integument, the authors of the Drinking Water Standards calculate that a concentration of 0.01 mg/l could be ingested for a life time

at a rate of two liters of water per day without reaching the concentration of 1 gram of silver. Similarly, they stated that 0.05 mg/l of silver could be consumed for 27 years without exceeding the silver deposition of 1 gram. McKee and Wolf point out, however, that this does not allow for the consumption of silver through foods such as mushrooms, or for concentration in cooked foods as discussed above.

Effect on Plants

Both the Drinking Water Standards and the work of McKee and Wolf indicate that silver is concentrated within food. In particular, McKee and Wolf note that mushrooms are known to have a very high concentrations of silver. The Drinking Water Standards report that any vegetable belonging to the family Brassicaceae such as cabbage, turnups, cauliflower and onions is capable of concentrating silver which might be found in the cooking water. As a result, the silver content of several liters of water could be ingested through the consumption of these vegetables when cooked. It was also pointed out that there is a probably increase in the absorbtion rate of silver in the presence of sulfur compounds in food.

Effect on Fish and Other Aquatic Life

The toxicity of silver, silver nitrate, and silver sulfate has been reported in the literature. It has been summarized in Table XXII-4.

In general, silver salts are reported as toxic to fish and aquatic life at concentrations ranging from 0.003 to 0.4 mg/l. It appears that most forms of fish and aquatic life are capable of surviving a concentration of less than 0.1 mg/l for at least one day. Some species of marine animals and plants are capable of concentrating silver as much as 1-3 mg/l from a sea water concentration of 0.0003 mg/l. (6) It, therefore, appears logical to assume that silver may be concentrated in fish and other aquatic life. If this is true, man and other mammals can then receive silver not only by direct consumption of water, but also through the ingestion of food grown or cooked in silver bearing water.

TABLE XXII-3
EFFECTS ON ANIMALS

<u>Species</u>	<u>Concentration (or Dose)</u>	<u>Remarks</u>	<u>Reference</u>
Man	1 g Ag, injected	Argyria	(66)
Man	10 g Ag, ingested	Lethal	(105)
Rat	400-1000 ug/l	Pathologic changes of kidneys, liver & spleen	(94)
Rabbit	0.25 mg/kg/day (11 mo.)	Effect on immunological capacity, conditioned reflexes, vascular, nervous & glial tissue of encephalon & medulla	(105)

TABLE XXII-4

SILVER TOXICITY TO FISH AND AQUATIC LIFE

<u>Species</u>	<u>Ag Concentration</u> <u>mg/l</u>	<u>Form</u>	<u>Remarks</u>	<u>Reference</u>
Salmon fry	0.04	AgNO ₃	Some killed	(66)
Salmon fry	0.44	AgNO ₃	Killed	(66)
Young eels	0.2	AgNO ₃	Max tolerated 24 hour	(66)
Guppies	0.0043	Ag	LD50	(66)
Sticklebacks	0.003	AgNO ₃	Lethal @ 15-18°C	(15,66)
Sticklebacks	0.004	AgNO ₃	1 wk survival	(66)
Sticklebacks	0.01	AgNO ₃	4 days survival	(66)
Sticklebacks	0.1	AgNO ₃	1 day survival	(66)
<u>Daphnia magna</u>	0.1	Ag	Killed	(15)
<u>Daphnia magna</u>	0.03	Ag	Med. threshold	(15,66)
<u>Daphnia magna</u>	0.0051	AgNO ₃	Immobilization	(15,66)
Tadpoles	0.1	Ag	Killed	(15)
<u>Lebistes retiolatus</u>	0.01	Ag	Killed	(15)
Adult barnacles	0.04	Ag ₂ SO ₄	90% killed	(15)

TREATMENT TECHNOLOGY - SILVER REMOVAL

Due to the value of silver, most of the treatment technology for its removal from waste waters is centered around its recovery. In addition to the previously mentioned recovery value of silver noted by Nemerow (14), Patterson and Minear (76) report that even dilute wastewaters ranging from 50 - 250 mg/l of silver have a net recovery value of \$1.60 to \$9.00 per thousand gallons. The basic methods for the recovery of silver fall into the four broad categories of precipitation, ion exchange, metallic replacement, (reduction exchange) and electrolytic recovery. Their respective efficiencies are summarized in Table XXII-5.

Precipitation

Precipitation of silver from solution normally utilizes the low solubility of silver chloride. Patterson and Minear report that silver chloride has a maximum solubility of 1.4 mg/l (as silver ion) provided silver chloride complexes are not formed. As most other metal ions in conjunction with chloride are soluble, it allows for silver recovery from mixed metal waste without prior waste stream segregation. Under alkaline conditions, the precipitation of hydroxides of other metals occurs along with silver chloride. Patterson and Minear report that acid washing other precipitates allows for the removal of the contaminating metal ions, leaving the insoluble silver chloride behind.

As reported by Nemerow, silver is often found in cleaning wastes in conjunction with cyanide. Cyanide must be removed prior to the precipitation of silver as a silver chloride. This may be achieved by oxidation of cyanide with chlorine which then releases chloride ions into solution allowing for the precipitation of silver chloride directly. Patterson and Minear pointed out, however, that in the event that cyanide concentrations greatly exceed that of silver, high chlorine concentrations may result from the cyanide oxidation, thereby greatly reducing the effectiveness of this removal procedure.

With respect to recovery of silver from photographic solutions, Patterson and Minear described the use of magnesium sulfate and lime in solutions containing high levels of organic acids, the use of sulfide to precipitate silver in the form of silver sulfide, and the use of hydrosulfide to precipitate both free silver and silver sulfide.

Ion Exchange

As one would expect due to the selective solubility of various silver salts, ion exchange has been found very useful in the recovery of silver from dilute photographic wash waters and plating rinse waters. (See Table XXII-5)

Patterson and Minear reported the use of a series of cation and anion exchange columns for the recovery of silver cyanide from plating rinse waters. While no final effluent levels were given, they did report that for one plant approximately 280 mg of silver were recovered for each liter of wastewater passed through the ion exchange columns.

TABLE XXII-5
TREATMENT FOR SILVER IN WASTEWATER
CONTAINING CYANIDE

<u>Method</u>	<u>Silver Concentration mg/l</u>	<u>Silver Effluent Concentra- tion mg/l</u>	<u>Ref.</u>
*Chl & P, bench scale	105-250	1-3.5	(76)
Chl & P, full scale	130-585	0.0-8.2	(76)
Chl & P, full scale	---	1 - 3	(97)
Chl, pH to 6.5, coag. with ferric chloride & lime, settle, pH to 8.0 & resettle)	0.7 - 40	0.1 or less	(76)
Chl & pH (coag. with ferric chloride & lime & settle)	---	0.1	(26,97)
Ion Exchange			
(a) Cation	0.055	0.0078	(58)
(b) Anion & Cation	0.055	0.0046	(58)
Ion Exchange	---	Trace	(59)
Metallic Replacement	---	95% Removal	(76)
*Chl - Chlorination			
P - Precipitation			

One work reviewed by Patterson and Minear indicated that there may be problems in recovering silver from resins, making the recovery of silver by ion exchange uneconomical for photographic waste. Another author indicated the use of an electrolytic process to remove silver from the ion exchange resin regenerant. (76)

Metallic Replacement

Metallic replacement, otherwise known as reductive exchange, consists of the precipitation of silver onto another metal. In order to form the silver precipitate, the silver ion must be substituted by another metal ion. Iron and zinc are common substitutes. Nemerow (72) reported that this is one of three methods recommended by the Eastman Kodak Company for the recovery of silver from photographic waste. Similarly, Patterson and Minear report the use of metallic replacement by silver plating plants. However, as the silver is replaced, the zinc and iron released must be removed from the wastewater by further treatment.

