



**United Nations
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UNEP(OCA)/MED WG.104/Inf.8
30 January 1995

Original: ENGLISH

MEDITERRANEAN ACTION PLAN

Meeting of MED POL National Coordinators

Athens, 18-22 March 1996

UNEP(OCA)/MED WG.111/Inf.7

**GUIDELINES FOR TREATMENT OF EFFLUENTS PRIOR
TO DISCHARGE INTO THE MEDITERRANEAN SEA**

In collaboration with:



WHO



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INTRODUCTION AND BACKGROUND

It is estimated that approximately 80% of the total pollution load of the Mediterranean Sea originates from land-based sources, and a preliminary survey of the overall situation was carried out between 1976 and 1977 within the framework of the Joint Coordinated Programme of Mediterranean Pollution Monitoring and Research (MED POL Phase I), which was operational between 1975 and 1981. In spite of the relatively short period of time (1½ years) provided for development and implementation of the survey, which did not allow for an in-depth study of each individual pollution source along the Mediterranean coastline, it was possible to achieve a comprehensive overview as well as a comparative evaluation of major point and non-point sources. One of the conclusions reached was that while domestic sources largely contributed organic matter (BOD or COD), microbial pollution and nutrients, as well as detergents from household uses and some metals, industrial waste discharges were responsible for considerable amounts of organic matter and suspended solids. Various industrial processes were also found to result in phenol and metal releases, while mineral oils were being largely introduced from refineries and crude oil terminals. A considerable proportion of both municipal and industrial waste was being discharged into the sea in the raw or partially treated state.

Apart from direct discharges into the sea, the report of the project also noted that agricultural run-off was responsible for a considerable portion of the nutrient input to the sea, and major rivers and drains were transporting an integrated load of domestic, industrial and agricultural pollutants from the entire drainage basin into the sea. Apart from contributing to a very high degree to the total pollution load of suspended solids, nutrients, metals and organic matter, these major rivers and drains were also carrying most of the pesticide residues from agricultural areas in the Mediterranean watershed.

The 1976-1977 survey of pollutants from land-based sources in the Mediterranean constituted a major technical input into preparations leading to the development of the Protocol for the Protection of the Mediterranean Sea against Pollution from Land-based sources, adopted and signed by the Governments of the region in May 1980. Under the terms of Article 5 and 6 of the Protocol, Contracting Parties have undertaken to eliminate pollution of the Protocol area from land-based sources from substances listed in Annex I to the Protocol, and to strictly limit pollution by substances or sources listed in Annex II. In both cases, the same articles also provide for elaboration, jointly or individually as appropriate, of the necessary programmes and measures to achieve this aim; in the case of Annex I substances, such programmes and measures also include, in particular, common emission standards and standards for use.

In addition, Article 7 of the Protocol also provides for the progressive formulation and adoption by the Parties, in cooperation with the competent international organizations, common guidelines and, as appropriate, standards or criteria dealing in particular with, *inter alia*, special requirements for effluents requiring separate treatment. The present document, which has been produced in compliance with the above terms within the overall framework of a calendar of activities approved by Contracting Parties for progressive implementation of the Protocol, attempts to summarize the main treatment options currently available for reducing the content of a number of pollutants listed in Annexes I and II to the Protocol (reproduced in Tables 1 and 2) in industrial and, where appropriate, municipal effluents.

The World Health Organization has been technically responsible for preparation of this document within the overall framework of the Long-term programme of pollution monitoring and research in the Mediterranean Sea (MED POL Phase II), operational since 1982.

Preparation of successive drafts of the document, which has been reviewed at a number of expert meetings, was entrusted to the Department of Environmental Engineering, Middle East Technical University, Ankara.

Up to the present time, as publication prepared within the framework of the MED POL programme had covered treatment options for effluents containing Annex I substances, and the first part of this document has therefore involved the breaking of new ground. The second part, covering Annex II substances, has drawn extensively on relevant material from the 1982 WHO/UNEP publication "Waste discharge into the marine environment", with comprehensive updating as and where necessary.

Table 1

Annex I to the Protocol for the Protection of the Mediterranean Sea
against Pollution from land-based sources

A

The following substances, families and groups of substances are listed, not in order of priority, for the purposes of article 5 of this Protocol. They have been selected mainly on the basis of their

Toxicity ;
Persistence ;
Bioaccumulation.

1. Organohalogen compounds and substances which may form such compounds in the marine environment.¹
2. Organophosphorus compounds and substances which may form such compounds in the marine environment.¹
3. Organotin compounds and substances which may form such compounds in the marine environment.¹
4. Mercury and mercury compounds.
5. Cadmium and cadmium compounds.
6. Used lubricating oils.
7. Persistent synthetic materials which may float, sink or remain in suspension and which may interfere with any legitimate use of the sea.
8. Substances having proven carcinogenic, teratogenic or mutagenic properties in or through the marine environment.
9. Radioactive substances, including their wastes, when their discharges do not comply with the principles of radiation protection as defined by the competent international organizations, taking into account the protection of the marine environment.

B

The present annex does not apply to discharges which contain substances listed in section A that are below the limits defined jointly by the Parties.

¹ With the exception of those which are biologically harmless or which are rapidly converted into biologically harmless substances.

Table 2

Annex II to the Protocol for the Protection of the Mediterranean Sea
against Pollution from land-based sources

A

The following substances, families and groups of substances, or sources of pollution, listed not in order of priority for the purposes of article 6 of this Protocol, have been selected mainly on the basis of criteria used for annex I, while taking into account the fact that they are generally less noxious or are more readily rendered harmless by natural processes and therefore generally affect more limited coastal areas.

1. The following elements and their compounds:

1. zinc	6. selenium	11. tin	16. vanadium
2. copper	7. arsenic	12. barium	17. cobalt
3. nickel	8. antimony	13. beryllium	18. thallium
4. chromium	9. molybdenum	14. boron	19. tellurium
5. lead	10. titanium	15. uranium	20. silver

2. Biocides and their derivatives not covered in annex I.

3. Organosilicon compounds and substances which may form such compounds in the marine environment, excluding those which are biologically harmless or are rapidly converted into biologically harmless substances.

4. Crude oils and hydrocarbons of any origin.

5. Cyanides and fluorides.

6. Non-biodegradable detergents and other surface-active substances.

7. Inorganic compounds of phosphorus and elemental phosphorus.

8. Pathogenic micro-organisms.

9. Thermal discharges.

10. Substances which have a deleterious effect on the taste and/or smell of products for human consumption derived from the aquatic environment, and compounds liable to give rise to such substances in the marine environment.

11. Substances which have, directly or indirectly, an adverse effect on the oxygen content of the marine environment, especially those which may cause eutrophication.

12. Acid or alkaline compounds of such composition and in such quantity that they may impair the quality of sea-water.

13. Substances which, though of a non-toxic nature, may become harmful to the marine environment or may interfere with any legitimate use of the sea owing to the quantities in which they are discharged.

B

The control and strict limitation of the discharge of substances referred to in section A above must be implemented in accordance with annex III.

PART I
ANNEX I SUBSTANCES

1. USED LUBRICATING OILS

1.1 General Properties of Used Lubricating oils

Used lubricating oils or waste oil refers to lubricating oils that have gone through their intended use cycle and must be disposed of or treated and re-used. Generally, the term embraces spent automotive lubricating oils and spent industrial oils including those used for lubrication, refrigeration, and process applications.

Lubricating oils are usually of lubricating base stocks, a fraction of crude petroleum that must be separated by vacuum distillation and synthetic chemical additives (UNEP/UNIDO, 1987), the majority of which are polynuclear aromatics (PNAs) (McCabe, 1989). Additives which may comprise up to 15 % of the oil by volume, are typically inorganics such as sulfur, nitrogen, trace and metals (McCabe, 1989), and they are combined with a base stock to improve its properties as a lubricant. However, recent studies have documented that additional compounds such as chlorinated solvents are also introduced either during use, or illegally blended with the used oil during storage. The presence of these compounds, which are suspected carcinogens and mutagens, is the basis of concern about waste oils in the environment (McCabe, 1989).

The definition of used lubricating oils in terms of Annex I to the Protocol for the protection of the Mediterranean Sea against pollution from land-based sources, to serve as a basis for national measures, is given as "any mineral-based lubricating oils which, through use, storage or handling, have become unfit for the purpose for which they were originally intended, in particular used oils from combustion engines and transmission systems, as well as mineral oils for machinery, turbines and hydraulic systems" (UNEP/UNIDO/WHO, 1989). It should be recognized that "used lubricating oils" are those made at least in part from petroleum (including chemical additives) but do not include lubricants that are wholly synthetic or chlorinated lubricating or insulating oils, e.g. those containing PCB's or PCT's. In addition, used motor vehicle lubricants should be included within the scope of the definition of used lubricating oils. However, discharges of oil from oil production, refining and storage installations; and other substances such as pesticide residues, gasoline, solvents, PCB's or hazardous wastes, or include oils with more than specified proportions of other substances should not be included.

The lubricating oils from the refinery process of crude oil are very complex mixtures of hydrocarbons. They contain linear and branched paraffins, cyclic alkanes and aromatic hydrocarbons (UNEP/UNIDO/WHO, 1989). The boiling points of these compounds are between 300 and 600°C. However, lubricating oils obtained from residual fractions contain some compounds with boiling points of up to 815°C (UNEP/UNIDO/WHO, 1989).

Similarly, for the purpose of EEC Directive 75/439/EEC on the disposal of waste oils, the definition of "waste oils" is given as "any mineral-based lubrication or industrial oils which have become unfit for the use for which they were originally intended, and in particular used combustion engine oils and gearbox oils, and also mineral lubricating oils, oils for turbines and hydraulic oils".

1.2 Sources and Inputs into the Mediterranean

The industries giving rise to used lubricating oils are the primary metals, fabricated metal products, machinery, electrical equipment, transportation equipment, chemical products, and rubber and plastic products. Automobiles, trucks, buses and heavy

machine equipment all use oil in their engines, gears, transmissions and hydraulic systems. Therefore, used lubricating oils are also generated from dealerships, service stations and garages. Types and amounts of used oil generated vary with the kind, age and size of the vehicles. Older cars produce more drained motor oil than newer cars, since they must be serviced more frequently. Lubricant used in a diesel engine is different than that is used in a gasoline engine.

Another source of used lubricating oils is terminals and airports at which the lubricants of both railroads and airplanes are collected. Both refrigeration units and shock absorbers also use lubricating oils and generate used oils. These oils are usually made from naphthenic base stocks.

Estimates of quantities of used lubricating oils reaching the sea would have to be based on detailed knowledge of the size, location, and disposal practices of the sources, the number of motor vehicles registered in coastal areas, and the appropriate "per capita" urban runoff amount in different regions.

The urban runoff contribution of the Mediterranean coastal area was estimated to be 48,500 t/a, on the basis of a coastal population of 133 million (UNEP/UNIDO/WHO, 1989). In estimating the total urban runoff contribution, a unit per capita contribution of 1.0 g/cap/d was taken as basis. Although there is a wide variation in per capita petroleum hydrocarbon contribution (Table 1.1), 1.0 g/cap/d was selected as the most reliable estimate.

The municipal wastewater contribution of oil and grease discharge from coastal areas may reach higher levels, such as 4.5 g/c/day which is calculated for Southern California (UNEP/UNIDO/WHO, 1989). Assuming that all wastewaters were discharged through municipal facilities, the municipal wastewater contribution was estimated to be under 218,500 metric tones per year. In these calculations, the total Mediterranean coastal population was taken as 133 million.

The amount of used lubricating oil reaching to the Mediterranean through coastal non-refinery effluent discharges was estimated to be 1.63 million kg per year, by calculating the number of employees in appropriate industries and utilizing the standard estimate for used oil generation per capita on the basis of the Industrial Standards International Classification (ISIC) for each category of employee (UNEP/UNIDO/WHO, 1989).

The total amount of used lubricating motor oils generated in Mediterranean coastal areas was approximated to be of the order of 375,000 metric tones per year (UNEP/UNIDO/WHO, 1989). In this estimation, the average amount of used lubricating oils per vehicle per year, and the total number of vehicles in coastal areas were taken as 25 liters and 15 million respectively.

1.3 Types of Wastes

The types of lubricating oils used in these industries vary widely according to the specifications for particular applications. For practical purposes, three types of used lubricating oils can be considered (UNEP/UNIDO/WHO, 1989):

1. used lubricating oils which can be reutilized;
2. contaminated used lubricating oils, i.e. those containing a certain proportion of toxic substances, while the main constituent remains the lubricating oil;
3. used lubricating oils present in various industrial wastes without, however, constituting the main constituent of such wastes.

Table 1.1

Per Capita Estimates of Petroleum
Hydrocarbons Contributions in
Urban Runoff (UNEP/UNIDO/WHO, 1989) and
Oil in the Sea (National Academy Press, 1985)

Location	Unit PHC Contribution (g/cap/d)
Philadelphia and Trenton	0.03
Narragansett Bay	2.7
Los Angeles (a)	1.9
Seattle	0.3
Sweden (b)	0.3

- (a) Single storm extrapolated to annual runoff
(b) Typical urban area (0.2 parking, 0.3 multi-family
and 0.6 single family)

During oil processing, several types of additives are employed for improving its physical and chemical properties depending on its future utilization. The most important additives are dispersants and detergents which can be as much as 20 per cent of the oil weight (UNEP/UNIDO/WHO, 1989). Besides detergents and dispersants, several dangerous compounds such as zinc diaryl or dialkyl dithiophosphates; molybdenum disulfide; zinc dithiophosphate and other organometallic compounds (Vasquez-Duhalt, 1988) are added for improving the quality of the oil. Therefore, the types of used oils vary according to the specifications for a particular industry. For example, metal working oils contain several additives to reduce wear on cutting and grinding tools. Quenching oils, used to cool hot metals require oxidation inhibiting additives such as barium sulfonate, zinc compounds, sodium nitrate. Transformer oils are mineral oils and they do not contain any additives. Hydraulic oils usually consist of paraffinic base stocks and contain rust and oxidating inhibiting additives such as zinc dithiophosphate. Motor vehicle lubricating oils also contain several additives.

In used lubricating oils, these additives are chemically changed, and the oil is contaminated with rust, soot, dirt, dust, lead, metal particles and water. Therefore, the type and amount of contamination in used lubricating oils depend on its specific use. Table 1.2 lists some compounds of potential concern and potential concentration ranges of these contaminants.

1.3.1 Polynuclear Aromatics

Polynuclear aromatic hydrocarbons such as four-, five-, and six-ring structures, which are present in the petroleum base stock and/or can be produced during the use of the oil, are known as potential carcinogens and mutagens. It is indicated that residual oils (No.6 fuel oil) often contain higher levels of PNAs (20 to 100 mg/kg) than waste oil (<50 mg/kg) and as a result, the substitution of waste oils for these virgin stocks would not have a significant effect on the environment (McCabe, 1989).

1.3.2 Halogenated Hydrocarbons

Halogenated hydrocarbons may be produced in oil during normal use cycle. Virgin lubricating oils typically contain less than 100 mg/kg of these compounds (McCabe, 1989).

1.3.3 Trace Metals

Trace metals are introduced into the oil as part of the lubricating package or from external sources such as the wear of metal parts. Metals such as zinc, chromium, aluminum, and barium are the metals that are introduced during the use. The other metal contaminant, lead is primarily introduced through the use of leaded gasoline in automotive engines. The concentration of lead in virgin oils is given as less than 2000 mg/kg (McCabe, 1989).

Table 1.2
Contaminants of Potential Concern in Waste Oils
(McCabe, 1989)

Organic Contaminants	Probable source	Approximate Concentration, µg/kg
Aromatic hydrocarbons Polynuclear (PNA) benzo(a)pyrene pyrene	Petroleum base stock	360-62000 1670-33000
Monoaromatics alkyl benzenes methalenes	Petroleum base stock	900000 440000
Chlorinated hydrocarbons trichloroethanes trichloroethylene	May be formed chemically during use of contaminated oil	18-1800 18-2600
perchloroethylene		3-1300
		Approximate Concentration, mg/kg
Metals barium zinc aluminum chromium lead	Additive package Engine or metal wear Contamination from leaded gasoline	60-690 630-2500 4-40 5-24 3700-14000

1.4 Waste Treatment Technology

Used lubricating oils may be either re-used or disposed of. They may be re-used as a lubricant following re-refining; or they may be used as a fuel in sludge or solid waste incinerators. Used lubricating oils may also be used as a component in making asphalt, spread to keep down dust on parking lots or roads, or painted on concrete forms of timbers (UNEP/UNIDO, 1987).

In disposing of the used lubricating oils, they may be dumped into a special landfill, or on to an unused lot of land in accordance with hazardous waste treatment requirements (UNEP/ UNIDO/WHO, 1989). The disposal of used lubricating oils into a landfill site is not exercised and nor allowed in EU countries. Another disposal alternative may be high temperature incineration which might cause air pollution problems due to the contaminants.

Spreading the used lubricating oil over the ground in controlled quantities and cultivating the ground might be another disposal alternative. In this way, the oil may be biodegraded (UNEP/UNIDO, 1987). However, great care should be taken in selecting the disposal site; no site should be used for the disposal of the used lubricating oils unless its geological and hydrogeological properties and its surroundings have been appropriately investigated and found to be satisfactory.

1.4.1 Re-Use of Used Lubricating Oils

1.4.1.1 Re-Use as a Fuel

Recycling of used lubricating oils to produce fuel oils is the primary option for re-use. Used lubricating oils might be utilized as a fuel or a fuel supplement in both of sewage-sludge incinerators and public solid waste incinerators. However, used oil burned as a fuel without any precaution for the removal of hazardous contaminants will cause air pollution problems. Therefore, great care should be taken in re-using used oils as fuel.

Reuse of used lubricating oils as a fuel following a reprocessing process such as settling, filtration, and dehydration which will produce a product that can be readily fired in a boiler (McCabe, 1989). The treatment steps are usually minimal in order to maintain the significant cost advantage over virgin oils. The physical treatment does not address the presence of chemical contaminants due to their extremely small particle size. More intensive treatment processes such as centrifugation, clay contacting, and distillation are available to address the problems of contaminants in used oils. However, the high costs associated with these treatment steps is a disadvantage. In general, it is more profitable to continue processing to produce a lubricating-oil base stock through re-refining process (McCabe, 1989).

Current trend in the regulation of recycled oils to be used as fuels indicate that compositional specifications will be applied. U.S. federal specifications for used-oil fuels, as promulgated in 1983, are presented in Table 1.3.

The mentioned specifications are generally equivalent to the worst case levels found in virgin fuels or levels which would not pose a significant health risk upon burning.

The specification for total halogens includes a "rebuttable" presumption that oils containing more than 1000 mg/kg of total halogens -even though concentrations are less than the 4000 mg/kg specification- have been adulterated by blending with hazardous wastes

(McCabe, 1989). Oils with more than 100 mg/kg of any one hazardous constituent are regulated as a hazardous waste fuel, and the burning of these is limited to high-efficiency boilers, industrial-process furnaces, or special burners for hazardous waste incinerators (McCabe, 1989).

Table 1.3

Used-Oil Fuel Specification
(U.S. Federal Register, 1983)

Constituent or property	Allowable level
Arsenic	5 mg/kg maximum
Cadmium	2 mg/kg maximum
Chromium	10 mg/kg maximum
Lead	100 mg/kg maximum
Total halogens	4000 mg/kg maximum
Flash point	37.7° C(100° F) minimum

The use of hazardous wastes as fuel is becoming increasingly attractive. By using hazardous wastes as a fuel supplement in certain production processes such as the cement manufacturing industry, substances and residues produced during incineration may be completely bound in the product without detriment to the environment or to the product. For example, heavy metals within the oil are incorporated in clinker if it is regenerated in a cement factory. The wastes such as waste oil, halogenated hydrocarbons, varnish and paint wastes, old tires and other rubber waste, industrial and sewage sludges with high calorific values etc., are accepted to be suitable for use in the cement production (WHO, 1983).

1.4.1.2 Re-Use as Lubricating Oil

The most desirable method of re-using used oils with a minimum environmental pollution is re-refining of used lubricating oils. Re-refining of used oil to base oil has been excited in industry since the late 1920s, and since then several technologies were developed; such as chemical and mechanical processes (IFP, 1979). However, the relative economics of disposal, versus recovery is extremely important. Whether used lubricating oils are collected and re-refined or disposed of, absent any government intervention, entirely depends on whether it is profitable to collect and to re-refine the oils. In general, as the price of crude petroleum increases, demand for products from used oil increases (UNEP, 1989). However, it is extremely important to consider the costs of environmental damages resulting from the disposal of used oils, for example, the cost may be contamination groundwater that serves as a source of drinking water. Thus, the principle purposes of government intervention to influence private decisions about used oil collection, re-use and disposal are to prevent or limit environmental damage, and as well as to conserve oil resources (UNEP, 1989).