Electrolytic Recovery

Nemerow also reported electrolytic recovery as a recommended method by Eastman Kodak for the recovery of silver. Patterson and Minear report that high wastewater concentrations are needed for the method to be effective. They indicated that most silver bearing wastewaters do not have sufficient concentration of silver to make the process feasible. They stated that while some units have been

effective at silver concentrations ranging from 100 to 500 mg/l, they have only noted consistent success in reducing silver from concentrations ranging from 5000 mg/l down to 500 mg/l. The cost of such a unit has been estimated to be as little as 400 dollars.

In summary, it is apparent that the value of silver makes it amenable to recovery processes at a net gain for the industry. Due to the low capital cost, it would appear that electrolytic recovery would be a first step for very high concentrations of silver wastewaters. Thereafter, the use of ion exchange, or precipitation with the chloride ion, would appear to be more feasible. While the efficiency of full scale ion exchange unit has not been reported in the literature reviewed, it has at least been shown in bench scale tests that very low effluent levels are obtainable. One must consider, however, the additional treatment steps which may be necessary for the destruction of the regenerate. This also appears to be the major problem for the metallic exchange treatment process. Generally, the recovery of silver by precipitation with chloride ion would appear the most feasible and it has been shown on the full scale process to achieve a final effluent concentration of less than 0.1 mg/l. Table XXII-6 reviews the costs for treatment of silver in wastewater.

TABLE XXII-6
COST FOR TREATMENT OF SILVER IN WASTEWATER
CONTAINING CYANIDE

<u>Method</u>	<u>Cost in \$1000/mgd</u>	<u>Reference</u>
P & S (chloride)	\$1000	(97)
	\$ 610	(97)
Chl, P & S (ferric chloride and lime)	\$210	(97)
	\$710	(97)
Ion Exchange	\$.18/lb Ag recovered	(76)
	\$1.75	(76)
Electrolytic Re- covery	\$400 capital cost	(72)
	(rate of flow not specified)	

P = Precipitation

S = Sedimentation

Chl= Chlorination

SUMMARY AND RECOMMENDATIONS

On the basis for the above discussion and literature review, the following conclusions are drawn:

- (1) Silver is found in the marine environment due to natural causes. Marine plants and animals contain silver above the ambient concentration of their water environment.
- (2) Considering only the consumption of silver in drinking water, the safe concentration of silver should be less than 0.1mg/l.
- (3) Some vegetables are capable of concentrating silver from water in which they are cooked, thereby providing an additional source of silver to man. Mushrooms concentrate silver during growth.
- (4) A silver concentration above 0.1mg/l is toxic to fish even for short durations. A silver concentration as low as 0.003 mg/l is toxic to stickleback fish under extended exposure.
- (5) While industrial waste concentrations may be relatively high, the value of silver makes removal by recovery economically attractive. Silver may be recovered by precipitation with the chloride ion, ion exchange, metallic ion exchange, and electrolytic recovery. Due to its low capital cost, electrolytic recovery is most advantageous

for concentrations of silver in the range of 5000 mg/l. For silver bearing wastewaters with a silver concentration from less than 5 to 600 mg/l the most effective treatment process appears to be precipitation and recovery by the chloride ion. At concentrations in the range of 50 to 250 mg/l silver has a net recovery value in the range of \$1.60 to \$9.00 per thousand gallons of wastewater.

- (6) Treatment of silver bearing wastewaters by chlorination, ferric chloride coagulants, pH adjustment, and settling is capable of obtaining a final effluent concentration of less than 0.1 mg/l.
- (7) Due to the value of the recovered silver, the next cost of silver recovery and treatment is substantially less than that of treating any other metal.

On the basis of the above conclusions, it is recommended that an interim effluent level be adopted at 0.1 mg/l. It is recognized that this level is above the maximum level for drinking water of 0.050 mg/l and that, possibly, ion exchange is capable of obtaining a 0.050 mg/l effluent level as a maximum condition. On the basis of the current data available however, the interim level should be adopted immediately. As soon as a methodology is available for a 0.050 mg/l effluent level, such a level would be recommended. In all cases, a final objective of 0.010 mg/l should be kept in mind.

CHAPTER XXIII SURFACTANTS

Surfactants are synthetic organic chemicals which have a high residual water affinity at one end of the molecule and a low residual affinity at the other. In discussing surfactants it is actually the methylene blue-active substances to which this chapter is addressed. These include not only the well known alkyl benzene sulfonates (ABS) and linear alkyl sulfonates (LAS), but many inorganic and organic compounds which may interfere with methylene blue. According to the 13th Edition of Standard Methods (1), "Organic sulfonates, sulfonates, carboxylates, phosphates, phenols - which complex methylene blue - and inorganic cyanates, chlorides, nitrates, and thiocyanates - which form ion pairs with methylene blue - are among the positive interferences. Organic materials, especially amines which compete with the methylene blue in the reaction can cause low results. Positive errors are much more common than negative when determining anionic surfactants in water."

Common sources of ABS and LAS are shown in Table XXIII-1. While many major industrial sources exist, municipal sewage contains a significant amount of surfactant.

In 1965, industry responded to the pressure to improve the treatability of surfactants by switching from ABS to LAS. The basic difference between ABS and LAS is the organic structure and, thereby, the biodegradability. ABS consists of a branched alkyl group generally attached to a non-terminal carbon which is more difficult to decompose through biological means than LAS

which has a straight chain alkyl group.

TABLE XXIII-1

MAJOR SOURCES OF SURFACTANTS AND REPRESENTATIVE CONCENTRATIONS (59)

A. Major Sources

Laundries
Car washes
Textile industry
Tanneries
Canning operations
General industrial clean-up operations
Municipal wastes

B. Commonly Found ABS Concentrations in Water

<u>AGENT</u>	<u>Source</u>	<u>Location</u>	<u>Concentration</u>
ABS	Detergent - industrial waste	—	0.6 mg/1
ABS	Surfactants	Italy-surface waters	3.5-100 mg/1
ABS	Anionic detergent	Czechoslovakia	.5 mg/1
ABS	Synthetic detergent	Wisconsin well	10 mg/1
ABS	Synthetic detergent	River and water supplies in 32 U. S. cities	0.14 mg/1 (average)
ABS	Sewage	In various U.S. cities	4-45 mg/1
LAS	Sewage	U.S. Cities	1-15 mg/1

ENVIRONMENTAL EFFECTS OF SURFACTANTS

Effect on Man

With respect to effects on man, Borneff (as reported in McKee and Wolf (66)) indicates that water supplies containing synthetic detergents are capable of dissolving carcinogenic compounds. Borneff concluded, "Drinking water obtained from rivers subject to contamination with wastewater containing detergents must be considered injurious to health" (66).

Volume 1 of the Water Quality Data Book (59) states that the maximum ABS concentration which produces no harmful effect in mammals over long periods is 0.5 mg/l. This concentration also produced no organoleptic effects when administered for long periods. The major difficulties created by detergents and other surfactants in domestic water supplies include those of foaming, turbidity, interference with treatment, and the production of tastes and odors. Under favorable conditions a concentration of 0.5-1 mg/l of surfactants may cause a light foaming condition. It is interesting to note that the tendency of ABS to cause foaming is greatest in clean water and decreases progressively as the polluttional load is increased. Similarly, the foaming power and stability of the foam are greater at a pH of 3 and of 9 than near neutrality (66).

Synthetic detergents in general, at a concentration of 3 to 5 mg/l, have been found to interfere with coagulation and floc formation at water treatment plants (66).

With respect to taste and odor conditions, an off taste in clean water has been reported in the ABS range of 1 to 40 mg/l. The work of Filicky et al. is summarized in Table XXIII-2 indicates the minimum perceptible (taste and odor) concentrations for various surface active agents. It is apparent that the minimum perceptible concentration varies with chemical compositions of the surfactants in solution. Chlorination of waters containing detergents may accentuate the unpleasant tastes and odors (66).

TABLE XXIII-2

MINIMUM CONCENTRATION OF A DETERGENT REQUIRED TO PRODUCE A PERCEPTIBLE TASTE AND ODOR, ALSO, TASTE AND ODOR THRESHOLD VALUES OF A 5 mg/l DETERGENT CONCENTRATION (AFTER FILICY, et al.) (66).