Waste Oil Collection

In some countries as in France, collection of waste oils from users is achieved by licensed societies. Every user in France (garage, greenhouse, commercial and pleasure harbour, etc), is bound to have its used oils collected by a licensed society. It's representative samples of collected oils are made for each user and kept for further investigation if there is a problem. And, in France, up to four societies can be authorized in each area instead of 1, to avoid monopoly situation.

In some circumstances, small independent oil collectors or some firms might collect used oils where and when demand for used oils is high and decline under contrary conditions. These opportunistic entrepreneurs compete with longer-established collection business, also often small, that respond to service calls, or enter into contracts to provide regular pickup or delivery services, or visit generators who usually have considerable quantities of used oils (UNEP/UNIDO/WHO, 1989).

Waste-Oil Re-refining

Rerefining process is the most aesthetically appealing option for dealing with used oils. The goal of re-refining process is to separate the components of waste oil in order to obtain a mineral base oil with the same characteristics as the original base oils. Regeneration of used oils is indicated as the most rational way of re-using waste oils, and in the disposal of the used lubricating oils, priority is given to the recycling of used oils, following their collection. However, while regenerating waste oils, necessary precautions should be taken to ensure that the operation of the regeneration plant will not cause any damage to the environment, and the product from re-refining process will not constitute any toxic or dangerous component. For example, according to EU regulations, all member countries are permitted to re-refine waste oils if the regeneration processes make it possible either to destroy the PCBs and PCTs or to reduce them so that the regenerated oils do not contain PCB/PCT beyond a maximum limit which in no case may exceed 50 ppm. In France, oils with a PCB content of less than 200 ppm and higher than 100 ppm can be regenerated whereas, oils with PCB higher than 200 ppm can not. For the disposal of this type of waste oils, incineration in a specialized treatment plant is required.

Virtually all re-refining processes start with a distillation step to remove water and light ends (the fuel fraction) from the feedstock. The most common re-refining processes are acid-clay, solvent-treatment-distillation-finishing, and distillation-hydrofinishing re-refining processes (McCabe, 1989). The acid-clay rerefining process involves mixing the feedstock with sulfuric acid in order to remove most of the contaminants. Inorganic species, such as trace metals form insoluble sulfates that settle out of the feedstock. Then, the product is neutralized through a clay-contacting step, and also, its color and odor is improved during this neutralization step (Figure 1.1). Solid waste products from this process are acid sludge and spent clay which exhibit the characteristics of a hazardous waste. Thus, there can be significant problems in disposing of these wastes.

Solvent treatment-distillation-finishing re-refining process use vacuum distillation in conjunction with a pretreatment using solvents such as butyl alcohol, isopropyl alcohol, and methyl ethyl ketone (McCabe, 1989). Solvents dissolves the lubricating oil, and the contaminants are removed in subsequent distillation steps (Figure 1.2).

In distillation-hydrofinishing re-refining process, following catalysts-assisted hydrofinishing step for the removal of contaminants, vacuum distillation is applied for the

separation of lubricating base stock from the lighter fuel cut and the heavy residues (McCabe, 1989)(Figure 1.3).

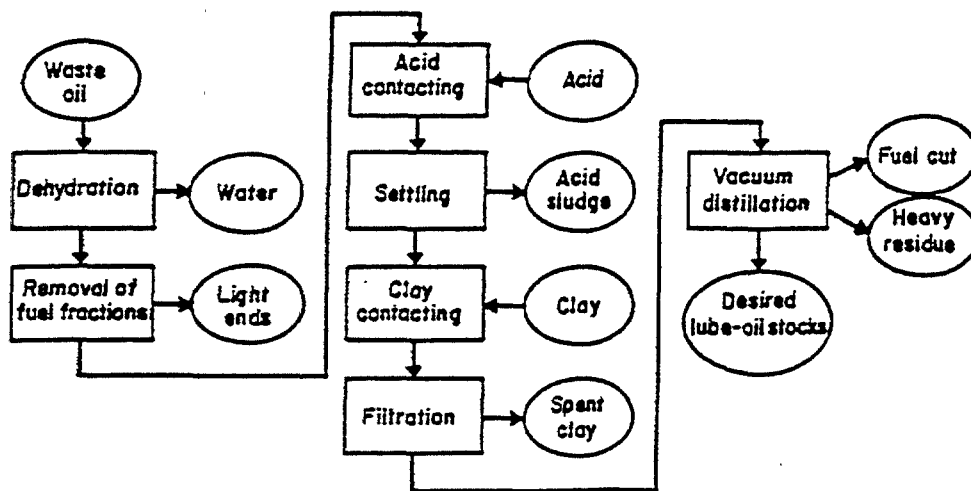


Figure 1.1 Acid-clay re-refining process.

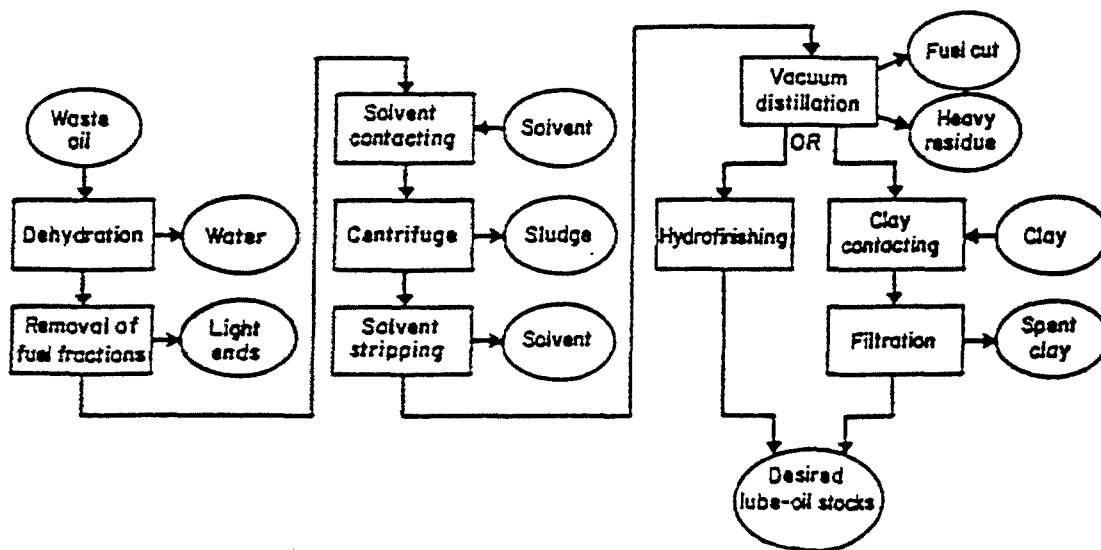


Figure 1.2 Solvent treatment-distillation-finishing.

In another re-refining process which is described for the waste oil from internal combustion engines (Hydrocarbon Processing, 1978) with a composition given in Table 1.4, the first stage is the elimination of the light hydrocarbons and water by distillation. In the second stage, all the impurities picked up during the use in an engine (including the additives and partly degraded polymers) are removed by extraction with propane. In the third stage the extracted oil is fractionated by vacuum distillation. The residue of vacuum distillation is submitted to a second extraction step by which metal content is reduced further. The base oils from vacuum distillation unit are finally hydrogenated in the fourth stage to improve the color and to increase the oxidation resistance of final oil with a composition given in Table 1.5. A distinctive feature of this process is given as the prevention of the production of acid sludges which is important from pollution point of view. In addition, it is stated that the extraction residue can be used as bitumen to waterproof tank, garrets, etc.

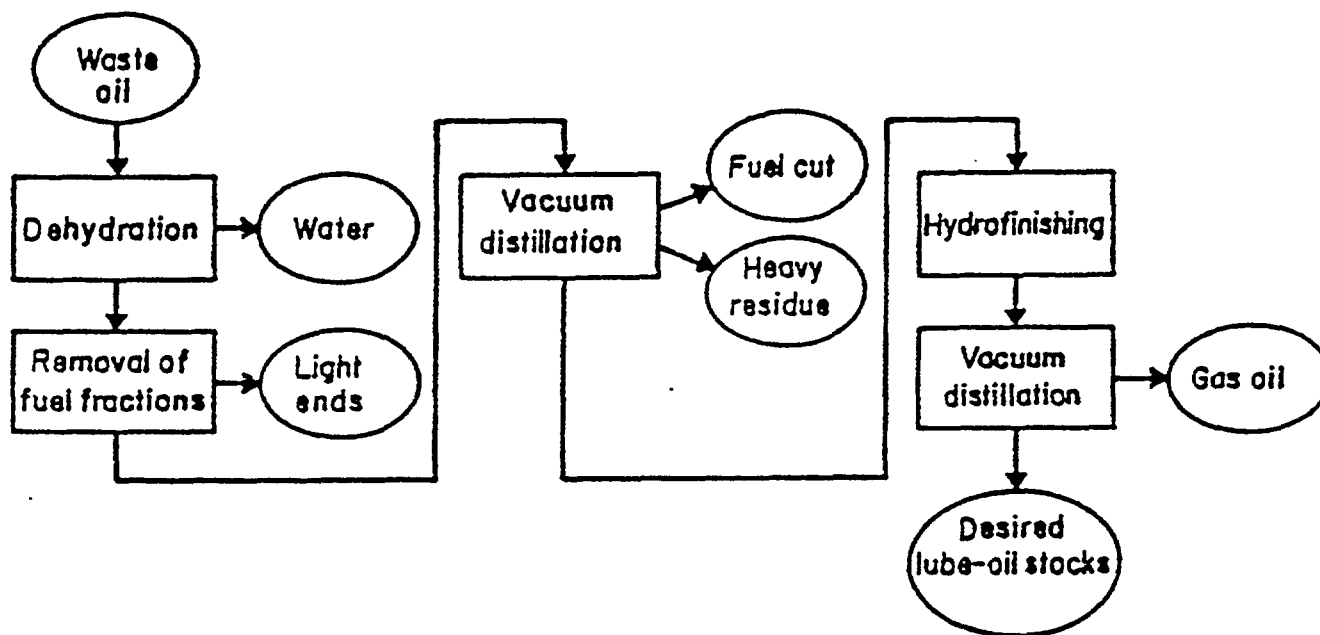


Figure 1.3 Distillation-hydrofinishing re-refining process.

Table 1.4

Waste Oil Composition from Internal Combustion Engines

Feedstock Composition	% weight
Water	7.1
Light distillates	3.4
Mineral oil (properties as follows)	89.5
Specific gravity	0.9104
Viscosity at 100° F, cS	116.1
Viscosity at 210° F, cS	13.2
Neutralization number, mgKOH/g	3.16
Sulfated ash, % wt	1.34
ASTM color	D8
Metal content, ppm	
Barium	400
Calcium	1560
Lead	2600
Zinc	900
Phosphate	850
Chlorine	650
Bromine	580
Copper, Tin, Aluminum, Silicon and Magnesium	traces

Table 1.5

Composition of Final Oil Following Re-refining

Parameter	Light oil	Medium oil	Bright stock
Yield on raw oil	23.4	40.8	18.1
Viscosity at 100° F, cS	28.90	79.54	369.6
Viscosity at 210° F, cS	4.900	9.250	25.22
Viscosity index	101	100	97
Carbon residue, % wt.	0.075	0.10	0.55
Sulfated ash, % wt.	0.04	0.04	0.04
ASTM color (D1500)	1.5	2	1.4
Oxidation test (IP 48)			
Viscosity at 100° F, cS (after oxidation)	34.10	86.86	436.1
Carbon residue, %wt (after oxidation)			
Viscosity at 210° F, cS	13.2		

1.4.2 Disposal of Used Lubricating Oils

1.4.2.1 Dumping into a Disposal Site

Disposal of used lubricating oils might be into the garbage or a landfill, or onto an unused lot of land. However, special care will of course be taken since used lubricating oil contains hazardous substances. Although controlled landfilling methods have proved adequate for municipal wastes and limited amounts of hazardous wastes, they are not suitable for the disposal of large quantities of hazardous wastes, primarily due to: (1) the possible percolation of toxic liquid wastes to the ground; (2) the dissolution of solids followed by leaching; (3) the dissolution of solids hazardous wastes by acid leachates from solid wastes, followed by leaching; (4) the possibility of the development of explosive or toxic gases; (5) the volatilization of hazardous wastes to the atmosphere (Tchobanoglous *et al.*, 1977). Therefore, great care should be taken in disposing of used lubricating oils. Both the site selection and the design in hazardous waste disposal require comprehensive preplanning and environmental impact assessment. Before designing the disposal facility, the followings will be taken as the fundamental considerations (Duvel, 1979):

1. The disposal area must be structurally sound, and environmentally acceptable.
2. The disposal system must conform to all applicable legal and regulatory requirements.

In design, it is absolutely essential to determine waste volume, waste production rate, and physical, chemical and engineering properties, such as moisture content, compression index, specific gravity, etc.. In site selection, there are four broad criteria categories: engineering; environmental; legal, regulatory and political; and economic. Engineering criterion include physical size, proximity, topography etc. Considerations such as quality of surface water, groundwater, air and as well as the protection of terrestrial and aquatic ecology are included under environmental criteria category.

In EU member countries, disposal of used lubricating oils into a landfill site or onto a lot of land is prohibited. Article 4 of the Directive 75/439/EEC states that all member states shall take the necessary measures to ensure the prohibition of:

- a. any discharge of waste oils into inland surface water, ground water, territorial sea water and drainage systems;
- b. any deposit and/or discharge of waste oils harmful to the soil and any uncontrolled discharge of residues resulting from the processing of waste oils;
- c. any processing of waste oils causing air pollution which exceeds the level prescribed by existing provisions.

Thus, EU Member States should take the measures necessary to give priority to the processing of waste oils by regenerating or re-refining.

1.4.2.2 Incineration

Incineration is a process for high-temperature oxidation of gaseous, liquid or solid wastes, converting them into gases and an incombustible solid residue. The flue gases are released to the atmosphere (with or without recovery of heat and with or without cleaning) and any slag or ash produced is deposited in a landfill (WHO, 1983).

Incineration of used lubricating oils or all hazardous wastes prior to land disposal is an excellent means of protecting the land environment. The organic fraction of the waste will be completely destroyed and only the inorganic ash will remain. When the organic structure is destroyed, toxicity will also be destroyed, unless the toxicity is due to other substances such as heavy metals. Therefore, the ash from incineration will only contain inorganic fraction, and has to be disposed of into an authorized land disposal site, or proper sanitary landfill for hazardous wastes, since the volume reduction achieved is very high.

Disposal of used lubricating oils might be achieved in municipal solid waste incinerators. However, as they are currently installed and operated, there are not designed to destroy hazardous materials. Their short-comings primarily include (Lindsey, 1975):

1. Inability to attain high temperatures for the destruction of hazardous substances;
2. Lack of adequate emission control;
3. A design or operation that results in unburned or only partially burned residues;
4. Lack of sufficient instrumentation to permit careful monitoring of operating conditions and combustion efficiencies.

One of the main criteria for using incineration for hazardous waste disposal is the virtually complete destruction of a given material. Successful incineration depends on the "three Ts" of good combustion: time, temperature and turbulence (WHO, 1983). Combustion time may be easily controlled by four methods: excess air ratio, radiant heat transfer, two-stage combustion, and direct heat transfer. However, residence time and turbulence in the combustion zone are related to the design of the incinerator and can only be marginally altered after the incinerator has been built.

There are several types or categories of incinerators available that may be used to thermally decompose various wastes. These include (Hitchcock, 1979) the:

1. Multiple-hearth furnace
2. Rotary kiln
3. Liquid-waste incinerator
4. Waste gas flare
5. Direct-flame incinerator
6. Catalytic combuster
7. Fluidized-bed incinerators
8. Wet-air oxidation unit
9. Molten salt incinerator
10. Multiple-chamber incinerator
11. Ship-mounted incinerator.

Each of these devices has advantages and disadvantages that must be evaluated prior to final process selection. Multiple-hearth either static or rotary sewage-sludge incinerators and fluidized-bed incinerators have a wide application for the destruction of some hazardous wastes (Coleman, 1985).

Multiple-Hearth Incinerators

Among the above mentioned types of incinerators, multiple-hearth incinerators are usually preferred by virtue of their specialized design, long retention times, capability for elevated temperatures, and adequate scrubbing facilities. Therefore, for incinerating used lubricating oils, multiple-hearth sewage-sludge incinerators might be utilized. Fig. 1.4 shows

a multiple-hearth-furnace incineration system. Such furnaces range from 1.5 to 7.5 m diameter and 3.5 to 22.5 m high. The selection depends on the waste feed, the required processing time and the type of thermal processing employed (Hitchcock, 1979).

Normally, waste material enters the furnace through the feed port in the furnace top. A vertically positioned center shaft rotates rabble arms and teeth, and spirals the sludge across the hearths. Waste retention time is controlled by the design of the rabble tooth pattern and the rotational speed of the central shaft. The residence time in a multiple-hearth furnace might change between 0.25 to 1.5 h.

Burners and combustion air ports are located in the walls of the furnace. The temperature (750-1000°C) in each hearth is controlled and adjusted by burner and air port modulation. The exhaust gas is cleaned by passing the hot gas through a precooler and then by spraying water to the cooled gas in a venturi throat.

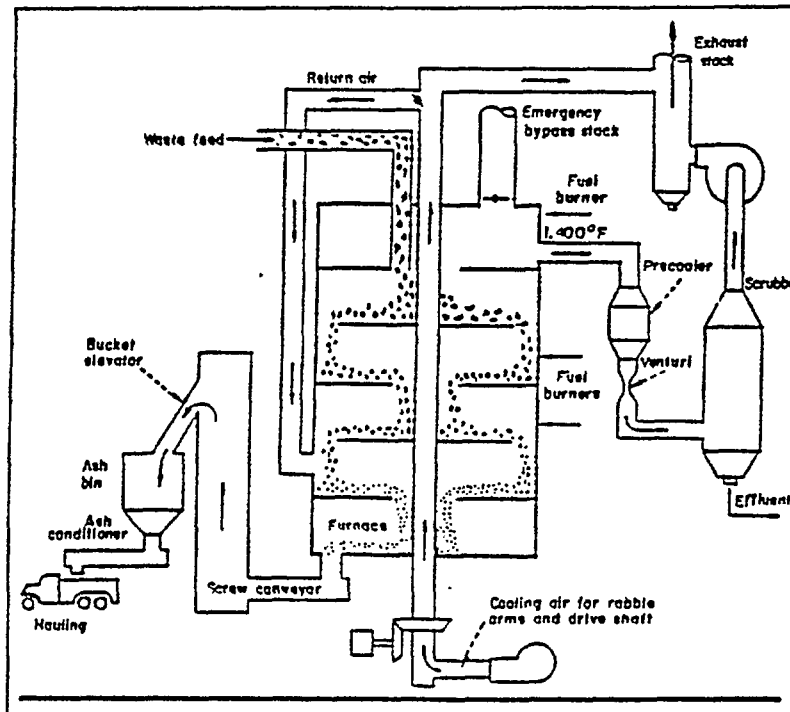


Figure 1.4. Multiple-hearth furnace

In this way, fine particulates are collected on the water droplets. The gas stream with entrained water then enters a particle disengagement unit, if additional cooling is required. The gas is now subcooled and discharged to the atmosphere through an induced-draft fan.

Rotary Kilns

A rotary kiln is a refractory lined steel cylinder which rotates at a very low speed and is mounted on a slight incline so that solid materials introduced at one end will move through the kiln and be discharged at the other end. The burner which is mounted at the same end of the kiln as the solids feed mechanism is fired with natural gas, oil or waste solvents. Solids retention time in the kiln varies from 10 minutes to 30 minutes, whereas the residence time of the combustion gases which are introduced at the burner end, is less than one second. Exhaust gases exit the kiln, which operates with as much as 100% excess air and oxygen, at temperatures of between 815°C and 1100°C. Afterburner insures the complete destruction of the waste materials which might leave the incinerator without complete destruction (Brady and Stratum, 1987).

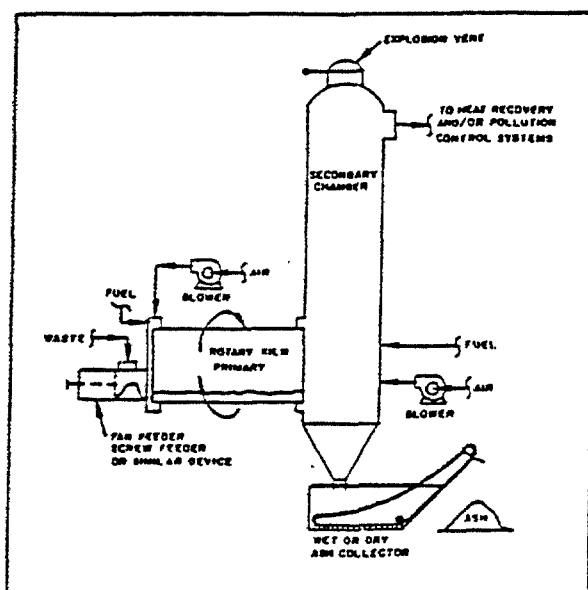


Figure 1.5 Rotary kiln incinerator (Brady and Stratum, 1987).