<u>Surface-Active Agent</u>	<u>Minimum Concentration Perceptible (mg/l)</u>	<u>Threshold Value of 55 mg/l Concentration</u>	<u>Type of Taste or Odor</u>
Taste Results			
Alkyl aryl sulfonate	0.6	8	Limey, chemical
Alkyl aryl sulfonate	0.6	13	Chemical, soapy
Alkyl sulfate	3.0	2	Solvent
Alkyl sulfonate	1.4	4	Bitter, soapy
Sulfonated amide	2.5	2	Chemical, soapy
Odor Results			
Alkyl aryl sulfonate	0.7	7	Limey, chemical
Alkyl aryl sulfonate	0.3	17	Soapy
Alkyl sulfate	0.2	25	Aromatic, solvent
Alkyl sulfonate	0.3	21	Kerosene, soapy

TABLE XXIII-2 (cont)

<u>Surface-Active Agent</u>	<u>Minimum Concentration Perceptible (mg/l)</u>	<u>Threshold Value of 55 mg/l Concentration</u>	<u>Type of Taste or Odor</u>
Sulfonated amide	2.0	3	Chemical, soapy

Effect on Domestic Animals and Wildlife

McKee and Wolf indicate that water containing surfactants has been found to dissolve the protective oil coating on water-fowl, thereby causing the feathers to become water-logged. They report that livestock will refuse to drink water containing surfactants. Small doses of surfactants put in the water supply of poultry is believed responsible for a rapid weight gain or loss; for example, a concentration of 5 mg/l sodium oronite was reported to give a 5 percent increase in the weight of baby chicks. Water Quality Data, Volume 1, lists surfactants within the acute toxicity ranking of organic chemicals found in fresh water. These values are tabulated in Table XXIII-3 according to their effect upon mammals.

Effect on Plant Life

McKee and Wolf found there were conflicting opinions as to the effects of surfactants on plants. One report they studied noted that a coating of LAS has a harmful effect upon the development of spinach, carrots, endive, lettuce and tomatoes. This was reportedly caused by a disturbance of the humidity balance within the soil, which allowed the soil to drain too rapidly. However,

a second report showed that surfactants are believed to promote water retention and retard penetration. On the basis of this conflict, no immediate conclusions can be drawn regarding the effects of surfactants on plant life.

Water Quality Criteria (6) indicates that within the marine environment detergents have been found to be more toxic in saline waters than in either fresh waters or tidal estuaries. The photosynthesis of marine kelp has been reported to be decreased by 50 percent after a 96 hour exposure to a surfactant concentration of 1.0 mg/l.

TABLE XXIII-3
SURFACTANT TOXICITY TO MAMMALS (66)

<u>Species</u>	<u>Substance</u>	<u>Conc. Level (or Dose)</u>	<u>Effect</u>
Human	LAS	100 mg/day (4 mo.)	no toxic effect on 6 men
Human	ABS	100 mg/day (4 mo.)	no effect
Dog	ABS	1000 mg/day (6 mo.)	no effect
Pigs, young	ABS	.1% in water (79 days)	no effect
Pigs, young	ABS	.2% in water (79 days)	stimulated growth
Pigs, young	ABS	.4% in water (79 days)	no effect
Rats	ABS	500 mg/l (2 years)	no effect
Guinea pig	ABS	2000 mg/l (6 mo.)	slight toxic effect
Guinea pig	LAS	2000 mg/l (6 mo.)	slight toxic effect
Rat	LAS	1.4-1.5 gm/kg	LD50 (single dose)
Mice	LAS	2.8 gm/kg	LD50 (single dose)

Effect on Fish and Other Aquatic Life

The effects of surfactants on fish and aquatic life are relatively well documented (6,66,59). The presence of surfactants in concentrations up to 0.14 mg/l are generally not toxic to fish and other aquatic life for short periods of time (66). However, trout reportedly have avoided waters containing as little as 0.001 mg/l (59).

Most of the earlier works in the literature dealt primarily with the effects of soaps and the ABS type surfactants, while the recent references include the effects of LAS surfactant as well. In general, McKee and Wolf show that the toxic concentrations of various ABS type surfactants, in either hard or soft water, vary from 3.6 to 5.6 mg/l as a 96 hour TLM. They also indicate that while the toxicity of ABS type surfactants is greater in hard water than in soft water, a decrease in the water temperature can make the surfactants just as lethal in soft water as in hard water. McKee and Wolf report concentrations of 5 mg/l of various detergents as having a lethal effect upon tadpoles, stickleback, roach, carp, and Daphnia. A concentration of 3 mg/l of well oxygenated clean water was found to produce a 50 percent mortality for rainbow trout within a 12 week period.

Table XXIII-4 indicates the varying degrees of toxicity of alkyl aryl sulfonates including ABS for different time exposures to various aquatic organisms. In comparison, Volume I of the new EPA Data Book has indicated a 96 hour TLM concentration for linear ABS (LAS) for three species: bluegill fingerling, 0.6 to 3.0 mg/l; flathead, 3.5 mg/l; and flathead (eggs), 3.4 mg/l in 24 hours.

Recommended stream criteria for surfactants are summarized in Table XXIII-5. While these are applicable as stream criteris, one must not consider the appropriateness of a unilateral application as effluent criteria without considering the current treatability of surfactants found in today's discharges.

TABLE XXIII-4

EFFECT OF ALKYL-ARYL SULFONATE, INCLUDING ABS, ON AQUATIC ORGANISMS (6)

<u>Organisms</u>	<u>Concentration (mg/l)</u>	<u>Time</u>	<u>Effect</u>
Trout	5.0	26 to 30 hours	Death
	3.7	24 hours	TL _m
	5.0		Gill pathology
Bluegills	4.2	24 hours	TL _m
	3.7	48 hours	TL _m
	0.86		Safe
	16.0	30 days	TL _m
	5.6	90 days	Gill damage
Fathead minnows	17.0	96 hours	TL _m
	2.3		Reduced spawning
	13.0	96 hours	TL _m
	11.3	96 hours	TL _m
Fathead minnow fry	3.1	7 days	TL _m
Pumpkinseed sunfish	9.8	3 months	Gill damage
Salmon	5.6	3 days	Mortality
Yellow bullheads	1.0	10 days	Histopathology
Emerald Shiner	7.4	96 hours	TL _m
Bluntnose minnow	7.7	96 hours	TL _m
Stoneroller	8.9	96 hours	TL _m
Silver jaw	9.2	96 hours	TL _m
Rosefin	9.5	96 hours	TL _m
Common shiner	17.0	96 hours	TL _m
Carp	18.0	96 hours	TL _m
Black bullhead	22.0	96 hours	TL _m
"Fish"	6.5		Min. lethality
Trout sperm	10.0		Damage
Daphnia	5.0	96 hours	TL _m
	20.0	24 hours	TL _m
	7.5	96 hours	TL _m

TABLE XXIII-4 (cont)

<u>Organisms</u>	<u>Concentration</u> (mg/l)	<u>Time</u>	<u>Effect</u>
Lirceus fontinailis	10.0	14 days	6.7 percent survival (hard water)
Crangonyx setodactylus	10.0	14 days	0 percent survival (hard water)
Stenonema ares	8.0	10 days	20-33 percent survival
	16.0	10 days	0 percent survival
Stenonema heterotarsale	8.0	10 days	40 percent survival
	16.0	10 days	0 percent survival
Isonychia bicolor	8.0	9 days	0 percent survival
Hydropsychidae (mostly cheumatopsyche).	16.0	12 days	37-43 percent survival
	32.0	12 days	20 percent survival
Orconectes rusticus	16.0	9 days	100 percent survival
	32.0	9 days	0 percent survival
Goniobasis livescens	16.0	12 days	40-80 percent survival
	32.0	12 days	0 percent survival
Snail	18.0	96 hours	TLm
	24.0	96 hours	TLm
Chlorella	3.6		Slight growth reduction
Nitzschia linearis	5.8		50 percent growth re- duction in soft water
Navicula seminulum	23.0		50 percent reduction in growth in soft water