Figure 1.5 shows a typical rotary kiln incinerator with secondary combustor or afterburner. The major advantage of the rotary kiln incinerators is its ability to handle solid waste materials with widely varied sizes, liquid wastes, high moisture content wastes and sludge-like materials, and materials which form molten slags (Brady and Stratum, 1987).

Fluidized-Bed Combustors

In these systems, the waste material is typically introduced by a screw feed mechanisms into the lower portion of the fluid bed. (Figure 1.6). Air, fuel, or a mixture of both, is introduced through a distributor plate below the solid bed to fluidize the solid material and provide for good fuel, air, and waste mixing. Lime or limestone can also be added to the feed material to adsorb the acid material that will be generated during the combustion process. most of the solid material is then removed by a primary cyclone collector before secondary pollution control systems (Brady and Stratum, 1987).

There are two advantages offered by these combustors over other systems (Brady and Stratum, 1987):

1. Solid adsorbent materials can be introduced with the waste feed to adsorb acid gases,
2. Solids residence time can be controlled by simply decreasing the feed rate and the ash removal rate while maintaining a constant temperature.

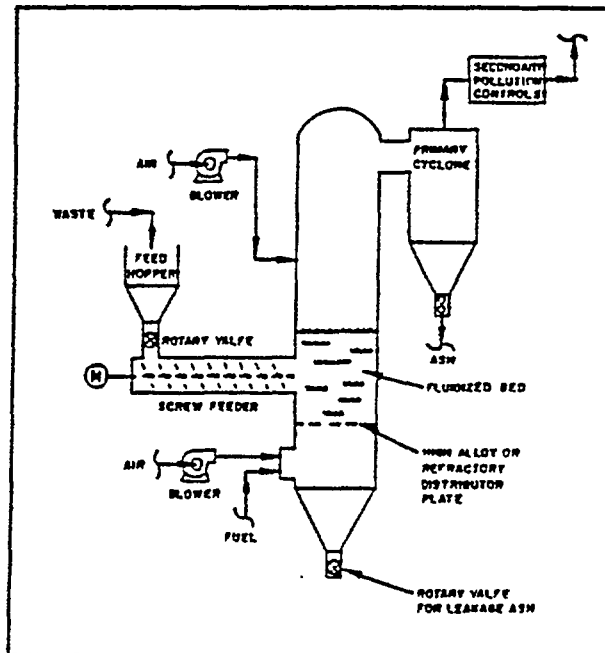


Figure 1.6 Fluidized-bed combustor (Brady and Stratum, 1987).

2. MERCURY

2.1 General Properties of Mercury

Mercury (atomic no.80) is silver-white colored and liquid at normal temperatures. It is the only metal known which is liquid at 0°C. It has an atomic weight of 200.61, melting point of -38.87°C, boiling point of 356.9°C, and specific gravity of 13.546 (Perry and Chilton, 1973). It has oxidation states of I and II (CRC, 1972).

Mercury oxidizes slowly and is insoluble in common solvents. It is not attacked by dilute hydrochloric and sulfuric acids but dissolves in dilute nitric acid and hot, concentrated sulfuric acid (Bidstrup, 1964). It is insoluble in water and alkalis.

Air in equilibrium with metallic Hg contains 13.2 mg/m³ at 20°C. Under ion equilibrium conditions the air over inorganic Hg salts can reach considerable conditions. At

equilibrium HgS reaches $100\text{ng}/\text{m}^3$ in dry air and $5000\text{ ng}/\text{m}^3$ in water-saturated air (Matheson, 1979).

All mercury for commercial use is practically obtained from the ore cinnabar, Hg(II) sulphide which has a very low solubility (solubility product : 10^{-53}) (WHO, 1986). Hg(II) forms covalent bonds and is strongly coordinated with -SH ligands of biological molecules, specially proteins (WHO, 1986).

Mercury forms hundreds of compounds. From eco-toxicological and environmental point of view the most useful and commonly accepted classification is (Goldwater and Stopford, 1977):

- Metallic mercury-liquid and vapor
- Inorganic salts ,such as sulfides,chlorides,nitrates and oxides
- Alkyl compounds such as those containing an ethyl or methyl radical
- Alkoxyalkyl compounds , usually of a complex nature
- Aryl compounds, particularly the phenylmercurials.

2.2 Sources and Inputs into the Mediterranean

The major natural sources of atmospheric mercury are land and ocean degassing, mercury ores, soils, and emissions from volcanoes.

Significant mercury deposits in the world belong to one of the Tertiary or Quaternary belts. the Circumpacific and the Mediterranean-Himalayan belt (UNEP/FAO/WHO, 1987). Map (Figure 2.1) showing the mercuriferous belts of the earth illustrates the wide distribution of the mercury in the Mediterranean basin (Australian Working Group, 1980). It is indicated that 65 per cent of the world's mercury resources are located in the Mediterranean basin which occupies only 1 per cent of the earth's surface (Table 2.1). Therefore, high mercury levels would be expected in the Mediterranean area which is under the influence of the Mediterranean-Himalayan belt.

Land and ocean degassing is another major natural mercury source. Although a precise quantification is difficult, Matheson (1979) suggested that 26,820 t/year of mercury is emitted to the atmosphere through land and ocean degassing. However, the estimate quoted by Miller and Buchanan (1979) is 18,500 t/year which is much lower than reported by Matheson.

The total global deposition of mercury estimated to be $4\text{ to }30\text{ mg Hg-T km}^{-2}\text{ year}^{-1}$ by Lindqvist *et al.*, (1984). However, the estimate for the Western Mediterranean is $50\text{ mg Hg-T km}^{-2}\text{ year}^{-1}$ (Buat-Menard and Arnold, 1978; Arnold *et al.*, 1983) which is higher than that of the total world. This difference was attributed to the industrial sources of Western Europe, and to a lesser extent, inputs into the atmosphere from volcanic activities by these authors.

Table 2.1

Reasonable Assured Mercury Resources and Yearly Production of Mercury
in 1975 (Bernhard and Renzoni, 1977)

	Production (tons)	Reserves (tons)	Ore Grades (%)
Mediterranean:			
Spain	1,622	87,000	1-2
Italy	1,048	21,000	0.5-0.8
former Yugoslavia	584	20,000	0.2-0.9
Algeria	458	?	?
Turkey	300	?	?
Tunisia	?	?	?
Total World	>4,012 8,585	>128,000 215,000	
Mediterranean in % of world	47	65	

Anthropogenic sources of mercury are numerous. The main importance for the marine environment are (UNEP/FAO/WHO, 1987):

- a. river runoff carrying anthropogenic wastes discharge into the river system,
- b. waste discharges directly into the marine environment, either as discharges as liquid effluents or through dumping (e.g. solid wastes, sewage sludge), and
- c. atmospheric inputs of anthropogenic origin.

The estimates of total pollution inputs from land-based sources to the Mediterranean Sea was made within the framework of MED POL-Phase I project (Table 2.2). However, it is pointed out that the estimates may not even be correct in their orders of magnitude due to lack of data.

The major industries discharging mercury bearing wastes are chlor-alkali plants and petrochemical plants. These industries and their waste specifications are discussed in Section 2.3.

The other important anthropogenic mercury releases, apart from above mentioned sources are from laboratories, dentist clinics and hospitals which discharge directly to sewage. High mercury levels in coastal sediments for which no apparent land-based source can be held responsible is attributed to the dumping of sewage sludges in the marine environment.

2.3 Mercury Bearing Wastewater

Mercury metal and mercury compounds are widely used in a variety of industrial applications. Discharge of mercury and its compounds should be strictly controlled and minimized because of its ability to convert to the highly toxic methyl mercury compounds.

Wastes containing mercury originate primarily from the chloralkali industry using the Downs, DeNora, or similar electrolytic cells. The second largest user of mercury is the electrical and electronics industry. The other industries in which mercury and its compounds appear in their wastes are explosives manufacturing, the photographic industry, pesticide and preservative industry and the paint industry (Patterson, 1985).

Table 2.2

Estimates on Inputs of Mercury in the Mediterranean
(UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984)

Region	Originating in coastal zones				Carried by rivers		total
	domestic		industrial		t/year	% total	
	t/year	% total	t/year	% total			t/year
I	0.04	2	0.6	24	1.8	74	2.5
II	0.28	1	2.7	8	30	91	33
III	0.04	1	0.2	7	2.5	92	2.7
IV	0.12	1	1.1	10	9.5	89	10.7
V	0.08	>0	0.5	1	40	99	41
VI	0.03	>0	0.16	2	9.6	98	9.8
VII	0.03	2	0.16	9	1.5	88	1.7
VIII	0.05	>0	0.2	2	14	98	14.3
IX	0.01	>0	0.05	1	7	99	7.1
X	0.07	1	1.2	17	5.6	82	6.9
Total	0.75	0.6	6.87	5.4	121.5 *	94	129.7

* In this amount 32 metric tons were considered as "background"

Mercury is also used as a catalyst in the chemical and petrochemical industry (Patterson, 1985). Pulp and paper operations have used mercurials as fungicides, and biocides (Cheremisinoff and Habib, 1972). Other sources of mercury wastes are research and hospital laboratories, sealants used in machines, and thermometers and manometers (Patterson, 1985). Table 2.3 gives the summary of mercury concentrations reported in industrial effluents.

Table 2.3

Levels of Mercury in Industrial Wastewater

Waste	Mercury, µg/L	Reference
Paper mill	20-34	Bouveng, 1979
Fertilizer mill	0.26-40	Bouveng, 1979
Smelting plant	20-40	Bouveng, 1979
Chlor-alkali plant	80-2000	Bouveng, 1979
	4600-5100	Smith and Ward, 1976
	1400-2800	Gurney, 1971
	3000-8000	Bieling <i>et al.</i> , 1975
	300-6000	Perry, 1974
	21500	Diaz <i>et al.</i> , 1977
Water-base paint	300	US EPA, 1975
Paint and ink formulation	0-120000	US EPA, 1980
Acetaldehyde production	20000	Irukayama, 1966
Fluorescent lamp production	2	Ohtsubo, 1977
Textile dyeing waste	15000	Chu and Ruane, 1978
Textile mill waste	11	Branden <i>et al.</i> , 1975
Rubber processing	0-720	US EPA, 1980

2.4 Principal Industries

2.4.1 Chloralkali Industry

2.4.1.1 Type and Size of Industry

Chlorine, sodium and potassium hydroxide are produced entirely by electrolytic methods from fused chlorides or aqueous solutions of alkali metal chlorides (Shreve, 1977). Mercury cells or electrolytic cells with mercury cathode are extensively used in chloralkali industries. The overall trend in the world seems to be towards installing an increased capacity in mercury cells for chlorine production, as against other methods of production (OECD, 1974).

Ideally, the mercury used in these cells is recyclable. However, mercury losses of these industries to waste discharges have been variously reported as 0.1 g per ton of chlorine produced (Patterson, 1975). A new mercury cell installation may require an initial charge of mercury of up to 450 kg per ton per day chlorine capacity (OECD, 1974).

In EU member countries, disposal of mercury is done according to EEC directives 82/176/EEC and 84/156/EEC.

The chloralkali plants may have a design capacity of 60000-75000 tones of chlorine per annum (BNF Metals Technology Center, 1979).

2.4.1.2 Types of Wastes

In the chloralkali industry, the main mercury losses appear to be in the spent brine and wash water. Caustic, one product of the chloralkali process has also been reported to contain very high levels of mercury (Table 2.4) (Patterson, 1985).

Wash waters arise in the following operations: cleaning of the electrolysis tanks, washing of the decomposers, stripping of the filters from the mercury containing sludges, washing of the cell room floor and cellar and occasionally rainwater (BNF Metals Technology Center, 1979). All wastewaters are collected and conveyed into a tank in which mercury will be separated from water.

Table 2.4

Mercury Content of Caustic from chlor-Alkali Plants
(Patterson, 1985)

Mercury, mg/L	Reference
0.07-18.8	Bouveng, 1979
125-150	Newell, 1971
7.0-42.0	Bouveng, 1968

2.4.1.3 Form of Wastes

Basically, the wastes originating from the use of mercury electrodes in the chloralkali industry contain mercury in elemental form.

Among the wastes generated, wash waters are alkaline and may contain globules of metallic mercury (insoluble) and other impurities, such as suspended solids, oil and grease. However, the spent brine is acidic and has a pH value of 3. The main characteristics of discharges from chloralkali industries is reported in Table 2.5.

2.4.1.4 Total Amounts

The total amount of wastes generated varies with the size of the plant. However, the amount of mercury losses was reported to be 0.1 kg-0.15 kg per ton of chlorine produced (Zugger and Ghosh, 1972; WHO, 1982). Table 2.6 presents the emission factors for the manufacture of sodium hydroxide through mercury cell process.

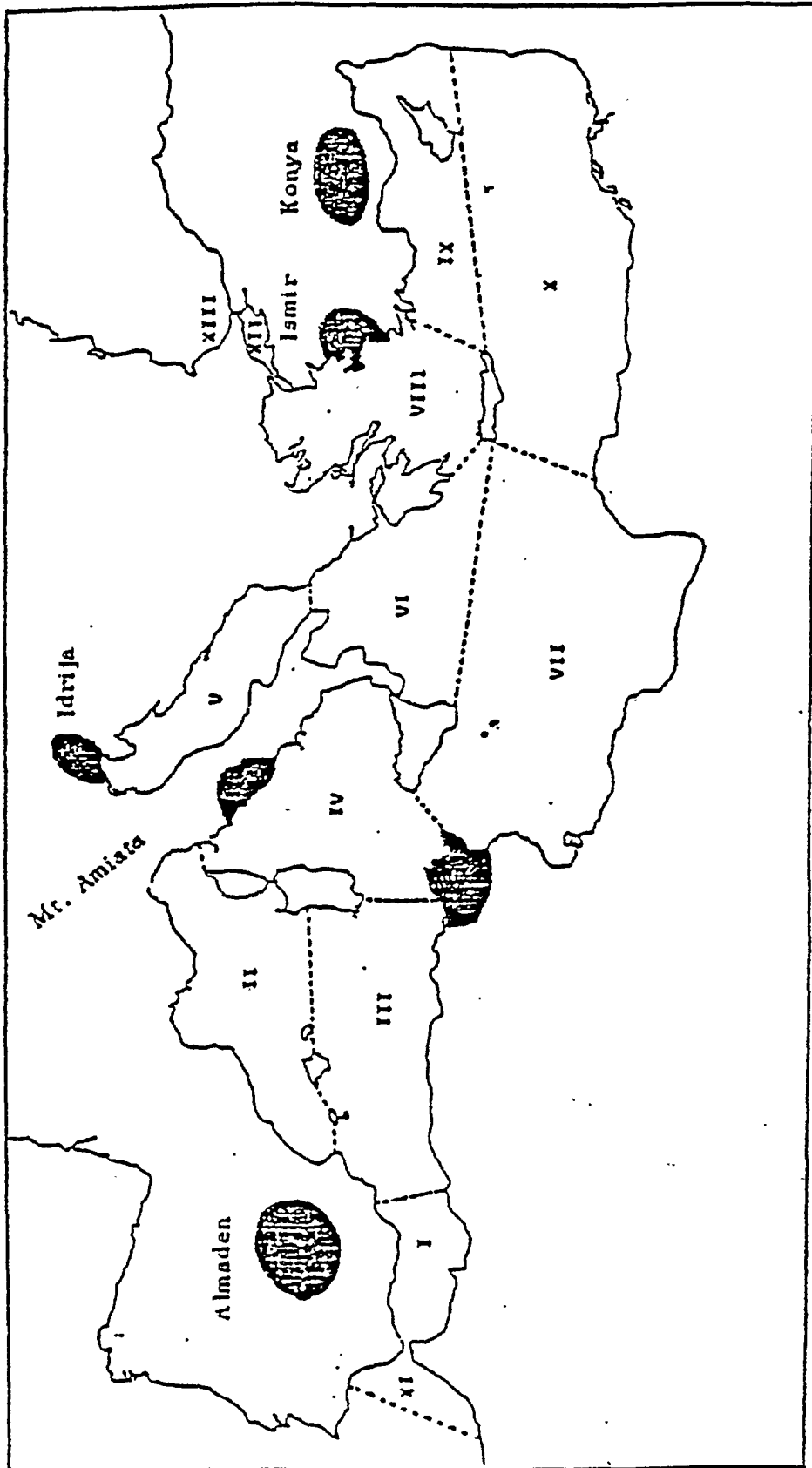


Figure 2.1 MED POL areas

2.4.2 Electrical Apparatus and Control Instruments

In electrical apparatus, mercury is used in fluorescent and mercury discharge lamps, and also in industrial power rectifiers. In control instruments, mercury metal is used in thermometers, gauges, barometers, pump seals, electrical switches etc. One other great use of mercury in these categories is as mercuric oxide in mercury cell batteries.

Table 2.5

Main Characteristics of Chloralkali Wastewaters
(Macchi *et al.*, 1985)

Parameters	Concentration (kg/t of Cl ₂)
Total mercury, mg/L	1-10
Dissolved mercury, mg/L	0.5-10
Total alkalinity (NaOH), mg/L	500-5000
Total Chlorides (NaCl), mg/L	10000-100000
Chlorine (Cl ₂), mg/L	0-100
Suspended matter, mg/L	150-400
Temperature, °C	20-40
pH	> 10

Table 2.6

Emission Factors for Wastewater from Mercury Cell* -Caustic Production
(WHO, 1982)

Parameters	Concentration (kg/t of Cl ₂)
NaOH	13.5
NaCl	211
H ₂ SO ₄	16
Chlorinated hydrocarbons	0.7
Na ₂ SO ₄	15.5
Cl ₂ (as CaOCl ₂)	11
Filter acids	0.85
Mercury	0.15
TSS [#]	2.2

* Produced by addition of HCl to acetylene.

[#] Produced by cracking ethylene dichloride.

2.4.3 Amalgamation , Dental Amalgams

Metallic mercury and/or inorganic mercury compounds are used in electrolytic processes for the recovery of metals such as zinc, gold, silver by amalgamation. Metallic mercury is also used in small proportions in amalgams with silver and tin for dental fillings. Losses from dental clinics are a potential source of environmental contamination.

2.4.4 Catalysis

2.4.4.1 Type and Size of the Industry

Mercuric chloride (HgCl_2) or mercuric sulphate (HgSO_4) are used as catalysts in the production of polyvinyl chloride (PVC) and polyvinyl acetate (PVA) (UNEP/FAO/WHO/UNIDO, 1987). In the production of PVC which is the fastest growing branch of the vinyl family, vinyl chloride is made from ethylene through the catalytic action of mercuric chloride, and PVC is produced by the emulsion polymerization. Emulsion polymerization is the most widely used process (Nemerow, 1978).

2.4.4.2 Types of Wastes

A vinyl chloride production facility generates a waste stream containing minor amounts of organics (4.5 g/ton) with significant amounts of NaCl, and FeCl_3 . However, the waste stream from the PVC operation is high in COD; having COD of 1200 to 1500 mg/L. The characteristics of wastewaters generated from a petrochemical plant is given in Table 2.7.

2.4.4.3 Form of Wastes

Wastewaters in the PVC production are generated from the centrifuges in which the polymer slurry mix is washed and dewatered. In addition to a high COD load, the effluent from the centrifugation step contains suspending agents, surface-active agents, catalysts, small amounts of unreacted monomer, and significant amounts of very fine particles of the polymer product (Nemerow, 1978). The waste generated from an average plant producing 45000 tons of vinyl resins a year contains 450 tons of BOD, and 70 tons of suspended solids (Nemerow, 1978).

2.4.4.4 Total Amounts

PVC producing plants produce between 0.4-0.8 tons of waste per ton of product (Nemerow, 1978). However, in vinyl chloride plants the waste produced per ton of product increases up to 8 tons.

2.5 Treatment

There are many types of treatment technology available for mercury control. Common methods include precipitation, ion exchange, adsorption, coagulation, and reduction of ionic mercury to elemental form and removal by filtration. The selection depends upon the chemical nature and initial concentration of mercury, the presence of other constituents in the wastewater that may interfere with that specific treatment, and the degree of mercury removal that must be achieved (Patterson, 1975).