TABLE XXIII-5

CRITERIA FOR SURFACTANT CONCENTRATION CONTROL

<u>Concentration</u>	<u>Effects</u>	<u>Ref.</u>
(1) 0.5 mg/l ABS	Max. dosage which produces no long term effects in mammals.	(59)
(2) 3.6 to 5.6 mg/l	TLm, LAS threshold limit for 96 hrs.	(66)
(2b) 0.6 to 3.5 mg/l	96 hr TLm for LAS on Bluegill fingerling flatheads, flathead eggs.	(59)
(3) ABS - 1/7 of 48 hr. TLm LAS - .2 mg/l or 1/7 of 48 hr. TLm	Recommended stream conc.	(6)
(4) 1.0 mg/l	Taste and odor and foaming problems.	(66)
(5) 0.5 mg/l	Max. desirable conc. for human consumption.	(66)

TREATMENT TECHNOLOGY-SURFACTANT REMOVAL

As the form of detergents and synthetic surfactants has changed over time, so has the reason for treatment. The early approach to treating wastes containing soaps was to handle them as other wastes with high BOD. In time, soaps were replaced by the ABS synthetic type which reduced BOD levels from industrial processes substantially. As mentioned previously, the pressure has been applied to the detergent industry to convert to the more readily degradable LAS type surfactants. At this time the state-of-the-art is centered around what form of soft detergents and what type of builders are most appropriate. Should the builder be high or low in phosphates? If phosphates are not used, what is a suitable substitute which is still effective as a cleansing agent, but is not toxic or harmful in some other means?

While the type of soap or detergent has been varying with time, the basic treatment processes remain biological treatment and chemical coagulation. Nemerow (71) indicates that chemical coagulation with alum yields a 90 percent removal of soap BOD from textile mills. He also states (72) that theoretically detergents may be removed to a level of approximately 0.2 mg/l by a combination of coagulation, filtration and adsorption. Table XXIII-6 lists the approximate efficiency of various treatment methods for mixed ABS-LAS and only LAS type detergents.

TABLE XXIII-4 (cont)

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SUMMARY AND RECOMMENDATIONS

On the basis of the literature review, the following conclusions have been drawn:

- (1) The term surfactants for this report includes all methylene blue-active substances which would be included by the Standard Method. While LAS is more prevalent in today's wastewaters, ABS is still used in some industrial operations.
- (2) The major effect of surfactants in water is their tendency to cause foaming, taste, and odor problems. Foaming has been found to decrease as the pollution load in the stream is increased and as the pH approaches neutrality.
- (3) Any taste and odor problem is usually found at and above a surfactant concentration of 1.0 mg/l and chlorination of surfactant bearing wastewaters accentuates the taste and odor.
- (4) The maximum desirable concentration of surfactants in water for human consumption is 0.5 mg/l.
- (5) Some plants have been found to be sensitive to surfactant concentrations in excess of 1.0 mg/l. For fish and other aquatic life toxicity of ABS ranges from approximately 3.0 to 6.0 mg/l. For fish and other aquatic life toxicity of LAS ranges from 0.6 to 3.5 mg/l.

(6) Theoretically, detergents may be removed to a level of approximately 0.2 mg/l by coagulation, filtration and absorption.

(7) Biological treatment or sand filtration is capable of removing 85% of the surfactants, measured as BOD.

On the basis of the foregoing, it is recommended that a uniform effluent criterion of 1.0 mg/l be established for all surfactants, as measured by the methylene blue technique, provided that no foaming is observed at the discharge or immediately downstream. It is further recommended that all dischargers be informed that their average surfactant concentration should be in the range of 0.5 mg/l.

TABLE XXIII-6

TREATMENT METHODS FOR SURFACTANTS (57)

<u>Method</u>	<u>ABS AND LAS Efficiency</u>	<u>Efficiency</u>
Biological:	(% removal as BOD)	(% removal as BOD)
Trickling Filter	52	77
Activated Sludge	67	86
Lagoon		71
Sand Filtration		85

Note: The softer LAS surfactant is easily degraded biologically while the harder ABS is not easily treated.

CHAPTER XXIV-TURBIDITY

SOURCES OF TURBIDITY

Turbidity is a physical parameter which expresses the optical properties of fine suspended matter in solution. This matter may be suspended material such as clay and silt, or organic matter, bacteria, plankton or similar organisms.

The analytical procedures for measuring turbidity vary from a crude visual comparison to comparisons with standard solutions of a kaolinite suspension using sophisticated light scattering measuring devices. The nephelometric method consists of measuring the intensity of light scattered at 90° to the light source. The Jackson candle method uses a standardized bees wax candle to measure the image of the flame as it passes vertically through a sample. It is the standard against which all other methods are based. Results are given in Jackson Turbidity Units (JTU).

To further confuse the issue the Nephelometric method uses turbidity free water to dilute samples having a turbidity greater than 40 Jackson Turbidity Units (JTU) (1). By now it should be apparent that the measurement of turbidity is subject to several variables. The procedures, however, are not the only source of variations. All methods of measuring turbidity are subject to false readings by the presence of debris, coarse sediments, gas bubbles, vibrations, "true color" and the individual optical properties of the particular material in suspension.

Colloidal mica, for example will give highly erroneous readings in comparison to many other materials.

Turbidity is present in most municipal and industrial discharges. Of particular note, however, are industries which use or manufacture large quantities of starch; clays; mineral substances such as zinc, iron, and manganese; fibers and sawdust; and eroded soils. Of special interest are the pulp and paper, mining, dredging, and logging industries (66).

ENVIRONMENTAL EFFECTS OF TURBIDITY

Effect on Man

The primary influence of turbidity in water used for human consumption is aesthetics. Turbidity, however, may be due to toxic trace metals, or disease producing bacteria and virus. Therefore, the turbidity limit has been set at 5 JTU in the Drinking Water Standards (94).

Effect on Man

The presence of turbidity in water used for food preparation, beverages, and high quality products is noted in the literature (66). Certain industries where turbidity is likely to have a deleterious effect are: ice making, laundries, beverage, and brewing, textiles, pulp and paper, steam boilers, and turbine operations.

A summary of the water quality needs of several industries is shown in Table XXIV-1.

TABLE XXIV-1TURBIDITY LIMITS FOR INDUSTRIAL WATER SUPPLIES (66)

<u>INDUSTRY</u>	<u>JTU</u>
Beverages	1-2
Food Products	10
Breweries	1-10
Boiler Feed Water	1-20 (Lowest for high pressure)
Pulp and Paper	
Alkaline Pulps	25
High Grade Paper	5-25
Fine Writing and Book Paper	10
Unbleached Kraft Paper	100
Bleached Kraft Paper	40
Groundwood Paper	50
Textiles	
Nitrocellulose	0.5
Rayon	1
Cotton	25
Cotton (Callaway mills)	0.3-0.5
Baking	10
Cooling Water	50
Ice Making	1-5
Tanning	20

TABLE XXIV-2

AVERAGE FATAL TURBIDITIES FOR FISH (66,6)

<u>Species of Fish</u>	<u>Ave. Exposure, Days</u>	<u>Turbidity, JTU</u>
Rock Bass	3.5	38,250
Channel catfish	9.3	85,000
Pumpkin seed sunfish	13.0	69,000
Largemouth	7.6	101,000
Golden shinner	7.1	166,000
Black bullhead	17.0	222,000

Effect on Fish and Other Aquatic Life

Turbidity may affect fish and aquatic life in four ways: (1) light penetration is decreased thereby decreasing photosynthesis and productivity of fish food organisms; (2) high concentrations of particulate matter can damage sensitive organs (e.g. gills); (3) it may interfere with normal predation and feeding patterns; and, (4) by excluding light, turbidity can modify the temperature structure of impoundments (66).