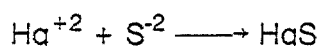
Table 2.7

Main Characteristics of Petrochemical Plant Wastewaters
(Beccari *et al.*, 1985)

Parameters	Concentration (kg/t of Cl ₂)
Total mercury, mg/L	1-10
Dissolved mercury, mg/L	0.5-10
Total alkalinity (NaOH), mg/L	500-5000
Total Chlorides (NaCl), mg/L	10000-100000
Chlorine (Cl ₂), mg/L	0-100
Suspended matter, mg/L	150-400
Temperature, °C	20-40
pH	> 10

2.5.1 Precipitation

Sulfide addition to precipitate mercury as mercury sulphide HgS which has a solubility product of 10^{-58} is the most common and preferred precipitation treatment reported (BNF Metals Technology Centre, 1979). This is done according to the following reaction (BNF Metals Technology Center, 1979):



The standard method of precipitating mercury is to adjust the pH to between 5 to 6 with sulfuric acid and then add a sulfide forming agent to a slight excess (Lanouette, 1977). Various mercury sulphide forming reagents such as sodium sulphide, sodium hydrogen sulphide, hydrogen sulphide, sodium dithionite, thiourea, etc. might be used.

Precipitation may possibly be combined with flocculation and sedimentation in a lagoon, and filtration or dissolved air flotation. These steps improve the collection of precipitated mercury sulphide, but do not enhance the efficiency of precipitation.

In sedimentation, collection of precipitate can be improved by addition of ferric chloride as a coagulant. All the waste water to be treated should be conveyed into a single tank and the treating reagent should be added at a controlled rate. A mercuric sulphide slurry will be formed and allowed to remain in that tank long enough to produce a suspension of uniform density (BNF Metals Technology Center, 1979). The slurry is then transferred into a mixing tank where a flocculent is added, then placed into another one where flocculation takes place (Fig.2.2). The HgS flocs precipitate out and is separated in a lagoon or clariflocculator from which the clear liquid overflows to the final neutralization step. The clear liquid can be treated by a further polishing stage. The slurry is then treated for mercury recovery, usually by retorting. Disposal to dried wells or mine shafts of proven environmental integrity is sometimes used (BNF Metals Technology Center, 1979).

In the filtration process, after mercury sulfide precipitate is formed, the slurry is filtered off by a special type of sand filter or a high pressure, leaf filter, and the filter cake is treated as above if the mercury is to be recovered (BNF Metals Technology Center, 1979).

Effluent mercury levels less than 0.2 and 0.1 mg/L can be achieved with the sedimentation and filtration process respectively (BNF Metals Technology Center, 1979). These figures are for an influent mercury level of 5-20 mg/L.

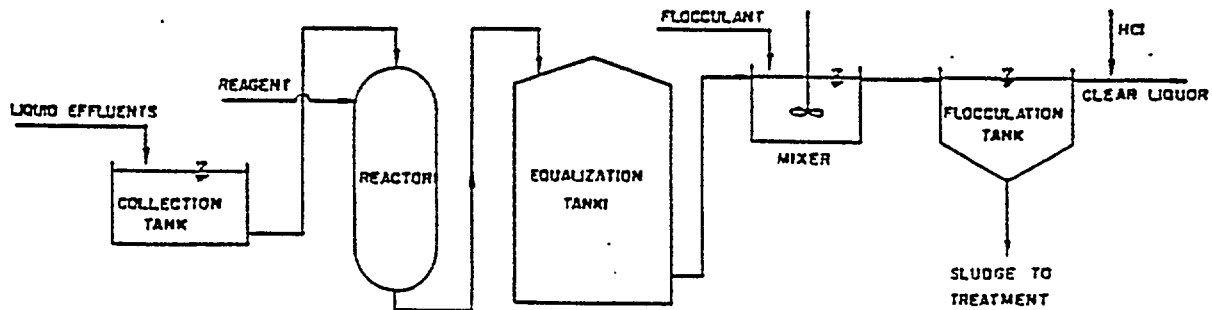


Figure 2.2 Precipitation treatment of mercury.

The sulphide precipitation process is reported to be the most convenient method for treating large volumes of effluents (such as wastes from chlorine production by the waste brine process). However, if the volume to be treated is relatively small, it is possible to use more sophisticated processes which are more expensive and can produce treated effluent at a lower concentration than the sulphide precipitation process (BNF Metals Technology Center, 1979). It is of course possible for these lower levels to be achieved by the sulphide precipitation process if it is backed up by a second stage (BNF Metals Technology Center, 1979).

Therefore, as reported by Macchi *et al.*, (1985), these conventional precipitation processes are not completely satisfactory in achieving mercury concentration below 10-20 $\mu\text{g/L}$. In addition, these processes produce a big quantity of sludges to be disposed of (Trivanti *et al.*, 1980).

In recent years, attention has been drawn upon a precipitation process utilizing some derivatives of starch (Marani *et al.*, 1980; Macchi *et al.*, 1985; Tiravanti *et al.*, 1985; Trivanti *et al.*, 1987). The processes proved efficient in removing Cd, Cr(III), Cu, Pb, Hg(II), Ag, either separately or in combination. Baccari *et al.*, (1985) studied the precipitation of mercury, or more specifically precipitation of mercury in chloralkali wastewaters, and indicated that, in the absence of chlorides and within the considered pH range (10-12), mercury can be removed quantitatively to a final residual level of $<20 \mu\text{g/L}$ by precipitation with starch xanthate if this reagent is added in 1:1 xanthate: mercury molar ratio. The presence of mercury chloro-complexes, such as those in solution containing 0.1 M NaCl at pH less than or equal to 9, affects the kinetics of precipitation reaction. Mercury removal to a residual level of $0.036 \mu\text{g/L}$ at pH 11 was reported in the presence of 0.1 M NaCl in a suitable time. And, process applicability of this precipitation technique to chloralkali wastewaters has been verified by Tiravanti *et al.*, (1987) in pilot plant tests.

2.5.2 Carbon Adsorption

In dealing with mercury removal by activated carbon, several factors, such as pH, activated carbon type and dosage, initial form and concentration of mercury, and contact time between the carbon and mercury-containing wastewater, effect the treatment efficiency. Increasing carbon dosages and increasing contact times improve the removal of both organic and inorganic mercury (Logsdon and Symons, 1973). Logsdon and Symons (1973) also reported that granular activated carbon is most effective in removing organic mercury and powdered carbon is almost equally effective for both the inorganic and the organic mercury. In general, organic mercury is more effectively removed than inorganic mercury (Patterson, 1975). Patterson (1975) also indicated that the highest percentage removals (85-99 per cent) result from carbon treatment of more concentrated mercury solutions. However, the lowest effluent mercury results from the treatment of lower initial mercury concentrations, although the relative efficiency is less. Thus, when mercury is present at a low concentration, the activated carbon process is able to achieve a low removal efficiency, less than 70 per cent. But a low effluent mercury level, such as 0.25 µg/L (Patterson, 1975). However, at high initial mercury concentrations such as 5-10 µg/L the yield is about 80 per cent removal and effluent levels are below 2 µg/L (Patterson, 1975). But, the results reported by Sigworth and Smith (1972) are not similar to those of Patterson (1975); Sigworth and Smith (1972) reported that methyl mercuric chloride could be reduced 30-54 µg/L to less than 1 µg/L by treatment in a granular activated carbon column.

The saturation adsorption capacity of certain type of carbon activated carbons for mercuric ions was reported as 138 mg/g. In addition, the adsorption capacity was found to be carbon particle size dependent possibly due to the fact that the solute molecules can not penetrate all the pores within the carbon particles.

Maruyama *et al.*, (1975) applied activated carbon adsorption following high lime treatment (600 mg/L), and reported that activated carbon adsorption increased removal to approximately 90 per cent, whereas the clarification and filtration following lime treatment removed 70 per cent of the initial mercury.

2.5.3 Ion Exchange

Ion exchange seems to be an effective means of removing inorganic mercury down to levels of 1 to 5 µg/L (Patterson, 1975). The most effective ion exchange treatment is reported to be a two system; on the slightly acidic side (Lanouette, 1977).

In general, ion exchange treatment of inorganic mercury involves the formation of mercuric chloride complex and the removal of this complex on an ion exchange resin. In removing negatively charged mercuric chloride complex, an anion exchange resin is utilized. This treatment systems especially allows the removal of mercury from the chloralkali wastes, since these wastes contain high background chloride concentrations (Patterson, 1975). In wastes where chloride is not high, cation exchange resins are utilized for mercuric ion removal. In addition, cation exchange resins containing -SH groups (mercaptans) are reported to be effective in adsorbing chloride-complexed mercury (BNF Metals Technology Center, 1979). DeJong and Rekers (1974) indicated that the mercury content of a chloralkali wastewater can be decreased down to less than 5 ng/l with the use of a specific resin, IMAC TMR containing thiol groups. In this process, as described by Rosenzweig (1975) wastewater first flows into an oxidation reactor together with a slight excess of sodium hypochlorite or chlorine (Fig. 2.3). Metallic mercury is oxidized or converted to ionic form with chlorine, and pH is controlled at about 3 in order to prevent problems in subsequent filtration from iron

hydroxides. Sand filter not only removes solids that might plug the ion-exchange beds, but also retains and oxidizes mercury droplets that might have passed through the oxidation reactor. Mercury-free solids are periodically discarded from the filter. The liquid is next dechlorinated, to prevent contamination of the ion-exchange resin in an activated carbon column. The liquid then passes to a pair of vessels containing the IMAC TMR ion-exchange resin. The resin does not contain any nitrogen compounds, avoiding formation explosive nitrogen trichloride. The resin maintains its performance under wide fluctuations of pH (1-14), temperature, and concentration of sodium, chlorate and sulfate ions (Rosenweig, 1975).

Resins can be regenerated up to five times. Use of hydrochloric acid solution as regenerant for chlor-alkali plants is recommended. For non-chlor-alkali services, a proprietary regenerant is offered.

2.5.4 Coagulation-Flocculation

Organic and inorganic mercury can be removed from wide variety wastewaters with the use of flocculants such as alum, iron salts and lime (Patterson, 1975). Patterson (1975) indicated that in the literature, effluent levels of mercury achieved by alum treatment range from 1.5 to 102 µg/L, and by iron treatment from 0.5 to 12.8 µg/L.

Maruyama *et al.*, (1975) applied lime as coagulant for mercury treatment and indicated that 70 per cent of the initial mercury (0.5 mg/L) can be removed following clarification and filtration. The lime dosage and the operating pH for the pilot plant were 600 mg/L and 11.5 respectively.

Logsdon and Symons (1973) reported that inorganic mercury can be removed effectively by both iron and lime coagulation while neither coagulant is effective in removing methyl mercury. The highest inorganic mercury removal was reported to be about 65 per cent by alum (20-30 mg/L) coagulation. However, the per cent removals of both methyl mercury and inorganic mercury were turbidity dependent; better removals were observed with higher initial turbidities.

2.5.5 Reduction Process

Mercury removal through the reduction process can be achieved with inorganic ionic mercury. In the process, there are two basic steps; reduction of mercury into elemental form by the help of a reductant and separation of metallic mercury by filtration or other solids separation techniques. A variety of reducing agents such as aluminum, zinc, hydrazine, stannous chloride, and sodium borohydride are available (Patterson, 1985). Reduction processes for inorganic ionic mercury removal do not appear to yield an effluent of below 100 µg/L (Patterson, 1975). Therefore, it is necessary to use a second polishing stage following the reduction process. However, the main advantage of these processes is that mercury can be recovered in metallic form.

Use of zinc dust for the reduction of mercury has been reported as effective in removing the mercury (Richard and Brookman, 1971). The tests performed on a mercury containing waste (432 mg/L) from a plant engaged in the production of both organic and inorganic mercurials revealed that mercury removal in excess of 99 per cent may be achieved. In the process, the first step is the adjustment of pH to 4.0, since the optimum removal was obtained at initial pH values between 4.0 and 6.0 (Fig.2.4). Following this, zinc powder is added, mercury is reduced to the elemental state, and a stable complex is formed with the excess of zinc. Subsequently, this compound is removed by a conventional solid-liquid separation method. The optimal zinc dosing for this waste was reported to be 3.8 kg of Zn/kg Hg and resulted in 99 per cent mercury removal.

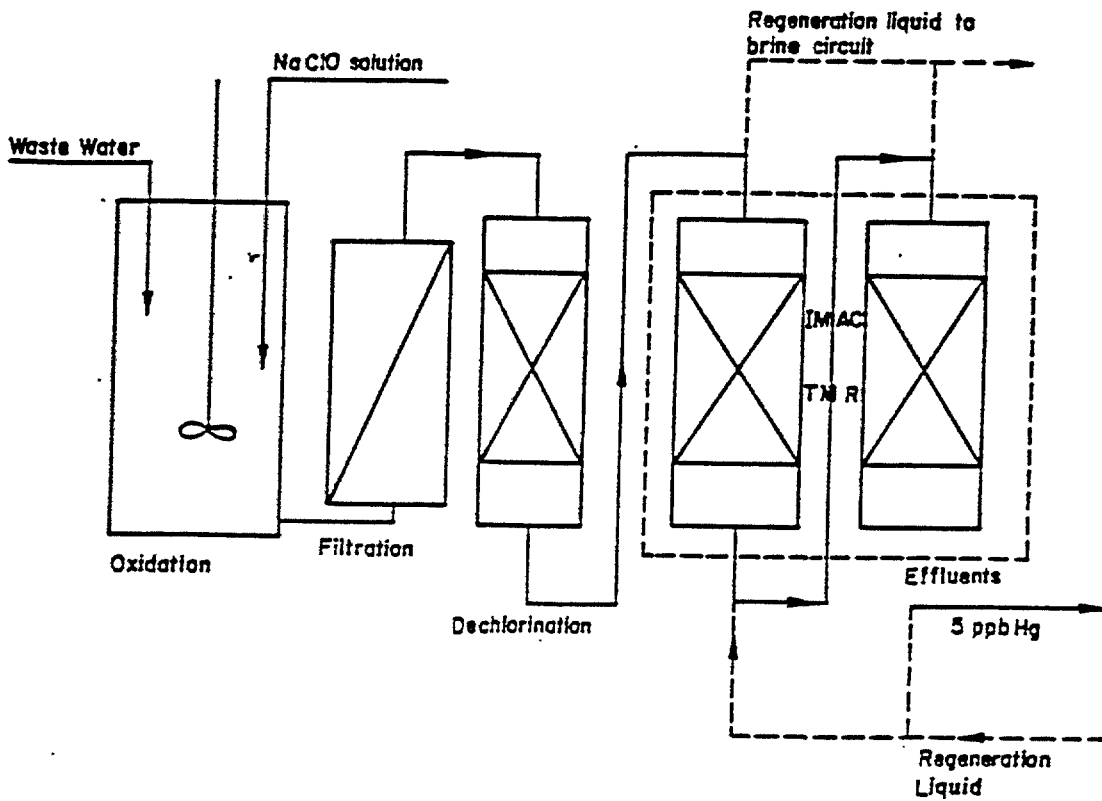


Figure 2.3 Ion exchange treatment of mercury.

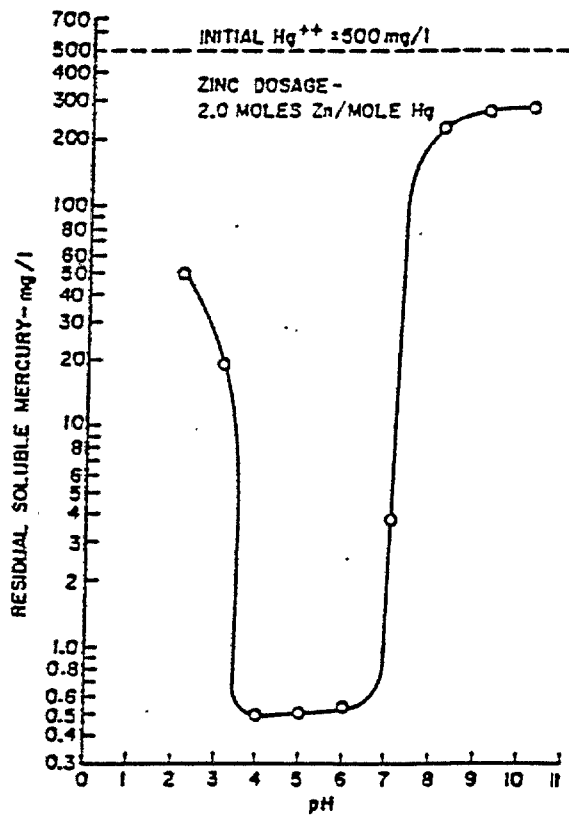


Figure 2.4 Effect of pH on the removal of mercury by zinc powder

3. CADMIUM

3.1 General Properties of Cadmium

Cadmium (atomic no. 48) belongs in Group IIb of the periodic table, and has an atomic weight of 112.40, specific gravity of 8.642, and melting point of 320.9°C (Perry and Chilton, 1973). Cadmium usually occurs in II oxidation state in all stable compounds (CRC Handbook of Chemistry and Physics, 1973). In the elemental form, it is insoluble in water (McKee and Wolf, 1977). Cadmium is similar in many respects to zinc and mostly occurs in small quantities associated with zinc ores, e.g. zincblende (ZnS), in which it occurs at 0.1-0.5 per cent (UNEP, 1984). The cadmium content of zinc ore, sphalerite might be as high as 5 per cent (Adriano, 1986). Cadmium is also found in ores such as Pb-Zn, and Pb-Cu-Zn (Adriano, 1986).

The most common cadmium compound is CdS. Cadmium forms a variety of complex amines, sulfur complexes, and chelates; and also hydroxides and complex ions with ammonia and cyanide, e.g., $\text{Cd}(\text{NH}_3)_4^{-2}$ and $\text{Cd}(\text{CN})_4^{-2}$ (Adriano, 1986). Cadmium also forms insoluble and highly stable hydroxides, usually hydrated with carbonates, arsenates, phosphates, oxalates, and ferrocyanides (Adriano, 1986). However; chloride, nitrite and sulphate salts of cadmium are highly soluble in water (McKee and Wolf, 1977).

3.2 Sources and Inputs into the Mediterranean

Cadmium is one of the rare elements in the earth's crust. Typical concentrations in various environmental matrices are given in Table 3.1. Therefore, due to geological weathering and erosion of the earth's crust, cadmium is transported into the marine environment through rivers and surface runoff.

Cadmium is also a minor part of the zinc fraction of the sulphide deposits of zinc, lead and copper. In addition, there are a few very rare cadmium minerals known, such as greenockite (CdS), cadmoseite (CdSe), monteponite (CdO), and ovavite (CdCO_3). Therefore, these deposits are natural cadmium sources and higher concentrations than the average cadmium concentrations can be found in these areas.

Table 3.1

Cadmium Concentrations (mg/kg) in Various Environmental Matrixes (GESAMP, 1984)

Matrix	Mean	Range
Igneous rock	0.15	0.001-1.8
Metamorphic rocks		0.04-1.0
Sedimentary rocks		0.3-11
Shales		up to 90
Marine clays	0.4	
Marine phosphorites		60-340
Agricultural soil, unpolluted	<1	

The main anthropogenic cadmium sources are ore mines and metallurgical industries. Since almost all cadmium is produced as a by-product of zinc, copper, and lead ore processing and refining, the main industrial cadmium sources are related to the mining of cadmium-containing ore, and primary production of cadmium, zinc, copper and lead. Cadmium concentrations in fumes of smelters treating copper, lead, nickel, and zinc sulfides can be high (Table 3.2). The industries giving rise to cadmium containing wastes are reviewed in Section 3.3.

The other important anthropogenic cadmium source to the environment is the disposal of sewage sludges. Immartino (1975) reported a cadmium concentration of 15 mg/L for one municipal incinerator scrubber water. Cadmium concentrations in the sewage of some Mediterranean cities are shown in Table 3.3.

3.3 Cadmium Bearing Wastes

Industries giving rise to cadmium wastes are non-ferrous metal production, metallurgical alloying, ceramics manufacture, electroplating, photography, inorganic pigments, textile printing, chemical industries, and mine drainage (Patterson, 1985). Phosphate fertilizer industry is another cadmium waste producer, if phosphoric acid is produced through the "wet-process". And, finally the sewage (domestic and mixed) also contains cadmium in high proportions relative to other metals (UNEP/FAO/WHO, 1989).

Table 3.2

Summary of Cadmium Inputs (metric tons year⁻¹) to the environment of the European Economic Community from Various Activities (Hutton, 1982)

	air	land	water
Volcanic action	20	ND	ND
Non-ferrous metal production			
Zn + Cd	20	200	5
Cu	6	15	ND
Pb	7	40	20
Production of Cd containing matter	3	90	108
Iron and steel production	34	349	ND
Fuel combustion			
coal and lignite	8	390	ND
oil and gas	0.5	14.5	-
Waste disposal	31	1434	ND
Sewage sludge disposal	2	130	33
Phosphate fertilizers	-	346	62
Total (estimate)	132	3009	273

ND= not detected

Table 3.3

Cadmium Concentrations ($\mu\text{g/L}$) in the Sewage of Some Mediterranean Cities
(UNEP/FAO/WHO,1989)

City	Mean	Range
Iskenderun	5	0.5-8
Mersin	2	ND-24
Antalya	-	0.1-0.3
Marmaris	0.3	ND-0.9
Valletta	0.25	-

ND = not detected

In primary zinc plants, cadmium is a major component of all waste streams due to the association of cadmium with zinc ores. The primary copper industry is another important but smaller source of cadmium wastes. Cadmium is one of the pollutants originating from copper smelting operation. Primary lead processing is another minor cadmium waste producer. The principle lead source, the mineral galena (PbS) frequently occurs with the mineral sphalerite (ZnS) which is the principle zinc source; therefore, lead, zinc, and cadmium commonly occur together, and cadmium is a major component of primary lead processing wastes (Williams, 1975).

In the metal plating industry, cadmium is mainly applied via electroplating or dipping to another metal as a thin coating for protection against corrosion (UNEP/UN/FAO/UNESCO/WHO/WMO/IMO/IAEA, 1985). Cadmium cyanide is a popular electroplating bath solution, due to the good adherence properties and fine-grained deposit formed. It is also widely used as a pigment in yellow and brown paints. One other important use of Cd is in Ni-Cd batteries. Cadmium is also a major component of some acid mine drainage wastewaters. However, the concentration of cadmium varies widely like other contaminants. Uncontrolled cadmium emissions from these major industries are given in Table 3.4. The principal uses of cadmium, in terms of total world consumption in 1984 are given as follows (Cadmium Association and Swedish Environment Protection Board, 1987):

Plating	25%
Pigments	22%
Batteries	27%
Stabilizers	17%
Alloys	7%
Others	2%

Thus, of the total industrial cadmium use, 98 per cent is utilized in electroplating, pigments, plastics stabilizers, alloying, batteries, and the remaining 2 per cent for television tube phosphorus, golf course fungicides, rubbercuring agents, and nuclear reactor shields and rods.

Table 3.4

Cadmium from Various Industrial Processes

Process	Uncontrolled emissions, mg/L	Reference
Plating Rinsewaters		
0.5 gph dragout	48	Nemerow, 1978
2.5 gph dragout	240	Nemerow, 1978
Large installations	15 avg, 50 max	Pinkerton, 1962
Plating Bath	23000	Nemerow, 1978
Bright dip and passivation plating bath	2000-5000	Lowe, 1970
Metal finishing plant	2-8	McDonald and Bajwa, 1977
Acid Mine Drainage	440-1000	Larsen, <i>et al.</i> , 1973
Acid Lead Mine Drainage	1000	McKee and Wolf, 1977
Primary Zinc Plant	0.02-2.4	Williams, 1975
Primary Lead Plant	1.9	Williams, 1975
Porcelain enameling	0.00-9.60	US EPA, 1980
Rubber processing	0.00-0.72	US EPA, 1980
Paint and Ink Formulation	0.00-0.81	US EPA, 1980

In EU member countries, disposal of cadmium is done according to EEC directive 83/513/EEC.

3.4 Principal Industries

3.4.1 Production and Use of Phosphate Fertilizers

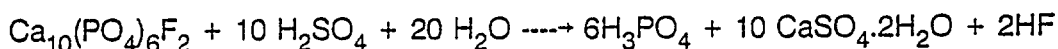
3.4.1.1 Type and Size of Industry

In the phosphate fertilizer industry, the production of phosphoric acid from phosphate rock is the only production with relevant waste products. Phosphoric acid is generally manufactured by the wet process. This method involves use of a strong acid to dissolve the phosphate rock. The most commonly used acids for this process are sulfuric and nitric, but hydrochloric acid can also be applied (Nemerow, 1978).

Cadmium emissions, in relation with the phosphate fertilizer industry occur in the wet process or in the production of phosphoric acid when sulfuric acid is used. This process involves four steps (Feenstra, 1978):

1. Dissolving phosphate rock in sulfuric acid
2. Holding the acidulate until the calcium sulfate dehydrate crystals grow to adequate size
3. Separating the acid and the calcium sulfate by filtration
4. Concentrating the acid to the desired level.

The reaction is as follows:



Hence, the cadmium in the ore is distributed between the acid and the calcium sulfate (gypsum).

3.4.1.2 Types of Waste

Since the gypsum produced is the only cadmium waste, cadmium discharges into water will obviously take place if the gypsum waste product is disposed off in land or sea or inland waters. Cadmium concentration in the gypsum (and in the fertilizer) produced depends solely on the cadmium content of the rock. The rock with a low cadmium content will cause less pollution than rock with a relatively high cadmium content.

The major cadmium releases from the fertilizer industry is expected to be in the product i.e. the fertilizers (UNEP/FAO/WHO, 1989). It was reported that the 56 per cent of the total Cd dispersion is via industrial fertilizers, while 48 per cent of this is due to phosphate fertilizers.

The other type of waste generated from phosphate fertilizer production or from phosphoric acid production is the liquid waste. This waste is known to contain high amount of fluoride due to the fluorine content of the phosphorus rock. In addition to fluoride, pollutants such as P_2O_5 , sulfate, calcium, ammonia, nitrate, copper might present in the liquid wastes. Table 3.5 and Table 3.6 indicate the average waste compositions for wet process phosphoric acid plants where gypsum is deposited and the supernatant water is recycled, and for plants with no such pond and no water recycle respectively.

3.4.1.3 Total Amounts

The amount of gypsum generated for every ton of phosphate (P_2O_5) is of about 4.75 tons (WHO, 1982). The gypsum may contain 10 per cent of the cadmium in the raw material if the initial cadmium concentration is high and up to 75 per cent if the initial concentration is low (Feenstra, 1978). Phosphate rock from countries exporting to the member countries of the EU are reported to have the following cadmium content (Feenstra, 1978):

USA(Florida)	5.5 - 16 mg/kg
Morocco	8 - 75 mg/kg
Senegal	70 - 90 mg/kg
Nauru Island	80 - 90 mg/kg
USSR (Kola peninsula)	0.1- 0.4 mg/kg

The amount of liquid waste for every ton of P_2O_5 produced is given as 2.8 m³/ton of P_2O_5 for a wet process phosphoric acid plant with ponds where gypsum is deposited and the supernatant is recycled; and as 670 m³/ton of P_2O_5 for plants with no such ponds (WHO, 1982).

Table 3.5

Liquid Waste Composition from a Wet Process Phosphoric Acid Plant with Ponds where Gypsum is Deposited and the Supernatant is Recycled (WHO, 1982)

Component	Concentration
P ₂ O ₅	25.2 kg/ton P ₂ O ₅
Fluoride	11.2 kg/ton P ₂ O ₅
Sulfate	8.4 kg/ton P ₂ O ₅
Calcium	2.2 kg/ton P ₂ O ₅
Ammonia	0.14 kg/ton P ₂ O ₅
Nitrate	0.14 kg/ton P ₂ O ₅
pH	1.0-1.5

Table 3.6

Liquid Waste Composition from a Wet Process Phosphoric Acid Plant with no Ponds (WHO, 1982).

Component	Concentration
SS	3900 kg/ton P ₂ O ₅
Fluoride (dissolved)	22.2 kg/ton P ₂ O ₅
Sulfate	82.2 kg/ton P ₂ O ₅
Sulfite	25.8 kg/ton P ₂ O ₅
Ammonia	6.1 kg/ton P ₂ O ₅
Copper	0.74 kg/ton P ₂ O ₅

3.4.2 Pigments and Stabilizers

Cadmium sulphide and sulpho-selenides are used as pigments in the manufacture of glass and some paints. Typical cadmium containing pigments are cadmium red, cadmium orange and cadmium lithophone (Shreve and Brink, 1977), and mixtures with other metals (e.g. Zn, Hg). Cadmium reds are made by roasting the precipitate obtained by mixing cadmium sulfate, sodium sulfite and sodium selenite (Shreve and Brink, 1977). Cadmium pigments are widely used in the plastic industry because of their brilliant color tone, heat stability (up to 600°C), good light, weather and alkali resistance (UNEP/FAO/WHO, 1989). These pigments are normally present in concentrations between 0.1-1.0 per cent of the weight of the base polymer (UNEP, 1984). In 1987, 22 per cent of the total cadmium production in the world was utilized in pigment production (UNEP/FAO/WHO, 1989). Approximately, 80 per cent of cadmium pigments are used within the plastic industry mainly for the production of high volume plastics such as polyethylene, polypropylene, polystyrene, etc. The rest is used in glass and ceramic glazers, artist's colors, enamels, printing ink etc. (UNEP/FAO/WHO, 1989).

Cadmium stabilizers which are used to protect polyvinylchloride (PVC) from decomposing are complex cadmium salts of organic acids (UNEP, 1984). Stabilizers can be in a liquid or in a solid form; a finished PVC article contains about 0.05 and 0.2 per cent cadmium when liquid and solid stabilizers are used respectively (Ernst, 1982). Cadmium discharges from inorganic pigment-industry plants range from 2 to 120 grams per day, with a plant average of 8 g/day (Barrett *et al.*, 1974).

3.4.3 Photography

3.4.3.1 Type and Size of the Industry

The processing of films requires the use of a large number of chemicals. Solutions containing a large number of thiosulfates and compounds of silver are utilized in film-developing and printing operations. In addition to these principal chemicals, there are various solutions in which the films are rinsed during processing.

The photographic industry is usually a small size industry, except for major film development centers (UNEP/WHO, 1986).

3.4.3.2 Types of Wastes

Two types of wastewater originate from the film-developing and the printing operation; the highly concentrated chemical replenishment or chemical-laden waste, and the dilute overflow of the spray or immersion-type wash tanks (Hennessy *et al.*, 1968). Each industry effectively recovers silver used in the photo development process and the remaining waste is generally discharged into a receiving body with minimum treatment.

3.4.3.3 Form of Wastes

The solutions are usually alkaline with a light white color (UNEP/WHO, 1986) and contain various organic reducing agents such as alcohols, ketones and glycol esters. Silver in ionic form is associated with $K_4(Fe(CN)_6)$, KBr, K_2S , $Na_2S_2O_3$, and Na_2SO_3 in the solutions. Although the waste characteristics changes with the industry, typically a photographic plant waste contains about 325 mg/L B.O.D.; 180-340 mg/L S.S.; and about 2000 mg/L total solids. The composition of a wastewater originating from a film-developing and printing operation is presented in Table 3.7.

3.4.3.4 Amount of Wastes

No information could be obtained regarding the amount of waste generated in film-developing. Control and surveillance of film-developing establishments is extremely difficult due to the smallness and vast distribution (UNEP/WHO, 1986).

3.4.4 Cadmium Electroplating Industry

3.4.4.1 Type and Size of Industry

Cadmium plating is a highly popular electroplating process among various industries such as automotive, appliances, radio, television, and electronics (Huang and Wirth, 1982) for the protection of steels, iron, copper, brass, and other alloys from corrosion. There are two main types of cadmium electroplating baths; cadmium cyanide bath and cadmium fluoroborate bath. The cyanide bath has a high throwing power and the ability to distribute

the deposit evenly. However, it is extremely poisonous and has low cathode current efficiency. The non-poisonous cadmium fluoborate bath has a high current density although it has much less throwing power than the cyanide bath (Huang and Wirth, 1982).

Table 3.7

Characteristics of a Film-Developing and Printing Wastewater
(Aita, 1984)

Parameter	Concentration, mg/L
pH*	8.29
Conductivity**	4.91
COD	1730
Ag	74
Cd	1.92
Fe	127
Zn	0.45
CN ⁻	<0.4
SO ₄ ⁻²	463
Ammonia	337

* pH unit; ** mS/cm

In the plating industry, cadmium can be efficiently substituted by zinc coating, sometimes together with chrome- and nickel-plating (UNEP/FAO/WHO, 1989). However, in places where water is condensed, cadmium is superior to others.

3.4.4.2 Types of Wastes

A typical cadmium plating process includes numerous steps in metal cleaning. The various acid dips, etches, and alkaline cleaning processes are designed to remove oils, grease, surface stains, oxide films or other substances which might cause uneven plating. Each step in the cleaning process is followed by rinsing, therefore large volume of rinsing waters are produced. Another waste producing operation is the periodic discarding of expended process solutions due to the accumulation of grease, oil, dirt, and metallic impurities (Huang and Wirth, 1982). Therefore, the total plant wastes are usually generated in the rinsing of processed items after removal from baths. However, accidental overflows from the plating solutions, dripping from work in progress between the various process solutions and rinse tanks, and finally the intermittent discharge of spent bath solutions (if they will not be re-used) will all contribute to the total plant wastes.

Typical cadmium plating wastewater contains 7-15 mg Cd/l, but some installations have reported as much as 50 mg Cd/l in the wastewater stream (Stittig, 1973; Lowenheim, 1978). However, cadmium concentrations in cadmium cyanide and cadmium fluorobate baths might be as high as 35.95 g/L and 94.36 g/L respectively (Huang and Wirth, 1982), whereas the typical cyanide concentration in cadmium cyanide bath is about 100 g/L (US-EPA, 1975).

3.4.4.3 Form of Wastes

The cadmium-cyanide electroplating wastes are normally aqueous turbid solutions with dissolved CN and Cd ions, associated are oils, grease, surface stains and detergents as well as suspended floating and dissolved metals (UNEP/WHO, 1986). However, the wastewater from cyanide-free cadmium-electroplating bath (which is suggested as an answer to simplified treatment needs) contains high amount of ammonium (Patterson, 1985).

The cadmium-fluoroborate electroplating wastes are aqueous solutions. They mainly contain cadmium and fluorides. The wastes are usually acidic and may include both insoluble and dissolved metals as well as floating scum and oil.

3.4.4.4 Total Amounts

The total volume of the wastes generated, usually expressed as gallons per finished number of metallic units, varies even more than the characteristics (Nemerow, 1978). However, no specific information is available related to the amount of waste generated.

3.4.5 Nickel-Cadmium Batteries

Cadmium hydroxide is the "active" material in the negative plate (electrode) of Ni-Cd batteries and is produced from cadmium oxide or cadmium nitrate in aqueous solutions. If cadmium hydroxide is directly applied from solution to the negative plate (which is called wet process), then liquid wastes and cadmium-containing sludges arise from the manufacturing process (UNEP, 1984).

The manufacture of Ni-Cd batteries in which cadmium acts as anode is the largest user of cadmium. In 1984, 27 per cent of the total cadmium produced was used in the manufacture of Ni-Cd batteries (Cadmium Association and Swedish Environment Protection Board, 1987).

There are two types of Ni-Cd batteries; pocket-plate cells and sealed cells (sintered plate). Open Ni-Cd batteries are usually larger and mainly used industrially. Therefore, cadmium (and nickel) is recovered from these batteries. However, many of the smaller cells are eventually thrown away and are disposed of with domestic rubbish. Attempts are being made to collect, and develop recovery treatments for small batteries in some countries.

Cadmium in Ni-Cd batteries can be recovered from the waste batteries by two different methods: by the dissolution in sulfuric acid followed by separation of the nickel and cadmium on the basis of their formation of amine complexes, or by melting the batteries with a reducing agent and distilling off the cadmium (UNEP/FAO/WHO, 1989).

3.5 Treatment

Limitations on a domestic water suppliers of 10 µg/L cadmium have been recommended by the U.S. Public Health Service (Lanouette, 1977). For drinking water, the WHO has a limit of 5 ppb Cd (Adriano, 1986). The US-EPA has a quality criteria of 10 ng/L maximum contaminant level for Cd in drinking water for humans (US-EPA, 1986). In addition, the US-EPA water quality criteria is 10 ng/L Cd for water and fish ingestion. In the quality criteria of the European Economic Community, limit value for cadmium discharges which must be complied with as from 1.1.1989 is given as 0.2 mg/L of discharge for all cadmium discharging industries (UNEP/FAO/WHO, 1989).

Cadmium is toxic to human beings when injected or inhaled. In addition, it acts synergistically with other elements such as copper and zinc to increase toxicity (McKee and Wolf, 1977).

Available treatment methods for cadmium include sulfide or hydroxide precipitation, ion exchange, electrolysis, ion flotation, electrodialysis, reverse osmosis, liquid-liquid extraction, cementation, and adsorption. These removal methods are essentially those employed for most heavy metals wastes encountered in the plating and metal processing industries. However, currently alkaline precipitation of cadmium as hydroxide or basic salts using lime, caustic soda or sodium carbonate followed by gravity settlement and sludge consolidation is the most widely used process (Dept. of Env., U.K., 1984). However, the maximum removal in precipitation process is pH dependent and some components (such as dispersants) of waste liquid stream can greatly influence the solubility of cadmium hydroxide. Therefore, if low cadmium residuals in solution is to be achieved, then alternate treatment processes such as sulphide precipitation and ion exchange should be applied. Primary precipitation of cadmium as hydroxide followed by secondary precipitation of residual cadmium as sulphide is also adopted (Dept. of Env., U.K., 1984). Table 3.9 summarizes the effluent cadmium levels through various cadmium removal technology.

3.5.1 Chemical Precipitation

Cadmium forms an insoluble precipitate as hydroxide, carbonate and sulfide forms. Precipitation in the hydroxide form occurs at alkaline pH values, usually with lime. Fig. 3.1 shows the theoretical precipitation curves for cadmium and for the other heavy metals as hydroxides.

As Fig. 3.2 shows, precipitation in the hydroxide form is dependent on high pH. Lanouette (1977) has determined that theoretical solubility of cadmium hydroxide is approximately:

pH	Solubility, mg/L
8	3000
9	30
10	0.03
11	0.003

Hence, with lime or caustic as the precipitating agent, pH should be maintained at 10-11 (Lanouette, 1977). Operating at such a high pH requires final treatment of the effluent discharge to lower the pH to an allowable limit of 9. Since, this pH adjustment will redissolve any remaining cadmium, all precipitate should be removed before this final pH adjustment. Freshly precipitated cadmium hydroxide has been reported to leave approximately 1 mg/L of residual cadmium ion in solution at pH 8 (Jenkin's *et al.*, 1964), but this is reduced to 0.2 mg/L at pH 10.4 (Patterson, 1977).

According to theoretical cadmium hydroxide solubility considerations, little additional treatment benefit should accrue from application of treatment pH above 10.0 (Patterson, 1977). However, many full-scale cadmium-precipitation treatment plants achieve effluent cadmium levels below 0.15 mg/L at lower pH (Table 3.8). Patterson *et al.*, (1977) explained this anomaly as preferential precipitation of cadmium as carbonate salt which is much more insoluble than is hydroxide salt. Minear and Patterson (1980) indicated that even modest background carbonate levels should greatly reduce the cadmium solubility (Figure 3.2).