Direct reduction of fish productivity occurred as the turbidity exceeded 25 JTU, and bottom organisms decreased from 249/sq ft to 36/sq ft due to silting (66). Aquatic insect productivity dropped by 85% below drag line operations. Studies have demonstrated a 41.7% drop in fish yield as turbidity increased above 25 JTU. When turbidity reached 100 JTU, the fish yield was only 18.2% of that in

clear ponds (less than 25 JTU). Similar reductions were found in plankton volumes. (Buck as reported in 6 and 66).

While Wolf and McKee report that fish thrive in waters with turbidities of 200 to 400 JTU, direct lethal effects to eggs are found above 1000 JTU within 6 days. Some of the average turbidities found to be fatal to fish are summarized in Table XXIV-2. In general, as turbidity approaches 20,000 JTU, harmful effects are observed even in adult fish (66).

It is recommended that turbidity in the receiving water due to a discharge should not exceed 50 JTU in warm water streams, 25 JTU in warm water lakes and 10 JTU in cold water streams, cold water or oligotrophic lakes (66).

TREATMENT TECHNOLOGY-TURBIDITY REMOVAL

The removal of turbidity is closely associated with the removal of suspended solids. When the turbidity of a particular wastewater is due to colloidal material, it can be removed by coagulation, sedimentation, and filtration.

SUMMARY AND RECOMMENDATIONS

On the basis of the above discussion, the following statements can be made:

1. Turbidity is a readily observable physical characteristic (not a pollutant itself) and the analytical procedures for turbidity are subject to internal and external variables.

2. Materials which cause turbidity are found in both naturally occurring and industrial discharges. Turbidity is objectionable in domestic water supplies for aesthetic reasons above a level of 5 JTU and is generally objectionable in water supplies because it is an indication of possible toxic and disease producing materials.

3. Many industries require waters with low turbidities (less than 10 JTU) for product quality reasons.

4. Materials which have turbidity in surface waters reduce fish and aquatic life production, water temperatures, and light penetration. Materials causing a turbidity above 1000 JTU begin to have direct lethal effects on fish reproduction, and above 20,000 JTU begin to harm adult fish.

5. Turbidity levels in surface waters should be maintained at or below 50 JTU in warm water streams; 25 JTU in warm water lakes, and, 10 JTU in cold water streams, and cold or oligotrophic waters.

On the basis of the review it is recommended that a uniform maximum effluent level of 50 JTU be adopted. It is further recommended that lower effluent levels be adopted when necessary to maintain the desirable receiving water quality of Summary No. 5 above.

CHAPTER XXV-ZINC

Zinc occurs in the natural aquatic environment as soluble Zn^{+2} salts, soluble inorganic and organic complexes and insoluble precipitates. At basic pH's, the hydroxides and carbonates are readily formed. Zinc occurs naturally and is abundant in rocks and ores in some areas. Table XXV-1 outlines several naturally occurring zinc levels in the environment. The literature contains references to zinc in the ores of lead, copper and gold.

Zinc is used in the automotive industry, viscose rayon production, groundwood pulp mills, and as a corrosion preventative in recycled cooling waters. Concentrations of zinc from major industrial sources as reported in the literature are summarized in Table XXV-2.

As reported by McKee and Wolff (66), zinc is used in a metallic form extensively. Various salts of zinc are noted for use in paint pigment, cosmetics, pharmaceuticals, dyes, and insecticides (66).

ENVIRONMENTAL EFFECTS OF ZINC

High concentrations of zinc in surface waters used for human and animal consumption and for plant irrigation have been found undesirable. Fish and other aquatic life much more sensitive to lower concentrations of zinc.

Effect on Man

Zinc has been found to be both an essential and beneficial element in human metabolism. It has been reported in the Drinking

Water Standards that several enzymes are dependent upon zinc (62). Zinc deficiency has caused growth retardation that is overcome only by an adequate daily intake through the consumption of food and water. Pre-school age children have been found to require 0.3 milligrams of zinc per kilogram of body weight as a daily requirement. The daily adult intake is reported to be 10-15 milligrams, with an excretion averaging about 10 milligrams daily through the feces and 0.4 milligrams through the urine (94). Table XXV-2 shows other zinc concentrations that affect man. McKee and Wolf reported that zinc bearing water should not be used in acid drinks, such as lemonade, due to the possible formulation of zinc citrate and other organic zinc compounds that may be poisonous.

TABLE XXV-1
NATURAL OCCURRING ZINC LEVELS IN THE ENVIRONMENT

<u>Source</u>	<u>Zn Concentration</u>	<u>Reference</u>
Most Plants	1-10 mg/kg	(66)
Cereals	as high as 140 mg/kg	(66)
Sea Water	0.01 mg/l	(6)
Marine Plants	as high as 150 mg/l	(6)
Marine Animals	6-1500 mg/l	(6)

TABLE XXV-2

INDUSTRIAL ZINC BEARING WASTE WATERS

<u>Process</u>	<u>Range</u>	<u>Average</u>	<u>Reference</u>
<u>Zinc Mining</u>			
Mine drainage	-	1450	(45)
<u>Metal Processing</u>			
Pickle bath waste	4300-41,400		(71,72)
Bright dipwastes	200-37,000		(71,72)
Copper Mill Rinse Waters	0.8-13.0	3.1	(65)
Brass Mill Rinse Waters	2.6-10.7	7.4	(65)
Brass Mill Pickle Waste	36-374		(96)
Brass Mill Rinse Waste	10-20		(48)
<u>Plating</u>			
General @ 100 gpm discharge	7.0-215	46.3	(71,72)
@ 50 gpm discharge	1.0-1.7	1.0	(71,72)
w/CN complex			
Plating bath		33,800	(71,72)
@ 0.5 gph drag-out		70	(71,72)
@ 2.5 gph drag-out		350	(71,72)
Plating waste	39-82		(72)
General	2.4-13.8	8.2	(76)
General	55-120		(76)
General	15-20	15	(76)
Zinc	70-150		(76)
Brass	11-55		(76)
Zinc	70-350		(76)
Brass	10-60		(76)
General	7.0-215	46.3	(76)
<u>Silver Plating</u>			
Silver bearing wastes	0.25	9	(71 per 76)
Acid waste	5-220	65	(71 per 76)
Alkaline	0.5-5.1	2.2	(71 per 76)
<u>Rayon Wastes</u>			
General	250-1000		(76)
<u>Automotive Ind.</u>			
General	1-12 16/100 cars		(72)

TABLE XXV-3
ENVIRONMENTAL EFFECT OF ZINC UPON MAN

<u>Effect</u>	<u>Zinc Concentration (mg/l)</u>	<u>Reference</u>
Gastrointestinal irritant	675-2280	(62)
Milky appearance to drinking water	30	(66)
Greasy film on drinking water (after boiling)	5.0	(66)
Taste threshold in spring water	27.2 (as ZnSO_4)	(66)
Taste threshold in distilled water	17.6	(66)
No known detrimental effects	11.2 to 26.6	(66,94)
" "	23.8 to 40.8	(66,94)
Nausea & fainting	30	(66,94)

Zinc may be eroded from zinc plated galvanized pipes and may appear in high concentrations in domestic water supplies. The Drinking Water Standards state that a dissolution of zinc could produce a concentration of 5 mg/l. This would be accompanied by a cadmium concentration of approximately 0.01 mg/l, and a lead concentration of approximately 0.05 mg/l. As a result, the 1946 Drinking Water Standard of 15 mg/l was reduced to a maximum desirable level of 5 mg/l. This level allows for the provision

of zinc, needed for the daily intake, while minimizing taste problems and the formation of an oily film on boiled water.

Effect on Plants

McKee and Wolf reported that while small amounts of zinc are needed for nutrition by most crops, zinc is found to be toxic when the nutritional value is exceeded by a very small amount. They reported that a deficiency of zinc has been found to cause poor growth and dwarfing of the leaves of fruit trees and causes chlorosis in corn. Zinc is present in most plants at a concentration of 1 to 10 mg/kg and as high as 140 mg/kg in cereals. Table XXV-1. Table XXV-4 outlines other environmental effects of zinc on plants and algae.