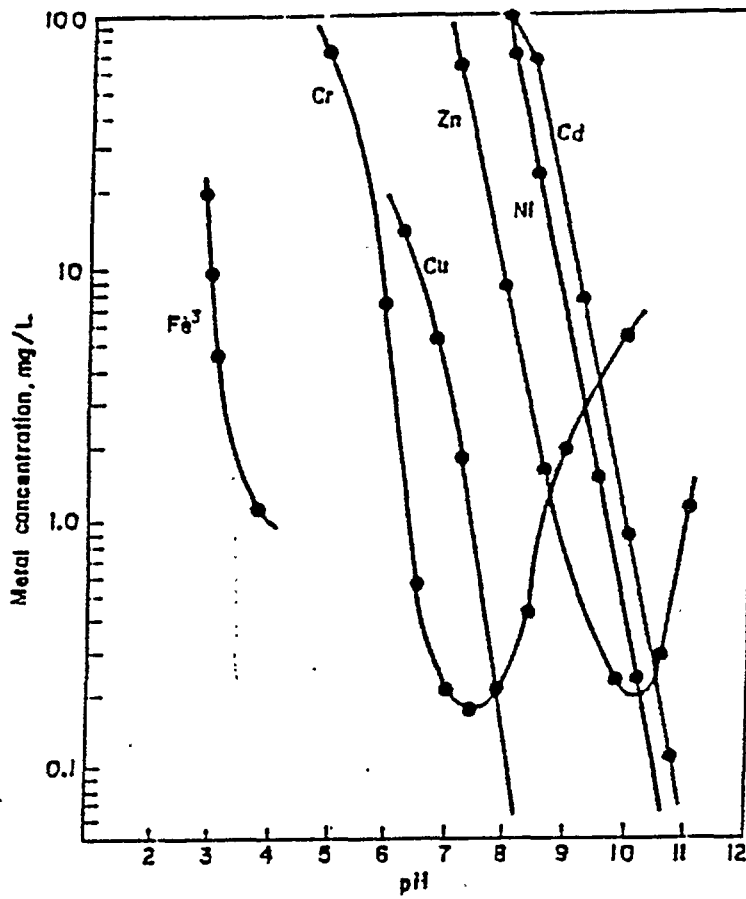


Figure 3.1 Precipitation of heavy metals as hydroxides (Lanouette, 1977)

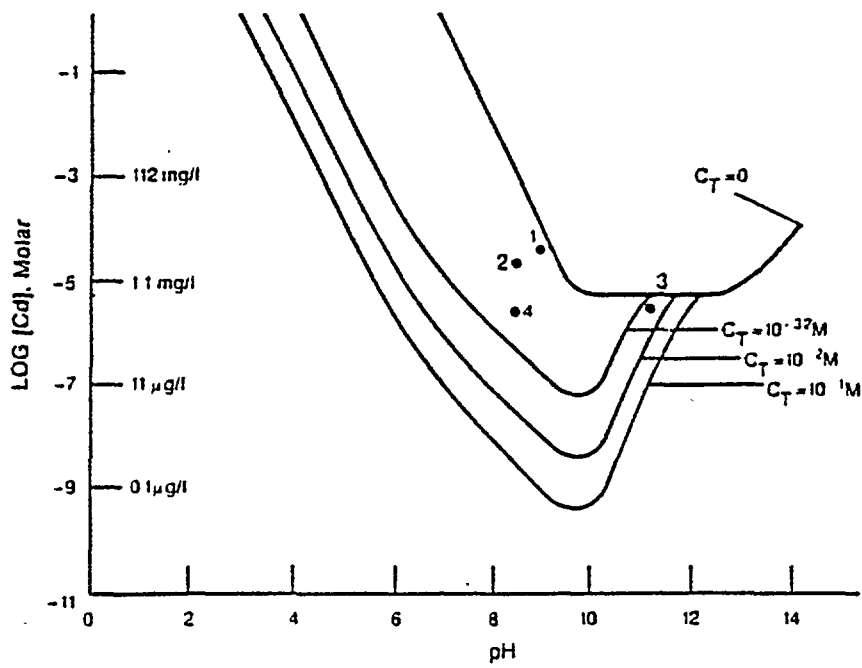


Figure 3.2 Effect of carbonate level on cadmium solubility (Minear and Patterson, 1977)

Table 3.8

Precipitation Treatment for Cadmium

Method	Treatment pH	Initial Cd (mg/L)	Final Cd (mg/L)	Reference
Hydroxide Precipitation	8.0	-	1.0	Jenkins <i>et al.</i> , 1966
Hydroxide Precipitation	10.0	-	0.10	Jenkins <i>et al.</i> , 1966
Hydroxide Precipitation	11.0	-	0.00075	Culp and Culp, 1974
Hydroxide Precipitation		1.5	0.13	Edwards and Benjamin, 1989
Hydroxide Precipitation	11.5	-	0.014	Maruyama <i>et al.</i> , 1972
Coprecipitation with Ferrous Hydroxide	6.0	-	0.050	Maruyama <i>et al.</i> , 1972
Coprecipitation with Ferrous Hydroxide	10.0	-	0.044	Maruyama <i>et al.</i> , 1972
Sulfide Precipitation	6.5	440-1000	0.008	Larsen <i>et al.</i> , 1973

Further benefits of iron addition is attributed to contaminant adsorption onto ferrihydrate (iron hydroxide); that is iron salts act both as coagulant and as adsorbent. Edwards and Benjamin (1989) investigated the potential for enhanced metal removal through adsorption on ferrihydrate and indicated that highly efficient metal removals from solution over the pH range 8 to 12.5 can be achieved. They regenerated and reused ferrihydrate 50 times to adsorb metals with no measurable loss in metal removal efficiency from both real and synthetic plating waste containing Cd,Zn,Cu,Cr(III),Ni,and Pb. Over time, the treated metals were concentrated in the (acidic) regenerant solution and may be recoverable. Therefore, the advantages of this process over precipitation are the sludge volume reduction and possible metal recovery.

Precipitation of cadmium can also be carried out with sulfide at lower pH values such as 6.5. It has been mentioned that various sulfide agents (BaS, Na₂S, NaHS, or H₂S) can be utilized as precipitating agent and this process yields lower concentrations (Table 3.3). In achieving low residual cadmium concentrations, sulfide precipitation is used as the secondary treatment following primary hydroxide precipitation. The more general application of sulfide precipitation technique is constrained due to a tendency for formation of colloidal precipitate, the toxicity and odor of hydrogen sulphide and the necessity to oxidize residual sulphide in emissions prior to discharge (Dept. of Env.;U.K.,1984).

One other precipitation technique for cadmium treatment is carbonate precipitation. The advantage in precipitating Cd with carbonate is that at pH 8.4, the residual soluble Cd concentration obtained is 1.2 mg/L; for the cadmium hydroxide system at pH 8.6, the maximum soluble Cd concentration is 126 mg/L (Patterson *et al.*, 1977). Therefore, treatment at a lower pH can be achieved with the carbonate system without sacrificing effluent quality. Patterson *et al.*, (1977) also reported that one other advantage of cadmium carbonate precipitation is the relative filtration rate achieved; cadmium carbonate precipitate has a filtration rate approximately twice that of cadmium hydroxide.

However, it is difficult to precipitate cadmium if other complexing agents (e.g., cyanide) are present. In that case the first treatment step is the removal of cyanide.

Cadmium plating wastes normally contain cyanide. Therefore, the effective removal of cadmium from plating baths or rinse waters is dependent upon the cyanide pretreatment before meeting in a segregated stream which is fortunately, easy and rapid as has been demonstrated for zinc and copper cyanide (Patterson, 1975; Patterson, 1985). Supplemental treatment may also encompass prior destruction of ammonium salts which could interfere adversely with precipitation (Dept. of Env.;U.K., 1984). In electroplating industry, lime addition for precipitation of cadmium wastewaters is the common practice (Patterson, 1985). Data presented in Table 3.9 for actual plant operation illustrate the lower limit of hydroxide precipitation treatment in the electroplating industry, since the plant for which the data are reported have been identified as "exemplary" plants by the US-EPA (1975). Patterson (1985) attributed the variations in treatment performance among the 10 plants of Table 3.8 to (1) ineffective cyanide destruction, (2) treatment pH applied, (3) background carbonate level, and (4) efficiency of precipitate solids separation.

Table 3.9

Results of Cadmium Precipitation Treatment
in the Electroplating Industry (USEPA, 1975)

Treatment pH	Cd concentration, mg/L	
	Influent	Effluent
6.0-9.5	-	0.03
6.6-9.5	-	0.01
6.5-8.0	-	0.30
7.2	-	0.01
8.2	-	0.03
8.8	-	0.21
10.5	3.10	0.05
-	-	0.02
-	-	0.05
-	-	0.02 ^a

^a Gravity clarification plus sand filtration

With cadmium chloride and cadmium acetate compounds in general, precipitation from solution as sulfides is recommended. Thereafter, sludge from precipitation will be dried and returned to suppliers for recovery (Noyes Publications, 1981). However, International Register of Potentially Toxic Chemicals expert consultation of UNEP (1985) recommended that these compounds should be converted to an insoluble form, the sludge will be filtered, solidified and deposited in a suitable landfill.

Chemical precipitation of cadmium may be accomplished by either batch or continuous treatment systems. A continuous treatment is usually preferred when wastewater characteristics are uniform or when volumes are small. Fig. 3.3 shows the typical continuous treatment system for heavy metals. The first process step is the pH adjustment for optimum precipitation. After the pH is adjusted a precipitating agent is added. The precipitating

agents most commonly used are lime and soda ash. The waste stream from the precipitation then flows to a clarifier where heavy-metal precipitate settles out, and clear treated overflow leaves the tank. The settled sludge is collected and usually dewatered by vacuum or high pressure filtration prior to landfill. The solids content of the settled sludge is increased to 15-25 per cent and 20-50 per cent from initial 2-10 per cent by vacuum and high pressure filtration respectively (Dept. of Env.; U.K.,1984). For sludges containing cadmium compounds; exceptionally chemical detoxification or chemical fixation is practiced, and then the sludge is deposited in a suitable landfill. Landfill at private sector and local authority sites employs both segregated deposition and co-disposal with domestic refuse and commercial waste (Dept. of Env.;U.K., 1984). Department of Environment of U.K. (1984) recommended that wastes containing brine solutions, mineral acids, cyanides, organic solvents and amine type substances should not be landfilled in proximity to cadmium-bearing wastes in refuse media particularly under aerobic conditions. The leaching tendency is accentuated in the presence of brine solutions.

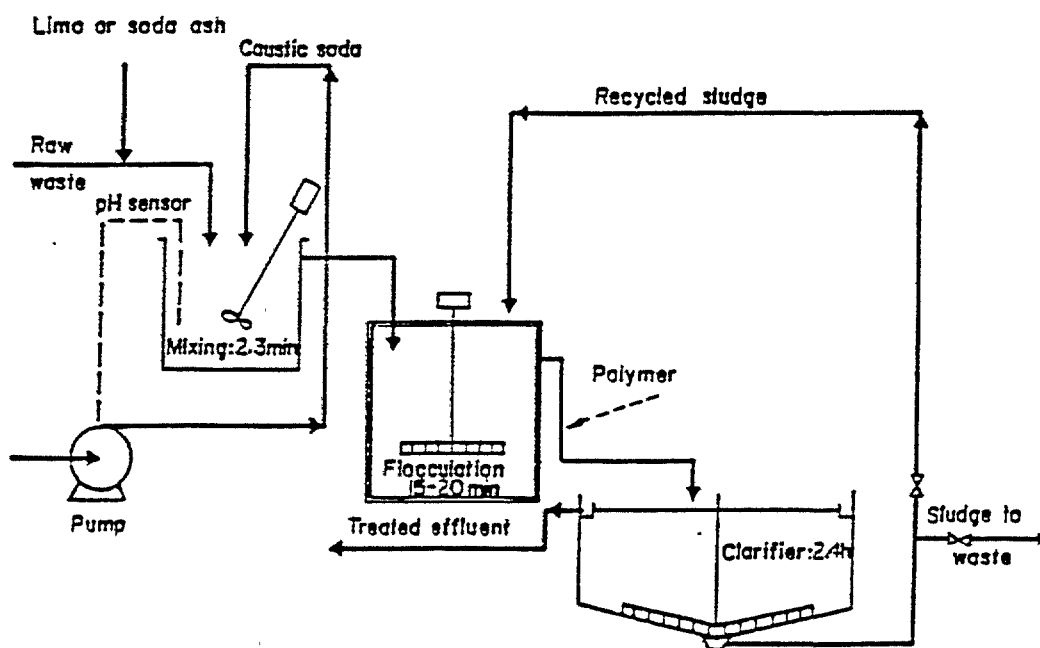


Figure 3.3 Typical continuous-treatment system for heavy metals.

However, International Register of Potentially Toxic Chemicals expert consultation of UNEP (IRPTC, 1985), with cadmium compounds in general, recommended return of the material to suppliers for recovery following precipitation and drying. Incineration of cadmium wastes is virtually out of question because of the high sublimality of the oxide (IRPTC, 1985).

3.5.2 Ion Exchange

Ion exchange process is an effective means of removing heavy metals from industrial waste streams. This can be used as a polishing treatment or recovery process for cadmium. A number of resins are available for removing cadmium from solutions containing a wide variety of other ions (UNEP/FAO/WHO, 1989). Strongly acid cation resins are suggested for recovering cadmium upon regeneration. The concentrated cadmium solution obtained upon regeneration of the ion exchange resin is often suitable for economical recovery procedures (Patterson, 1985). The recovery value of cadmium is estimated at \$3.17-15.85/10 m³, at a solution concentration of 50-250 mg/L cadmium (Digregorio, 1968). Installation cost is given as \$29-1226/10 m³/d capacity depending upon the ion exchange resin and regeneration configuration, with operating costs of \$1.37-1.74/10 m³ treated (Zievers and Novotny, 1971).

3.5.3 Activated Carbon Adsorption

The removal of cadmium from wastewaters has become a subject of interest in recent years. Derouette and Porta (1982) reported that the adsorption capacities in the order of 5 to 10 mg Cd/g of activated carbon with residual concentrations around 1 ppm is achievable, in the case of basic solutions.

Huang and Wirth (1982) studied the adsorption characteristics of Cd(II) from Cd(II)-BF₄ plating solution, and reported that at all pH values, powdered activated carbon exhibited greater Cd(II) removal capacity than the granular one. The rate of Cd(II) removal at pH 7 was found to be proportional to the cadmium concentration, the carbon dose, and the available surface sites.

Based upon the results obtained, Huang and Wirth (1982) proposed two activated carbon adsorption systems: 1-Completely mixed flow reactor (CMFR); and 2-the column reactor (CR). In the CMFR mode of operation (Fig.3.4), the powdered carbon is dispersed in the adsorption tank where the pH is kept neutral. The pH in the adsorption tank was suggested to be neutral to prevent the precipitation of Cd(OH)₂ which could hinder the solid-liquid separation operations that are to follow later. The Cd(II)-laden activated carbon particles are separated from the solution for regeneration via clarification and thickening. Then, the carbon is regenerated by an acid (H₂SO₄) wash and centrifuged for reuse.

Column reactor (CR) is another possible treatment scheme. The main advantages of the column operation are its ease in regeneration, and compactness in installation (Fig.3.5). At exhaustion, the influent is disconnected and used carbon is regenerated directly in the exhausted column with H₂SO₄.

The adsorption capacity of 0.0337 g Cd/g carbon was reported at neutral pH, for Nuchar SA type activated carbon (Huang and Wirth, 1982). And, depending on the preliminary economical analysis, the feasibility of activated carbon adsorption process for the removal of cadmium was demonstrated.

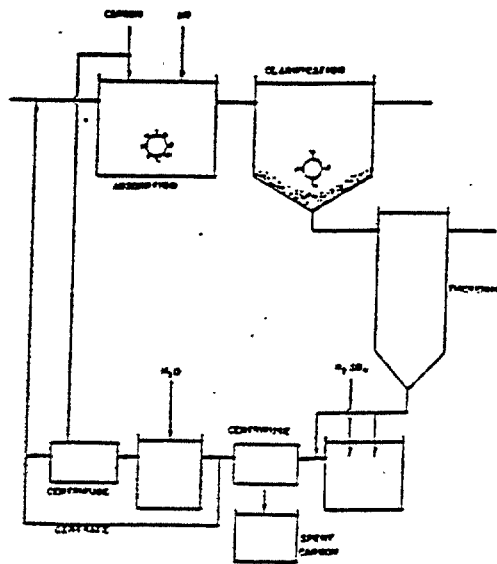


Figure 3.4 Schematic diagram of proposed CMFR activated carbon system with carbon regeneration (Huang and Wirth, 1982).

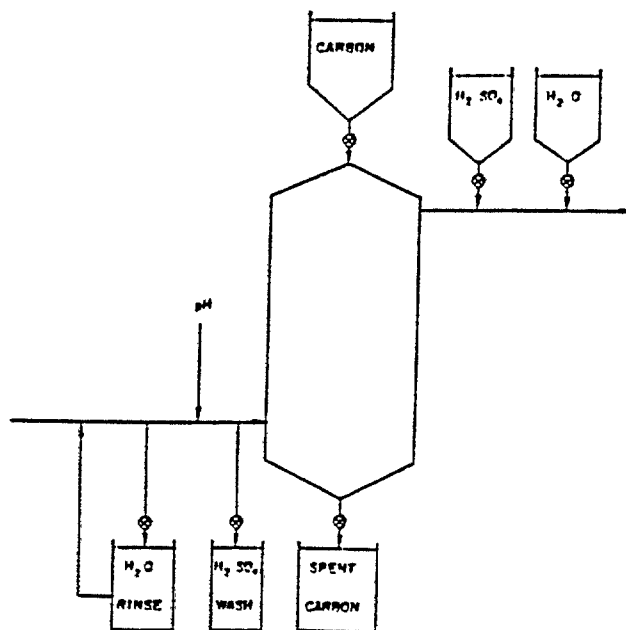


Figure 3.5. Schematic diagram of proposed CR activated carbon system with carbon regeneration (Huang and Wirth, 1982)

3.5.4 Electrochemical Recovery

Electrochemical recovery of cadmium is a treatment alternative for the cadmium plating industry. A fluidized bed electrochemical reactor is applied for the recovery and recycling of cadmium. The metal recovered is a massive deposit suitable for direct recycling to the plating bath as soluble anode material (Tyson, 1984). And, metal is recovered and reused when it otherwise would flow wastefully to drain or effluent treatment, and the value of the metal so recovered can be credited against the equipment and operational costs (Tyson, 1984).

Table 3.10

Payback for Evaporative Recovery System at Superior Plating
(Williamson and Natof, 1985)

Treatment Process	Range of Removal %	Range of Eff. Conc., µg/L
Activated carbon adsorption		
granular	76-95	<1.5-<40
powdered	NM	<1.5-<10
Chemical oxidation		
ozone	NM	<2-250
Chemical precipitation with sedimentation		
lime	0->99	ND-80
alum	38-88	12-47
polymer/unspecified	0-99	5-100
FeCl ₃	NM	<2
sodium carbonate	67->99	<1-<5
sodium hydroxide	22->99	ND-930
combined precipitants	11->99	ND-<80
Chemical precipitation with filtration	0->99	ND-19
Chemical reduction	NM	BDL-2
Coagulation and flocculation	99	BDL-<10
Filtration	0->99	ND-97
Flotation	0-99	BDL->72
Oil separation	>98	BDL-200
Reverse osmosis	0-60	<0.5-48
Sedimentation	0->99	BDL-200
Ultrafiltration	67-93	BDL-200
Activated sludge	0-99	BDL-13
Aerated lagoon		2

BDL = below detection limit; ND = not detected; NM = not meaningful

3.5.5 Other Processes

Other than the above mentioned processes, reverse osmosis and electro dialysis has been claimed to be successful and economical means of treating wastewater in treating wastewater in the plating industry (Patterson, 1985). However, the removal of cadmium via chemical precipitation is indicated as the most conventional treatment technology, although organic and inorganic complexing agents in the waste stream might reduce the effectiveness of the treatment. Table 3.10 indicates the results obtained using different methods of treatment of wastes containing cadmium, U.S. EPA (1981).

4. ORGANOTIN COMPOUNDS

4.1 General Properties of Organotin Compounds

Organometallic tin compounds or organotin compounds have one or more carbon-tin covalent bonds. There are four series of organotin compounds depending on the number of carbon-tin bonds. These are mono-, di-, tri-, and tetraorganotin compounds with the general structure $R\text{SnX}_3$, $R_2\text{SnX}_2$, $R_3\text{SnX}$ and $R_4\text{Sn}$ respectively. In practically important organotin compounds, R is usually a butyl, octyl, or phenyl group and X, a chloride, fluoride, oxide, hydroxide, carboxylate, or thiolate.

Essentially, in all organotin compounds, tin is in oxidation state +4 (WHO, 1980). However, there is only one well established organotin compound with tin in the oxidation state of +2; which is the tin(II) cyclopentadienyl, $C_{10}H_{10}\text{Sn}$.

Organotin compounds dissolve readily in common solvents, such as alcohol, ethers, and halogenated hydrocarbons. However, their solubility data are incomplete. The solubility in water at ambient temperatures is of the order of 5 to 50 mg/L (WHO, 1980). For diorganotin compounds (excluding dimethyltin derivatives), the solubility in water is of the order of 10 mg/L or less, and decreases with the length of the alkyl chains (Table 4.1).

The uses of organotin compounds can be divided into two main categories: nonbiocidal and biocidal (UNEP/FAO/WHO/IAEA, 1988). The main nonbiocidal use is for polyvinyl chloride (PVC) stabilization. Diorganotin compounds are used for preventing PVC degradation induced by UV light, and prolonged exposure of heating (Evans, 1974; Blunden *et al.*, 1984). Another important nonbiocidal use of organotin compounds is as catalysts in the production of polyurethane foams, and in the room-temperature vulcanization of silicones, since they are chemically reactive (WHO, 1980). Other minor nonbiocidal uses are for heat stabilization of materials other than PVC (such as rubber paints, cellulose acetate, polyethylene) (Thompson *et al.*, 1985); and for waterproofing of paper and textiles (Luijten, 1972; UK DOE, 1986). The specific uses of various organotin compounds are given in Table 4.2.

Table 4.1

Aqueous Solubility of Some Organotin Compounds
(from Blunden *et al.*, 1984)

Compound	Solubility in dist. water, mg/L
Me ₂ SnCl ₂	20000
Bu ₂ SnCl ₂	4-50
Bu ₂ Sn(OAc)	6
Bu ₂ Sn(O.C.Oct ¹) ₂	6
Oct ₂ SnCl ₂	<1

4.2 Sources and Inputs into the Mediterranean

The biocidal applications account for about 30 per cent of total worldwide use of organotin compounds (Blunden *et al.*, 1985). A major use is as fungicides and acaricides in agriculture. Another important biocidal use which is rapidly increasing in recent years, is as an antifouling agent in water; microorganism, plants, and animals can settle on submerged parts of boats, ships, docks, and in some cases in marine water-cooling pipes of coastal power stations and of industrial plant (UNEP/FAO/WHO/IAEA, 1988). The total biocidal use is roughly divided equally between uses in agriculture as wood preservatives, and for antifouling treatments (UNEP/FAO/WHO/IAEA, 1988).

There is no information in the literature on the amounts of organotin compounds discharged into the Mediterranean. However, it seems that the main source relates to the biocidal use of triorganotin compounds in antifouling compounds (UNEP/FAO/WHO/IAEA, 1988). Antifouling paints, containing mainly bis(tributyltin) oxide, tributyltin fluoride, and triphenyltin salts are used in cooling water pipes, in paints for boats, ships, and marina structures and in some cases in marine water cooling pipes. Triorganotin coated cooling water pipes are utilized in cooling water systems of electric power plants, chemical and steel industries. The amount of tributyltin compounds discharged into the sea through a cooling water line is approximated as 1.7-48 kg/d whereas the total input from 100 large ships each with 1500 m² painted surface is about 15 kg/d (UNEP/FAO/WHO/IAEA, 1988). Thus, the load from cooling water pipes is relatively significant.

The load from small boats and large ships is generally through diffusion of tributyltin and triphenyltin, which could be assumed as negligible on the total Mediterranean basin. However, high contamination levels can be expected in places such as marinas, moorings, dry docks, and harbors.

The input of organotins into marine environments from the agricultural use differs from the antifouling treatment in that their use will generate secondary nonpoint sources, since their use is characterized by dispersive application to land by leaching into water. In contrast to use in agriculture, the use as an antifouling agent is in the aquatic environment itself, and this type use will create a much more important pollution source.

However, there is no information available on triorganotin levels in the Mediterranean area, with the exception of some methyltin measurements in coastal environments of Turkey (Tugrul *et al.*, 1983; Salihoglu *et al.*, 1987).

The load due to non-biocidal use of organotin compounds does not seem to have a great pollution potential for the Mediterranean. As the major use of organotin compounds (essentially diorganotins) is as a stabilizer in PVC, the pollution potential of this use must be evaluated. However, there is only little information available about the fate of diorganotin compounds arising from stabilized PVC, or other materials produced by means of catalysis by organotin derivatives (UNEP/FAO/WHO/IAEA, 1988). However, the current use of stabilized PVC in beverage bottles and food packaging indicates that the rate of release of diorganotin derivatives into water should be very low (Blunden *et al.*, 1984). However, the leachate from a landfill is known to contain organotins. Considering that the most of the use and disposal sites are far from the marine environment, and certain time period will be taken for them to reach the sea, the organotin loads of these contaminants reaching the Mediterranean by way of leaching, runoff and transportation via water, would be negligible.

4.3 Organotin Compounds Bearing Wastes

Commercially, the most important category of organotin compounds are dialkyltin derivatives. They are utilized as heat and light stabilizers in the production of PVC plastics to prevent degradation during manufacture, and during the use. Another important commercial use of dialkyltin derivatives is in the production of polyurethane foam products. Dialkyltin compounds such as dibutyltin diacetate or -dilaurate are used as urethane and esterification catalysts (WHO, 1980). In addition, dialkyltin derivatives such as dibutyltin diacetate and dibutyltin dilaurate are also used as curing agents for silicone rubbers (WHO, 1980).

However, monoalkyltin derivatives are not widely used commercially. They are used as heat stabilizers in PVC plastic film production. The other category, trialkyltin derivatives are used in agriculture as non-systematic fungicides and acaricides. The tetra-alkyltin are used as intermediates in the manufacture of other organotin compounds.

4.4 Principal Industries

4.4.1 Drydock Facilities

4.4.1.1 Type and Size of Industry

Tri-organotin compounds particularly tributyl and triphenyl-tin derivatives are widely used in marine paints as antifouling agents. At the end of the useful life of an antifouling paint, the remaining paint is removed in a drydock. Hence, the wastewater generated during these operations contain organotin compounds.

Table 4.2

Uses of Organotin Compounds (from Bluden *et al.*, 1984)

Use		Compounds
	R_3SnX	
Agriculture (fungicides, etc.) (acaricides)		Ph_3SnX (X=OH, OAc) (cyclo- C_6H_{11}) $_3SnX$ ((PhMe $_2$ CCH $_2$) $_3Sn_2O$
Antifouling paints (biocides)		Ph_3SnX (X=OH, OAc, F, Cl.) $Ph_3SnO.CO.CH_2CBr_2.CO.OSnPh_3$ Bu_3SnX (X=F, Cl, OAc) (Bu_3Sn) $_2O$ $Bu_3SnO.CO.CH_2CBr_2.CO.OSnBu_3$ $Bu_3SnO.CO.(CH_2)_4.CO.OSnBu_3$ (-CH $_2$ CMe(CO.OSnBu $_3$)-) $_n$
Wood preservative fungicides		(Bu_3Sn) $_o$ Bu_3Sn (naphthenate) (Bu_3Sn) $_3PO_4$
Stone preservation		(Bu_3Sn) $_2O$
Disinfectants		$Bu_3SnO.CO.Ph$ (Bu_3Sn) $_2O$
Molluscicides		Bu_3SnF (Bu_3Sn) $_2O$
	R_2SnX_3	
Heat and light stabilizers (PVC)		$R_2Sn(SCH_2.CO.OOct^i)_2$ (R=Me,Bu,Oct,BuO.CO.CH $_2$ CH $_2$) ($R_2SnO.CO.CH:CH.CO.O$) $_n$ (R=Bu,Oct) $R_2Sn(O.CO.CH:CH.CO.OR')$ $_2$ (R=Bu; R'=Oct) $Bu_2Sn(O.CO.C_{11}H_{23})_2$ $Bu_2Sn(SC_{12}H_{25})_2$
Catalysts (silicones, polyurethane foams, transesterification reactions)		$Bu_2Sn(O.CO.R')$ $_2$ (R'=Me, Oct, C $_{11}H_{23}$) (Bu_2SnO) $_n$
Anthelmintics (for poultry)		$Bu_2Sn(O.CO.C^i_{11}H_{23})_2$
	$RSnX_3$	
Heat stabilizers (PVC)		$RSn(SCH_2.CO.OOct^i)_3$ (R=Me,Bu,Oct,BuO.CO.C $_2$ H $_4$) ($BuSnS_{1-5}$) $_4$
Catalysts (transesterification reactions)		($BuSn(O)OH$) $_n$ $BuSn(OH)_2Cl$

4.4.1.2 Types of Wastes

Wastewaters generated from drydock facilities may contain approximately 100 µg/L of organotin compounds (Argaman *et al.*, 1984). The maximum organotin discharge concentration might be 500 µg/L (Argaman *et al.*, 1984).

4.4.1.3 Form of Wastes

The wastes generated will be turbid with dissolved and floating material.

4.4.1.4 Total Amounts

Total production quantities will be dependent on the particular drydock facility.

4.4.2 Organotin Compounds as Stabilizers of PVC

In the production of rigid and flexible PVC plastics, including food-grade PVC for wrapping and containers, about 0.5-2.0 per cent by weight of dialkyltin derivatives are utilized (WHO, 1980).

However, no reliable information is available regarding the quantity and the quality of PVC production facility wastes.

4.4.3 Paint Industry

4.4.3.1 Type and Size of the Industry

The paint industry consists of the process of mixing organic and/or inorganic pigments with a suitable vehicle and grinding them to a satisfactory fines, color, and consistency (Nemerow, 1978). In manufacturing paints, several substances such as oils, resins, solvents, plasticizers, pigments, extenders, and dyes are all used. A wide range of organic solvents is used in paints that are not water-based, including aliphatic, aromatic and terpene hydrocarbons, alcohols, ketones, glycols, glycolethers and glycol ether esters. The industry may vary in size from small units to large industrial complexes. With small paint industries, wash water is often used with make-up water on subsequent batch mix operations; therefore, the volume of discharge is reduced. However, in large paint manufacturers the volume of waste discharge is high and the waste contains a large range of the paint types and colors (Williams, 1974).

4.4.3.2 Types of Wastes

In the manufacture of paints, wastes which are classified as hazardous (WHO, 1983), arise either as dirty solvents from plant cleaning or as reject batches of paint. Wash-down solvents are generally reused until unacceptably contaminated before disposal and recovery (WHO, 1983). Such waste wash-down solvents typically contain a number of compounds of various heavy metals used in paints as pigments, fungicides, flame retardants or anti-corrosion additives in a wide range of concentrations. The compatible pollutants in the paint industry's wastewater are regarded as suspended solids, and chemical oxygen demand.

Toxic heavy metals likely to be present in paint industry wastes include antimony, barium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, tin and zinc (WHO,

1983). In addition to these pollutants, the paint industry's wastewater contains several solvents as indicated above.

4.4.3.3 Form of Wastes

The paint industry's wastewater are colored with some suspended matter, and pH varies according to the combination of dyes utilized.

4.5 Treatment

In the literature, there are few studies reported on the treatment of wastes containing organotin compounds. One of the alternative treatment methods is the activated sludge process. Biodegradable organotin compounds such as methyltins can be removed through biological oxidation; however, complex synthetic organotins such as triorganotin biocides cannot be removed, since they are non-biodegradable. For some organotin wastes, another method of treatment is coagulation. For example, the paint industry's wastewater is usually treated by chemical means; coagulation and flocculation followed by sedimentation is applied for these wastewaters.

4.5.1 Coagulation

US EPA (1979) suggested the application of physicochemical treatment methods for the treatment of paint industry wastewaters. Following the coagulation with the application of a coagulant such as lime, alum, ferric chlorine etc. , and a coagulant aid, the waste stream might be subjected to settling. And, the overflow from the settler might be treated further biologically, for increasing the treatment efficiency, since BOD removal efficiency for physicochemical treatment is reported to be only 20 per cent for an influent BOD of 10778 mg/L (EPA, 1979). It is also reported that the removal efficiency of the physicochemical treatment for tin is 86 per cent if the influent level is 858 µg/L. Segregation of waste from the emulsion section and final paint preparation section is recommended.

Williams (1979) showed that chemical coagulation with the use of hydrated aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$ and hydrated lime calcium hydroxide $Ca(OH)_2$ is effective in treating paint industry wastewaters. Polyvinyl acetate and acrylic paint wastewaters were tested, and 86 per cent COD removal achieved in the presence of both of these coagulants. The pH of the media was suggested to be slightly alkaline to have better removal efficiencies.

However, it is extremely important to evaluate the treatability of wastewater on a case-by-case basis, because chemical coagulation may not have significant effects on some of the organotin compounds.

4.5.2 Activated Sludge Process

Biological treatment or more specifically activated sludge process may be applied for the wastewaters containing organotin compounds provided that microorganisms are protected against shock load, rapid pH variations and accidental leakages. The effectiveness of the biological treatment also depends on the biodegradability characteristics of the waste. Williams (1979) reported a 75 per cent C.O.D. removal for an acrylic paint wash water sample without any attempt to acclimate the microorganisms. Thus, higher removal efficiencies might be expected with acclimated cultures.

It is reported that the nature of organic compound has a marked effect on the toxicity while the anionic radical is not as important. N-butyl organotins have the most profound effect on such organisms as gram positive bacteria, fungi, mollusks and fish. This indicates that the prime biocide in such antifouling paints, tributyl tin oxide can effect the performance of activated sludge systems and, if not degraded in the treatment plant, may effect higher forms of aquatic life in the receiving water (Argaman, 1984).

Slesinger and Dressler (1978) reported that 20 to 13 per cent of tributyl tin oxide can be degraded in 126 days at initial concentration of 10 and 1.0 mg/L, respectively.

Stein and Kuster (1977) studied the effect of triorganotin compounds on the activated sludge process. They found that tributyl tin fluoride was inhibitory at 5.0 mg/L and tributyl tin oxide at 10 mg/L. In transient shock loading 2.0-5.0 mg/L tributyl tin oxide caused a marked drop in BOD removal when applied to an acclimated system. Subsequent shocks had a lesser effect as the system became acclimated to tributyl tin oxide.

Bokranz and Plum (1971) found the inhibitory threshold level of tributyl tin chloride to various bacteria between 0.2 and 3.1 mf/l. Argaman *et al.*, (1984) indicated that unacclimated biological cultures can be inhibited by tributyl tin oxide concentrations as low as 25 µg/L. However, tolerable dose for a well acclimated culture reported to be over 8000 µg/L. However, they have observed adverse effect on sludge settleability at 100 µg/L tributyl tin oxide. Shock loadings of 500 and 1000 µg/L tributyl tin oxide had no effect on soluble organic removal but resulted in impaired settling and higher effluent suspended solids.

5. ORGANOHALOGEN COMPOUNDS

5.1 General Properties of Organohalogen Compounds

The definition of the term "organohalogen compound" accepted by UNEP is "an organic chemical compound containing any of the chemical elements bromine, chlorine, fluorine or iodine in any form" (UNEP/FAO/WHO/UNIDO, 1987). Industrial fluids or polychlorinated biphenyls (PCBs), and pesticides and their degradation products are included under this title. The list of organohalogen compounds consists of more than one thousand substances (UNEP/FAO/WHO/IAEA, 1989). Approximately, 20 per cent of these substances are pesticides, and the rest are miscellaneous compounds (UNEP/FAO/WHO/IAEA, 1989). Little interest has been shown to industrial compounds with the exception of polychlorinated biphenyls.

DDT and Its Metabolites

One famous group, DDT (dichloro-diphenyl trichloroethane) and its metabolites are used against a wide variety of agricultural and forest pests and against insect pests.

In the environment can be degraded by solar radiation or metabolized in organisms. Dehydrochlorination gives the metabolite DDE and dechlorination the metabolite DDD.

Hexachlorocyclohexane (HCH)

The other compound hexachlorocyclohexane (HCH) is the one used as an agricultural pesticide. HCH can exist in seven stereo-isomers but the technical product

contains only five of these, the most common being alpha, beta, gamma and delta. The gamma-isomer known as lindane is the one normally used as an agricultural pesticide.

HCH is considered as one of the less persistent organochlorine pesticides. It decomposes under alkaline conditions to yield trichlorobenzene.

Aldrin/Dieldrin/Endrin

In addition to HCH, aldrin, dieldrin and endrin are also used as pesticides. Aldrin is an alicyclic chlorinated hydrocarbon and is therefore less resistant to oxidation than the aromatics, being rapidly converted to the epoxide, dieldrin, which is also used as a pesticide. Further degradation of the epoxide dieldrin does take place but much more slowly. Endrin is a stereoisomer of dieldrin and is one of the most toxic of the chlorinated pesticides.

Polychlorinated Biphenyls (PCBs)

One of the most famous groups, PCB's are similar to DDT's and used widely in industry. PCBs possess many useful characteristics. They are very stable, have a low vapor pressure, low flammability, high heat capacity, low electrical conductivity, and a high dielectric constant. PCBs are produced commercially by the chlorination of biphenyl with anhydrous chlorine. Chlorine substitution to the biphenyl molecule (which has ten sites available for substitution) can occur at any one or more of the ten numbered locations. As a result, there are 209 individual chemical species which fall under the generic classification of "PCBs". Commercially produced PCBs are mixtures of chlorinated biphenyl isomers and homologues. Impurities found in commercial PCBs can include polychlorinated naphthalenes (PCNs) and polychlorinated dibenzofurans (PCDFs). Unfortunately, these chemicals can enter the human body through the skin, lungs, and gastrointestinal tract, and are accumulated in fatty tissue. They may cause adverse reproductive effects, developmental toxicity, and tumor development in humans. They also tend to bioaccumulate in the food chain.

Because of their excellent electrical insulating properties, the largest application of PCBs is in electrical equipment. Table 5.1 indicates the applications of PCBs in United States, before the US EPA implemented controls on the production and use of PCBs.

Table 5.1

Applications of PCBs by Amount in United States (McCoy, 1989)

Uses	Amount, tons/year
Transformers	165000
Capacitors	320000
Plasticizers	57000
Hydraulic fluids and lubricants	40000
Carbonless copy paper	22000
Miscellaneous industrial uses	13000
Heat-transfer fluids	10000
Petroleum additives	1000

Heptachlor/ Heptachlor epoxide

Another organohalogen compound which is used as an insecticide is heptachlor/heptachlor epoxide. In the environment it is degraded or metabolized and is more commonly found as its epoxide.

Hexachlorobenzene (HCB)

Hexachlorobenzene is a fully chlorinated compound formed when all the hydrogen atoms in benzene are substituted by chlorine atoms. It is generally accepted to be stable and persistent. It is a general fumigant and a fungicide, and therefore used widely in grain storage.

5.2 Sources and Inputs into the Mediterranean

Although the list of organohalogen compounds consists of more than one thousand substances, the followings are normally included in the list of organohalogen compounds by UNEP (UNEP/FAO/WHO/UNIDO, 1987):

Industrial fluids: Polychlorinated biphenyls (PCBs)

Pesticides and their

degradation products:

- p,p'-DDT
- o,p'-DDT
- p,p'-DDD
- o,p'-DDD
- p,p'-DDE
- o,p'-DDE
- chlordane
- aldrin
- dieldrin
- endrin
- endosulfan
- toxaphene
- heptachlor
- heptachlor oxide
- hexachloro cyclo hexane (HCH) (mixed isomers)
- gamma - HCH (lindane)

For chlorinated pesticides, there are no sales or production statistics for the Mediterranean countries. Consumption figures of the Mediterranean countries for 1973/1976 period are shown in Table 5.2. However, Cyprus, Egypt, Greece, Israel, Italy, Libya and Turkey reported to FAO that in 1985 no chlorinated pesticides were used in their countries for agricultural purposes (UNEP/FAO/WHO/IAEA, 1989).

PCBs have been produced industrially since 1929 and were or are manufactured in many industrial countries, including some Mediterranean countries. As it was mentioned previously, PCBs are nowadays used primarily in the electrical industry, in capacitors and transformers. Some production figures for PCBs for some Mediterranean Countries are given in Table 5.3.

Halogenated hydrocarbons can reach the marine environment through atmospheric deposition, agricultural run-off, rivers and discharge of industrial and municipal wastes. Concentrations of PCB's in the near ocean atmosphere at Monaco were monitored over a two year period (Villeneuve, 1985). An increase in PCB concentrations of one order of magnitude was noted with an increase of temperature of 20°C. It was also noted that the winds blowing from north/northwest are loaded with industrial discharges and this results in higher PCB concentrations in the atmosphere. PCB measurements taken during various cruises aboard research ships in the Mediterranean sea gave an average of 0.23 ng/m³ for 1975 cruises and 0.07 ng/m³ for 1977 cruises (from Villeneuve, 1985).

Project Med X of MED POL-PHASE I estimated a total organochlorine pesticide load of 90 tons per year to the Mediterranean Sea from land-based sources carried by surface run-off, either directly or through rivers. This project does not include polychlorinated biphenyls and was based on a number of assumptions as to use patterns, with the end result being expressed as a percentage of the field used pesticides entering the sea. The results obtained from this study suggested that the minimum input occurs in Area VII 2.9 t/a (3%) and the maximum in Area II 14.9 t/a (17%) (Figure 5.1 and Table 5.4). However, it is reported that the reliability of the data for Area II are questionable since France provided no agricultural use data (UNEP/FAO/WHO/IAEA, 1989).

Surveys of chlorinated hydrocarbons in marine environments along the French coast (Elder, 1976) have shown that high concentrations occur near the mouth of the Rhone river. Similar results were obtained by Burns and Villeneuve (1982) working off the Var river estuary near Nice. Contamination of the waters and sediments of the Tiber estuary with polychlorinated biphenyls and hexachlorobenzene was studied in 1976 and 1977 (Puccetti and Leoni, 1980). PCBs were detected in all samples analyzed at mean levels of 0.297 µg/L(1976) and 0.135 µg/L(1977).

The powerful influence of the sewage outfalls on the chlorinated hydrocarbons concentrations was indicated by Voutsinou-Taliadouri and Satsmadjis (1982). In another study, El-Sebae and El-Amayen (1979) investigated the potential effects of pesticidal pollutants carried by the river Nile and its associated canals and drainage systems. The concentrations of some chlorinated hydrocarbon pesticides were measured as 0.34 to 0.95 µg/L in Mahmoudieh canal water and as 0.19 to 0.95 µg/L in a chicken slaughter house wastewater (Table 5.5).

5.3 Wastewaters Bearing Organohalogen Compounds

Organohalogen compounds reach the marine environment through agricultural run-off, rivers and discharge of industrial and municipal wastes.

The major user of organohalogen compounds is the pesticide manufacturing industry, whose discharges contain varying amounts of organohalogen compounds. The other user is the pulp and paper industry which uses these compounds as fungicides, and biocides. The Other major sources of organohalogen wastes are petroleum refineries, research laboratories, iron and steel work, foundries, and the electrical industry in which PCB's are used in capacitors and transformers.