Effect on Domestic Animals and Wildlife

Animals, like man, require small amounts of zinc in their daily diets. The acidic effects of zinc in the drinking water for animals is apparently of little concern. Table XXV-5 summarizes the effects of zinc on animals.

Effect on Fish and Other Aquatic Life

The sensitivity of fish and aquatic life to zinc has been found to vary with the species, age and condition of the fish as well as the physical characteristics significant in determining the toxic effects of zinc are the hardness of the water, the calcium and magnesium concentrations, the pH, the temperature, and the concentration of dissolved oxygen.

TABLE XXV-4
TOXIC EFFECTS ON PLANTS

<u>Type of Plant (66)</u>	<u>Zinc Concentration (mg/l)</u>		
Orange & Mandarin seedlings	3		
Flax	5		
Water hyacinths	10		
Oats	25-100 (as ZnSO ₄)		
<u>Plankton (6)</u>	<u>22°C</u>	<u>27°C</u>	<u>30°C</u>
<u>Nitzschia cinearis</u> (soft water, 44 mg/l CaCO ₃)	4.29	1.59	1.32
<u>Navicular seminulum</u> (soft water, i.e. 44 mg/l CaCO ₃)	4.05	2.31	3.22

TABLE XXV-5
EFFECTS ON ANIMALS AND WILDLIFE (66)

<u>Type of Animal</u>	<u>Zinc Concentration (mg/l)</u>	<u>Effect</u>
Pigs	1,000 (in milk)	lameness and malnutrition
Laying hens	10,000 (in drinking water)	Reduced egg production, less water consumption, loss of body weight
Rats	50 (in drinking water)	No harmful effect

From the toxicity data in Table XXV-6 it is apparent that the toxicity of zinc to fish life is substantially reduced as the hardness of the water is increased. It is also apparent that the toxicity may decrease slightly with an increase in temperature. There is some discrepancy as to whether it is water hardness, as CaCO_3 , or whether it is the concentration of calcium and magnesium (reported CaCO_3) which controls the toxicity of zinc. While most of the studies on the toxicity of zinc on fish life report variations in relation to water hardness, a report (15) on the toxicity of zinc to plankton referred to the concentration of calcium and magnesium as the critical factors. Results of the study are summarized in Table XXV-4. It is interesting to note from this study that the toxicity of the zinc increased rather than decreased with an increase in temperature for plankton rather than decreased as shown in most of the fish studies.

A review of the literature indicates that copper may have a synergistic effect on the toxicity of zinc. McKee and Wolf reported that 1 mg/l of zinc in the presence of 0.025 mg/l of copper was as toxic to fish life as 8 mg/l of zinc alone. Similarly, the work of Sigler *et al.*, as reported in the water Quality Criteria Data Book Volume 3 (25) indicates that a concentration of 0.6 mg/l of zinc in the presence of 0.048 mg/l of copper was toxic to salmon in soft water. In hard water, McKee and Wolf reported that the threshold concentration of a mixture containing 0.56 mg/l of zinc and 0.44 mg/l of copper was about that which was to be expected assuming no synergism. One is therefore lead to conclude that copper may have

a synergistic effect with zinc only in soft waters (15-20 mg/l as CaCO_3).

TABLE XXV-6

TOXICITY OF ZINC ON FISH LIFE AND EFFECT OF HARDNESS, TEMPERATURE
& pH CONCENTRATIONS, mg/l

<u>Species</u>	<u>Water</u>	<u>Temperature</u> <u>18-20</u>	<u>°C</u> <u>30</u>	<u>Ref.</u>
<u>Lepomis</u>	Soft	2.9 - 3.8	1.9 - 3.6	(15)
<u>Macrochirus</u>	Hard	10.1 - 12.5	10.2 - 12.2	(15)
"	Soft	2.86 - 3.75	0.9 - 2.10	(15)
"	Hard	6.60 - 9.47	6.18 - 9.50	(15)
<u>Physa</u>	Soft	0.79 - 1.27	0.62 - 0.78	(15,66)
<u>Heterostrophia</u> (pond snail)	Hard	2.66 - 5.57	2.36 - 6.36	(15,66)
<u>Pimephales</u>	Soft	0.96	-	(15)
<u>Prumelas</u>	Hard	33.4	-	(15)
<u>Zepomis</u>	Soft	5.46	-	(15)
<u>macrochirus</u>	Hard	40.9	-	(15)
<u>Bluegill Sunfish</u>	Soft	2.9 - 3.8	1.9 - 3.6	(66)
"	Soft	4.2	-	(66)
"	Hard	10.1	- 12.5	(66)
"	Hard	12.5	- 12.9	(66)
<u>Flathead</u>	Soft (50 mg/l)		4.9 @ pH = 8.0	(15)
<u>Minnow</u>	Hard (200 mg/l)		32.3 @ pH = 6.0	(15)

According to McKee and Wolf, the toxicity of zinc salts is also increased as the concentration of dissolved oxygen decreases. The effect of dissolved oxygen on zinc toxicity is the same found for lead, copper, and phenols. They reported a lethal concentration at 60% saturation to be about 85% the lethal concentration at 100% saturation.

McKee and Wolf reported that zinc may also be dangerous to oysters in small concentrations. In large amounts, it has been known to impart a blue-green color. They reported that snails have a toxic limit of 1.0 mg/l zinc in natural waters. McKee and Wolf report that zinc, like several other metals, has been found to be concentrated by various forms of aquatic life. Studies with radioactive Zn^{65} , indicate concentration factors to range from a low of 290 to a high of 200,000.

TREATMENT TECHNOLOGY-ZINC REMOVAL

Removal of zinc from industrial wastewater, plating wastes in particular, may be greatly enhanced by good housekeeping, spill prevention plans, recycling, and countercurrent rinsing. Zinc wastes are more amenable to treatment following concentration of wastewater and a reduction of total flow. The removal of zinc from industrial wastewaters is normally carried out either by chemical coagulation and precipitation, or by a recovery step.

Precipitation

As zinc hydroxide has a limited solubility above a pH of approximately 8.8, it may effectively be removed from wastewaters under alkaline conditions. Lime is normally used to raise the pH, due to its availability and low costs. In acidic industrial wastes, which may be high in sulfates, calcium sulfate will also be precipitated with the zinc hydroxide, forming large volumes of sludge. As a result, the cost of treating wastes with high sulfate concentrations

may be substantially greater due to sludge disposal.

Since zinc bearing wastewaters also often contain substantial concentrations of cyanide and chromium, the cyanide must be oxidized following reduction of the chromium from the hexavalent to the trivalent form prior to precipitation of zinc and other trace metals. The efficiency of zinc removal by chemical precipitation is summarized in Table XXV-7.

The works of Patterson and Minear (76) discussed a new process by DuPont which utilizes hydrogen peroxide, catalyst and stabilizers to oxidize cyanide and promote the formulation of metal oxide in lieu of the hydroxide. As the oxide of metals are most amenable to filtration, lower final effluent levels might be obtainable. A full-scale changeover of this type has been described in the literature (96). The Velco Brass & Copper Company of Kennelworth, New Jersey, converted a former sulfuric chromic acid or ammonium bifluoride-chromic acid pickle to a sulfuric acid-hydrogen peroxide pickle with stabilizer agents. As a result, their previous zinc discharges of 36-375 mg/l have been reduced to their current level of 0.08-1.6 mg/l. This process has reduced their previous costs of \$195 per day without treatment to \$194 per day for total operating cost plus amortized installation costs. A summary of the capital costs for zinc removal by lime coagulation and precipitation is summarized in Table XXV-8. With respect to the operating costs, Patterson and Minear reported that for the General Electric plant referred to in Table XXV-7, treating 30,000 gallons per day the cost was \$3.79 per 1,000 gallons. Other operational costs reported by Patterson and Minear were as low as \$.34 per 1,000 gallons.

TABLE XXV-7

EFFICIENCY OF ZINC REMOVAL BY CHEMICAL PRECIPITATION

<u>Process</u>	<u>Initial</u>	<u>Zinc Concentration mg/l Effluent</u>	<u>Reference</u>
Zinc coag. & precip. & settle	General	0.5-2.5	(97)
	20	Less than 1.0	(76)
	10-20	1-2	(48)
	55-120	Less than 1.0 (av.)	(76)
	Copper Brass fabrication	0.5-2.5	(76)
	Plating wastes	3-4	(61)
Lancy integrated	Plating wastes	0.5	(61)
Zinc coag. & Precip. Settle & Filter	General	0.1-0.3	(97)
	Copper-Brass fabrication	0.1-0.5	(76)
	2.2-6.5 (16 ave.)	0.02-0.23	(76)

TABLE XXV-8

CAPITAL COST OF ZINC REMOVAL

<u>Process</u>	<u>Flow</u>	<u>Cost, \$</u>	<u>Cost, \$/1000 Gal.</u>	<u>Ref.</u>
Lime coag. & precip.	1 MGD	100,000	100	(97)
& settle	10	600,000	60	(97)
Lime coag., precip.	1 MGD	300,000	300	(97)
settle & filter	10 MGD	1300,000	130	(97)
	50 MGD	4600,000	108	(97)
(1957)	0.3 MGD	276,000	9200*	(76)

*Includes vacuum filter cost of \$30,000

Recovery Process

While precipitation, ion exchange, evaporation, and simple process modifications may be utilized for the recovery of zinc, Patterson and Minear have indicated the following: "Unless other process modifications are necessary, or extremely high levels of zinc are present and minimal purification of recovered material is required, zinc recovery is generally not economical."

In contrast with the report of Patterson and Minear, the works of McGarvey, et al. (65) state, "the recovery and disposal of copper and brass alloy metals from washwaters prior to discharge in the stream might be accomplished successfully by employing high capacity ion exchanges such as Amberlite, IR-120. Either the sodium or hydrogen cycle may be used..." Further analysis of this study

indicated that copper, zinc and chromium could be precipitated from the chloride regenerate and recovered by chemical means, or they could be wasted. While Patterson and Minear report that recovery of zinc is generally not economical, or as economical as lime precipitation, they report that recovery by evaporation resulted in substantial savings for one plant. Evaporative recovery preceded by process modifications reduced a total of 3,000 gallons an hour to 50 gallons an hour. It also resulted in chemical savings of more than \$18,000 a year. By following the breakpoint formula presented in the report of Patterson and Minear it is apparent that zinc recovery might be beneficial for large operations with concentrated zinc wastes. It is also questionable whether Patterson and Minear had compared the cost of recovery with simple precipitation and sedimentation or whether they had included the additional cost of filtration. The reports by McGarvey and Patterson and Minear do agree on one point. Zinc may be recovered from precipitates by dissolution with acid. It is also apparent that the total cost of treatment facilities may be recovered from precipitates by dissolution with acid. It is also apparent that the total cost of treatment facilities may be substantially reduced by a reduction in the volume of wastewater to be discharged.

In summary, zinc concentrations in waste waters can be reduced by lime coagulation precipitation and sedimentation to a final

effluent concentration of up to 2.5 mg/l and may be further reduced to a maximum concentration of 0.5 mg/l by filtration.

SUMMARY AND RECOMMENDATIONS

On the basis of this discussion the following statements can be made about zinc:

1. Zinc is abundant in rocks and various metal ores. The marine environment contains 0.01 mg/l of zinc in water, up to 150 mg/l in marine plants, and from 6 to 1,500 mg/l in marine animals, apparently due to natural causes.
2. Major industrial sources of zinc bearing wastewaters are mining and smelting of zinc, metal alloys, and plating operations.
3. Zinc is a necessary nutrient to man, animals, and plants in limited amounts. Surface waters used for irrigation of plants should not contain more than 5 mg/l zinc due to damaging effects. Zinc concentrations in surface waters should be less than 50 mg/l for animal and wildlife watering.
4. Domestic water supplies should not contain more than 5 mg/l zinc for aesthetic reasons.
5. Zinc toxicity varies with respect to the species, age, and condition of fish as well as the water hardness, pH, dissolved oxygen, and other trace metal concentrations. The presence of copper will increase the toxicity of zinc in soft waters. Most forms of fish and aquatic life can withstand short exposure (at least one hour) to a zinc concentration of 1.0 mg/l in both soft

and hard waters. Reductions in the dissolved oxygen of surface waters will increase the toxicity of zinc.

6. Zinc bearing industrial wastewaters can currently be treated by lime coagulation, precipitation, settling, and possible filtration to a maximum effluent level of less than 1.0 mg/l. The cost to reach an effluent level of 1.0 mg/l is within a reasonable economic range, compared to removing other pollutants.

On the basis of the above discussion, it is recommended that a uniform effluent level for zinc be established at 1.0 mg/l. In applying this effluent limit to industrial and municipal discharges, consideration must be given to the concentration of other trace metals such as copper and their synergistic effects. With respect to average operating conditions, of a zinc removal treatment process, the effluent should only contain a zinc concentration in the range of 0.1 to 0.5 mg/l.



APPENDIX

A: References	A-1 -- A-9
B: Water Quality Criteria Recommendations for Total Residual Chlorine in Receiving Waters for the Protection of Freshwater Aquatic Life by W. A. Brungs and Staff	B-1 -- B-9
C: Capital and Operating Costs	C-1

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WATER QUALITY CRITERIA RECOMMENDATIONS FOR TOTAL RESIDUAL
CHLORINE IN RECEIVING WATERS FOR THE PROTECTION OF
FRESHWATER AQUATIC LIFE

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The recommendations are:

<u>TYPE OF CRITERIA</u>	<u>RECOMMENDATION FOR TOTAL RESIDUAL CHLORINE</u>	<u>LEVEL OF PROTECTION</u>
continuous	0.01 mg/liter	This level would probably not protect trout reproduction, some important fish food organisms and could be partially lethal to sensitive life stages of sensitive fish species.
continuous	0.002 mg/liter	This level should protect most aquatic organisms.
intermittent	A. 0.1 mg/liter <u>not to exceed 30 minutes per day.</u> B. 0.05 mg/liter <u>not to exceed 2 hours per day.</u>	These levels should not result in significant kills of aquatic organisms or adversely affect the aquatic ecology.

The above recommendations in clean water require the use of the amperometric titration method that is among the most accurate for the determination of free or combined available chlorine. The method is largely unaffected by the presence of common oxidizing agents, temperature

variations, and turbidity and color, which interfere with the accuracy of the other methods. Simpler methods, such as orthotolidine, are best suited for the routine measurement of total residual chlorine, but are commonly affected by the above interferences and provided appreciably lower values than actually occur (Standard Methods, 1971). These colorimetric methods may provide a measure as low as 10% or less than the real level depending upon interferences.

Despite the fact that there are several significant studies in progress to evaluate the effects of total residual chlorine in waste and cooling waters, there are available sufficient data to make rather accurate estimates of criteria to protect freshwater aquatic life. Studies are being conducted by the National Water Quality Laboratory on sewage plant effluent, the City of Wyoming, Michigan on domestic and combined sewage plant effluent (EPA Demonstration Grant, 17060 HJB), the Michigan Water Resources Commission on chlorinated power plant condenser cooling waters, and the University of California, Berkeley, on the toxicity of treated municipal effluents. It is probably that the results of these studies will either confirm or necessitate more stringent criteria recommendations.

The recommendations for continuous total residual chlorine levels are based on the maximum levels that would provide for the successful completion of life cycles, including reproduction, of aquatic organisms and the relative persistence of total residual chlorine in the environment (Table 1). Obviously the persistence of chlorine is greater than

commonly thought and it clearly does not disappear in minutes as is often stated. The Michigan Water Resources Commission observed fish mortality in cages up to one mile below a sewage outfall (Basch, 1971). In other studies by the same organization, during which total residual chlorine was not measured, fish were killed in cages up to 4 miles downstream (Fetterolf, 1970).

Many of the recent investigations of chlorine toxicity have included analytical determinations of total residual chlorine to which the test organisms were exposed. These more recent studies have also utilized continuous flow procedures which alleviate the problem of gradually declining total residual chlorine concentrations characteristic of static, or standing volume, bioassays. Despite the fact that nearly 120 publications, reports, etc., were read and evaluated prior to making the above recommendations, 15-20 of these papers provided the basis for the recommendations. A summary of these data is shown in Table 2.

Trout and salmon appear to be the most sensitive fish species (Holland, et al., 1960; Merkens, 1958; Arthur, 1971; Basch, 1971; Conventry et al., 1935; Sprague and Drury, 1969; Taylor and James, 1928; and Tsai, 1971). Some fish food organisms such as scuds, cladocerans, and protozoans are also rather sensitive (Arthur, 1971; Arthur and Eaton, 1972; Hale, 1930; Biesinger, 1971). Smallmouth bass are almost as sensitive as trout (Tasi, 1971 and Pyle, 1960) while crayfish, snails, mussels, bullfrog tadpoles, oligochaetes, algae, and stoneflies are

generally more resistant (Sinclair, 1964; Kott, et al, 1966; Learner and Edwards, 1968; Panikkar, 1960; Arthur, 1971; and Coventry, et al, 1935).

The recommendations for discontinuous total residual chlorine in fresh water are on less firm ground due to the scarcity of data on toxic effects during a few minutes to a few hours of exposure. Probably the most pertinent data, again developed by the Michigan Water Resources Commission, observed in a power plant discharge canal erratic swimming by fish of several within 6 minutes of the initiation of chlorination by the plant. At this time the total residual chlorine was 0.09 mg/liter (Truchan, 1971). After 15 minutes there were dead fish at a total chlorine residual of 0.28 mg/liter. Other studies have shown rainbow trout killed in 2 hours at 0.3 mg/liter (Taylor and James, 1928), brook trout median mortality was 90 minutes at 0.5 mg/liter and smallmouth bass median mortality was 15 hours at 0.5 mg/liter (Pyle, 1960). Trout fry were killed instantly at 0.3 mg/liter (Coventry, et al, 1935). Chinook salmon, which have been introduced into Lake Michigan, started to die in 2.2 hours at 0.25 mg/liter in salt water (Holland, et al, 1960). Arthur (1971) has shown that the 1-hour median tolerance limit was slightly above 0.7 mg/liter for fathead minnows, yellow perch, and largemouth bass although the 12-hour median tolerance limits for these species is between 0.3 and 0.5 mg/liter. Unfortunately, no extensive studies have been conducted to determine the fate of aquatic organisms upon returning to water containing no total residual chlorine following

a brief exposure to lethal concentrations. Preliminary studies with Daphnia Magna, a cladoceran, indicate that they did not recover from a 4-hour exposure to what would have been a lethal concentration (0.125 mg/liter), after being returned to uncontaminated water (National Water Quality Laboratory, 1971). In this latter study some fathead minnows were killed in 2 hours at 0.45 mg/liter and 20% were killed in 7 hours at 0.2 mg/liter.

These data indicate the chlorination of cooling water should be avoided whenever possible to reduce undue stress or risk to the aquatic environment resulting from commonly-occurring excessive use of chlorine.

When chlorine is added to water for the purposes of disinfection, reduction of biochemical demand or antifouling, the dissolved materials in the water acted upon are oxidized or combine with chlorine. The addition of chlorine to compounds slows the degradation rate of the compound and is in part responsible for lower or reduced biochemical oxygen demand of a chlorinated waste. Chlorine residual is commonly stabilized by the addition of ammonia and the resulting chloramines persist for much longer periods of time than does the hypochlorite ion. Chlorine is known to combine with organoamines, phenols, lipids, thiocyanate, aromatic hydrocarbons, several pesticides and carcinogens, terpenes and humates.

Experiments are currently underway in several laboratories to assess the extent of the hazards of these organochlorine compounds and to identify them.

We further realize that our recommendations run counter to the minimal recommendations for total residual chlorine in municipal sewage effluent (usually 0.5 to 1.0 mg/liyer). For this reason it is advisable that our Agency seriously consider the feasibility of alternate disinfection procedures to avoid the problem of toxicity and the formation of potentially harmful organochlorine compounds.

TABLE 1

Decline in Total Residual Chlorine with Time in Static
Bioassay Chambers*

TOTAL RESIDUAL CHLORINE (mg/liter)					
<u>INITIAL</u>	<u>2HOURS</u>	<u>7 HOURS</u>	<u>24 HOURS</u>	<u>48 HOURS</u>	<u>72 HOURS</u>
2.10	1.90	1.66	1.09	0.47	0.10
1.02	0.96	0.83	0.42	0.12	0.001
0.50	0.41	0.32	0.18	0.001	0.001
0.26	0.18	0.15	0.04	0.001	0.001
0.13	0.07	0.035	0.001	0.001	0.001

* Nine volumes of Lake Superior water were mixed with one volume secondary sewage plant effluent and the mixture was split and then chlorinated to the initial concentrations.

TABLE II

Selected Summary of Toxic Effects of Total Residual Chlorine
on Aquatic Life.

SPECIES	EFFECT ENDPOINT	RESIDUAL CHLORINE CONCENTRATION, MG/LITER	BRUNGS' REFERENCES
trout fry	lethal(2 day)	0.06	Coventry et al, 1935
rainbow trout	96-hr. TL50 a	0.14-0.29	Basch, 1971
rainbow trout	7-day TL50	0.08	Merkens, 1958
rainbow trout	lethal (12 day)	0.01	Sprague & Drury, 1969
rainbow trout	avoidance	0.001	Sprague & Drury, 1969
brook trout	7-day TL50	0.083	Arthur, 1971
coho salmon	7-day TL50	0.083	Arthur, 1971
pink salmon	100% kill(1-2 day)	0.08-0.10	Holland et al, 1960
coho salmon	100% kill(1-2 day)	0.13-0.20	Holland et al, 1960
pink salmon	max. non-lethal	0.05	Holland et al, 1960
coho salmon	max. non-lethal	0.05	Holland et al, 1960
brook trout	not found in streams	0.015	Tsai, 1971
brown trout	not found in streams	0.015	Tsai, 1971
fathead minnow	96-hr. TL50	0.05-0.16	Zillich, 1969 & Zillich & Wuerthele, 1969
fathead minnow	7-day TL50	0.082-0.115	Arthur, 1971
walleye	7-day	0.15	Arthur, 1971
black bullhead	96-hr. TL50	0.099	Arthur, 1971
white sucker	7-day TL50	0.132	Arthur, 1971
yellow perch	7-day TL50	0.205	Arthur, 1971
largemouth bass	7-day TL50	0.261	Arthur, 1971
smallmouth bass	not found in streams	0.1	Tsai, 1971
scud	safe concentration	0.0034	Arthur & Eaton, 1972
scud	safe concentration	0.012	Arthur, 1971
cladoceran		0.001	Biesinger, 1971
fish species diversity	50% reduction	0.01	Tsai, 1971
protozoa	lethal	0.1	Hale, 1930
fathead minnow	safe concentration	0.0165	Arthur & Eaton, 1972

aTL50 = median tolerance limit

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CAPITAL AND OPERATING COSTS

Individual cost data are presented in the individual sections when such data exist. However, in the treatment of municipal and industrial effluents, a finite number of unit operations are required for the treatment of the wastewater.

Cost data have been prepared by Burns and Roe (23), Datagraphics Inc. (28), Smith (86) and Mitchel (69). These published data include capital, operation, and maintenance costs for the individual processes. Also the total costs, including debt service for the process, are presented. Most of the data were prepared over a different period of time. Hence the cost index is not the same for all of the charts. When the costs for a plant are compared, care must be taken to assure that the same cost index is used for all comparisons.