Table 5.2

Pesticide Consumption by Agriculture in some of the Mediterranean Watershed
(excluding Albania, Algeria, France, Malta, Monaco, Morocco, former Yugoslavia, 5 regions of Italy
(UNEP/FAO/WHO/IAEA, 1989)

Kind of pesticide	Consumption (t active ingredient per year)											Total	estimated area treated (10 ³ km ²)
	Cyprus 1976	Egypt 1976/76	Greece 1973	Israel 1974	Italy ¹ 1975	Lebanon 1973	Libya 1974	Spain ² 1976	Syria ² 1976	Tunisia 1973/74	Turkey 1976		
1. Organochlorine compounds	14.9	743.3	85.5	132.3	2972.4	35.3	5.8	323.2	65.8	39.0	1266.8	5684.3	216.3
1.1 DDT and related compounds	11.2	169.3	-	10.3	866.4	-	-	12.7	36.7	-	864.1	1970.7	29.1
1.2 HCH and lindane	0.6	21.9	-	25.0	1563.7	-	1.7	122.3	9.1	36.0	163.0	1943.3	126.6
1.3 Cyclodienes (aldrin, dieldrin, endrin, etc.)	0.1	98.7	-	0.8	-	-	2.0	99.2	6.3	3.0	81.2	291.3	15.4
1.4 Other organochlorine compounds	3.0	453.4	85.5	96.5	542.3	-	2.1	89.0	13.7	-	158.5	1444.3	44.4

¹ Except Piemonte, Valle d'Aosta, Lombardia, Trentino Alto Adige and Umbria regions
² Mediterranean watershed only

Table 5.3

Manufacturers, Trade Names of PCBs and 1980 production figures
(after Geyer *et al.*, 1984)

Country	Manufacturer	Trade name	Production (tons)
France	Prodelec	Phenoclor, Pyralene	6557 ¹
Italy	Caffaro	Fenoclor, Apirolio	1479
Spain	Cross, S.A.	Fenoclor	1241

Table 5.4

Estimated Annual Pollution Loads of Organochlorine Pesticides
in the Regional Mediterranean Sea Areas (UNEP/FAO/WHO/IAEA, 1989)

Mediterranean Region	Pollution load tons/year	% of total
I	6.4	7
II	14.9	17
III	10.4	12
IV	12.1	13
V	14.0	16
VI	6.1	7
VII	2.9	3
VIII	7.4	8
IX	6.7	7
X	9.1	10

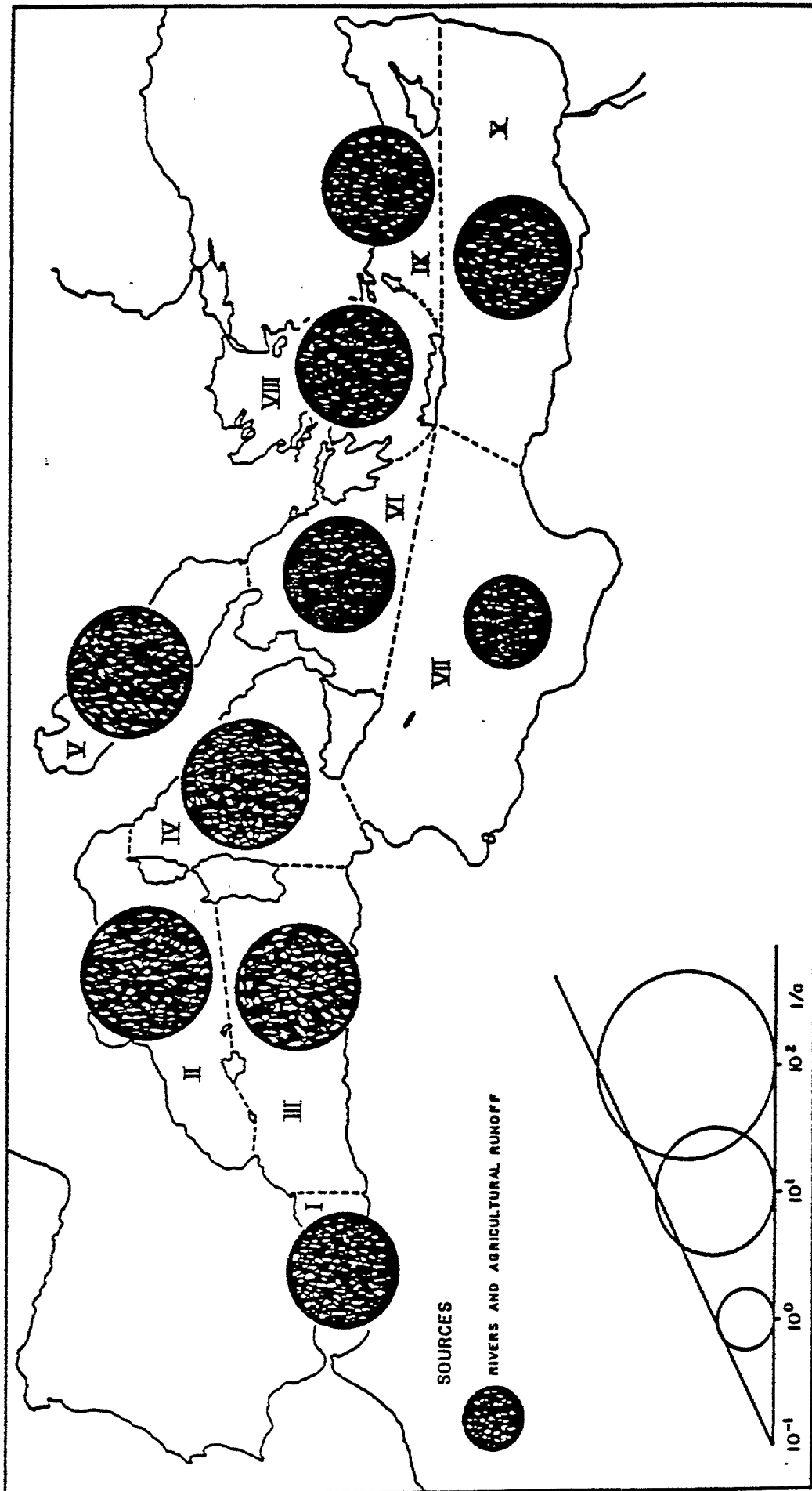


Figure 5.1 Regional contributions of organochlorine pesticides (UNEP/FAO/WHO/IAEA, 1989).

Table 5.5

Chlorinated Pesticides in Alexandria City Municipal Waters
(El-Sebae and El-Amayem, 1979)

Pesticide	Canal raw water	Slaughter-house wastewater, µg/L
HCH	0.39	0.19
Lindane	0.34	0.63
Heptachlor	0.70	0.19
p,p' DDT	0.65	0.95
o,p' DDT	0.95	0.25

5.4 Principal Industries

5.4.1 Pesticide Manufacturing Industry

5.4.1.1 Type and Size of Industry

The consumption of organochlorine pesticides reaches to about 5700 tons per year in Mediterranean countries, (for years 1973-1977) excluding Albania, Algeria, France, Malta, Monaco, Morocco, former Yugoslavia, and five regions of Italy; the main type being the DDT and related compounds, and BHC and lindane (UNEP/FAO/WHO/IAEA, 1989). However, there are no statistics available on the production of halogenated hydrocarbons in the Mediterranean Countries (UNEP/FAO/WHO/IAEA, 1989).

5.4.1.2 Type of Wastes

The wastes are aqueous solutions of organics. Depending on the type of pesticide manufactured, and the individual process steps, wastewaters with different characteristics will be discharged. Pesticide manufactured wastes may be characterized by BOD, TSS, COD, and TOC. The wastes may contain varying amounts of organohalogen compounds. Table 5.6 gives the concentration of several organohalogen compounds in pesticide manufactured wastes (Patterson, 1985).

5.5 Treatment

In general, a broad array of treatment technologies is available to control the organic priority pollutants or organohalogen compounds. However, none of these technologies is uniformly applicable to all of these organic compounds. Steam stripping is effective but expensive.

In addition, if the recovery is not an objective then this treatment process results in a contaminated condensate which requires additional treatment.

Activated carbon treatment is also effective for many of the toxic organic compounds. But, it is expensive too. Biological treatment which is the least costly option is effective in treating many of the toxic organic compounds.

The disposal of organohalogen compounds might be achieved through landfilling or incineration as the other toxic organic wastes. Landfilling is only allowed in special cases in EU countries. Table 5.7 shows the recommended disposal methods for some of the organohalogen compounds, whereas Table 5.8 indicates the U.S. EPA's approved disposal methods of PCBs.

Table 5.6

Organohalogen Compound Concentrations in Pesticide
Manufactured Wastes (Patterson, 1985)

Compound	Concentration, µg/L
Aldrin	410
Dieldrin	700
Chlordane	2610
Endrin	2210
Heptachlor	530
Heptachlor epoxide	68
Tetrachloroethylene	77
Carbon tetrachloride	24500
Hexachloronaphthalene	350
2-Chlorobutadiene	575
Hexachlorobutadiene	1320
Hexachlorocyclopentadiene	6810

5.5.1 Adsorption

One of the most widely adopted techniques for the removal of organohalogen compounds is adsorption. For this purpose, several adsorbents such as bentonite, saturated clay, hydrous aluminum silicate, and activated carbon might be utilized (UNEP/WHO, 1986). However, among these adsorbents, activated carbon is the one which is most widely used from the point of view of application, and safe ultimate disposal of the toxic compound.

For activated carbon adsorption, the process suitability must be checked each time. Inspection of an adsorption isotherm is a relatively simple method of determining the feasibility of using activated carbon for a particular application. An isotherm shows the division of adsorbable adsorbate between the adsorbed phase and the solution phase at equilibrium in certain temperatures. From inspection of the isotherm, it can be determined whether or not the desired degree of adsorbate removal is achievable with the particular activated carbon tested. Once the capacity of the particular activated carbon is determined, the theoretical carbon demand for the given wastewater can be calculated. It should be noted that this approach will provide an estimate that is frequently lower than the actual size and cost since it assumes equilibrium conditions and complete utilization of the carbon

capacity-assumptions that are generally violated in full-scale systems. Table 5.9 presents Freundlich isotherm data on carbon adsorption of some of the organohalogen compounds. One must be aware that Freundlich is often utilized due to its simplicity, while Langmuir isotherm is usually describe better the adsorption processes in wastewaters.

Table 5.7
Disposal Methods of Some Organohalogen Compounds
(IRPTC/UNEP, 1985)

Compound	Disposal method	Comment
DDT	Incineration at high temperatures	Dissolve in a solvent, and scatter the solution into a furnace with afterburner and alkali scrubber
DDE	Incineration	a. Incinerate at 850°C with off gas scrubbing equipment to adsorb hydrogen chlorine b. Incinerate at 1200°C for 1-2 seconds
Aldrin	Incineration Landfilling [#]	Incineration in polyethylene on a small scale Small amounts may be sprayed over a landfill
Dieldrin	Incineration Landfilling [#]	
Endrin	Incineration Landfill [#]	Large amount should be incinerated Absorption and burial at least 0.5m deep

[#] In EU member countries landfilling is only allowed in special cases

Efficiency of adsorption in removing organic compounds depends on the relative absorbability of the individual components. The main factor affecting the absorbability is the correlation between compound solubility and ratio of adsorbed to residual soluble concentration: solubility (Patterson, 1985). Factors such as pH, temperature, and ionic strength affect the solubility, and therefore the adsorption. As solubility decreases, adsorption capacity increases. Verschueren (1983) reported the following correlation

$$\log P = 8 - 0.66 \log S$$

where P= gram of amount of compound adsorbed per gram of activated carbon in equilibrium with initial concentration of compound in solution,
S= solubility in µg/L.

Molecular weight and polarity also affect the absorbability. Nonpolar molecules are more strongly adsorbed than are polar molecules. And, in general aromatic and substituted aromatic compounds are more adsorbable than are aliphatic compounds. (Patterson, 1985).

Table 5.8
USEPA's Allowable Methods of PCB Disposal# (McCoy, 1989)

Type of PCB material	PCB high efficiency			Approved alternative methods
	PCB	incineration (boiler)	PCB landfill	
Liquid PCBs, spills > 500 ppm	X	X	X*	Chemical dechlorination Chemical dechlorination
50-500 ppm	X	X	X*	
Nonliquid PCBs, spill residues, > 50 ppm (contaminated soil, rags, or other debris)	X			Transformer disposal Capacitor disposal Municipal solid waste Municipal solid waste@
All dredged materials and municipal sewage-treatment sludge > 50 ppm PCB transformers@ (>5ppm)	X		X	
PCB large capacitors > 50 ppm	X		X	Municipal solid waste@
PCB small capacitors	X		X	
PCB hydraulic machines containing > 50 ppm	X		X@	Municipal solid waste@
Other PCB articles, > 50 ppm PCB containers > 500 ppm > 50, < 500 ppm	X		X@	

In general, disposal of waste containing < 50 ppm PCBs is not regulated.

* Liquid can not be ignitable; i.e. flashpoint cannot be below 140° F.

@ Drained of free-flowing liquid; hydraulic machines must be flushed with suitable solvent if PCB concentration > 1000 ppm.

Table 5.9

Freundlich Parameters for some Organohalogen Compounds
(Patterson, 1985)*

Compound	pH	K	1/n
Aldrin	5.3	651	0.92
Dieldrin	5.3	606	0.51
Endrin	5.3	666	0.80
Heptachlor	5.3	1220	0.95
Alpha-BHC	5.4	303	0.43
Beta-BHC	5.4	220	0.49
Gamma-BHC	5.3	256	0.49
PCB-1221	5.3	242	0.70
PCB-1232	5.3	630	0.73

* These data were generated using pulverized Calgon Filtrasorb 300 activated carbon, at initial chemical concentrations of 1.0 mg/L, and at indicated pH.

Full-scale activated carbon treatment systems do not achieve the maximum carbon loadings predicted from isotherm tests, as it was mentioned previously. However, improved efficiency can be achieved usually by connecting two or more adsorbers in series (Fig.5.2). When the effluent from the second, or polishing bed begins to approach the desired objective, just the first, bed is removed from service. This assures maximum carbon efficiency.

Activated carbon treatment costs vary widely, depending upon carbon exhaustion and attrition rates, and plant size.

5.5.2 Stripping

Both air and steam stripping can be applied for the treatment of organohalogen compounds. The extent of removal of a compound by air stripping is governed by several factors such as air and liquid pollutant concentrations, air and liquid temperatures, air-to-liquid ratio, etc.

Diffusion and mass transfer rates are a function of power input, packing medium, and depth (for packed tower strippers), hydraulic regime, air bubble or water droplet size (Patterson, 1985).

One principal factor in air stripping is the tendency of the compound to establish an equilibrium between the gas and the liquid phases which is defined by Henry's law. Henry's law constant is like a partition coefficient which describes the relative tendency for the compound to partition between the gas and the liquid at equilibrium, in accordance with the following equation:

$$H = C_g / C_l$$

where H = Henry's law constant
 C_g = Concentration in gas phase
 C_l = Concentration in liquid phase

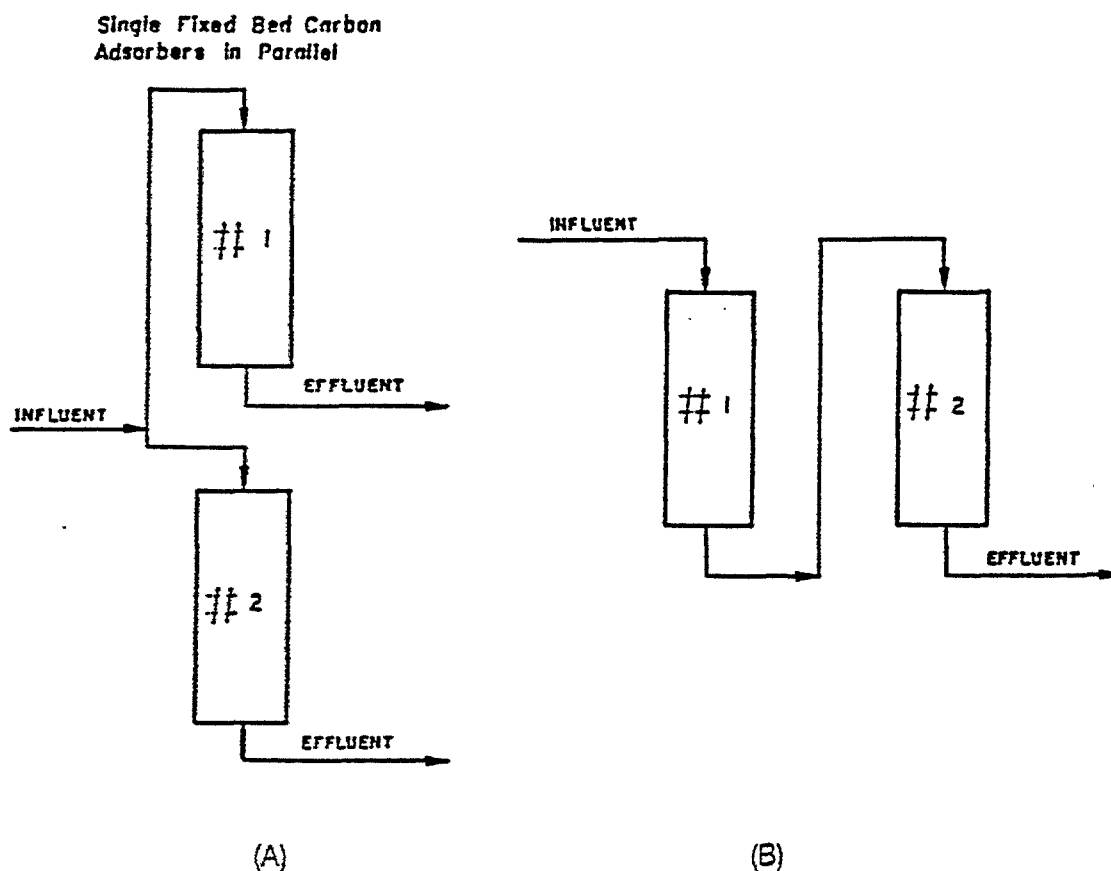


Figure 5.2 Process configuration used for carbon columns
(A-columns in parallel, B-columns in series).

Table 5.10 gives the values for H and solubility for some organohalogen compounds.

The removal efficiency depends not only on its equilibrium partition ratio but also on the contact opportunity, or intensity and duration of aeration (Patterson, 1985). Increased air:liquid ratio and increased contact time increase stripping efficiency up to the equilibrium defined by Henry's law. A 98 per cent removal efficiency was reported for dichlorobromomethane by air stripping in a packed tower in 11.8 min detention time. The influent concentration and air:liquid ratio stated to be 0.225 mg/L and 200 respectively in this pilot plant work (Patterson, 1985). However, the per cent removal with an influent dichloro-bromomethane concentration of 0.12 mg/L was 74 while the detention time and air:liquid ratio were 1.6 min and 32 respectively (Patterson, 1985).

Steam-stripping is defined by the boiling point of the organic compound. A compound with relatively low boiling point (< 150°C) together with an acceptable Henry's law constant value would exhibit a good steam-stripping characteristics. In one study on steam-stripping of carbon tetrachloride, initial compound levels of 100-200 mg/L were reduced to 0.16 mg/L (Strier, 1980).

Table 5.10

Henry's Law Constant and Compound Solubility for some
Organohalogen Compounds (Patterson, 1985)

Compound	H(at 25° C)	Solubility, mg/L
Aldrin	0.021	0.027
Dieldrin	0.024	0.19
Heptachlor	0.062	0.56
PCB-1242	0.023	0.24
PCB-1254	0.35	0.212
PCB-1248	0.14	0.054
PCB-1260	0.29	0.0027
BHC-Alpha	0.013	0.275
BHC-Beta	0.53	5.0

A typical stripper system operating at atmospheric pressure is shown in Figure 5.3. Wastewater containing organohalogen compounds is preheated and fed to the top of the stripper column. On the other side, low pressure steam is introduced to the column from the bottom of the stripper and they form a mixture. Certain fraction of this mixture is vaporized and leaves the stripper column from the top. This vapor is condensed, and separated in a decanter from which the water is returned to the wastewater inlet line, while organic layer of the condensate is removed for final disposal (Nathan, 1978). This system can also be operated under vacuum. Although vacuum operation does not require a feed-bottom exchanger, it increases the total investment cost, since vacuum operation requires additional equipment.

Stripping by simple aeration is undesirable due to transformation of pollutant from the liquid phase to the atmosphere.

5.5.3 Biological Oxidation

Although the organic priority pollutants are generally considered to be toxic, the extent of toxicity is a function of both the relative toxicity of the individual compounds and of the absolute level (exposure level). The responses of either an aerobic or anaerobic biological treatment processes might be any one or combination of the followings (Patterson, 1985):

- a. Inhibition
- b. Non-biodegradability
- c. Chemical conversion
- d. Biodegradation
- e. Acclimation-degradation
- f. Sorption.

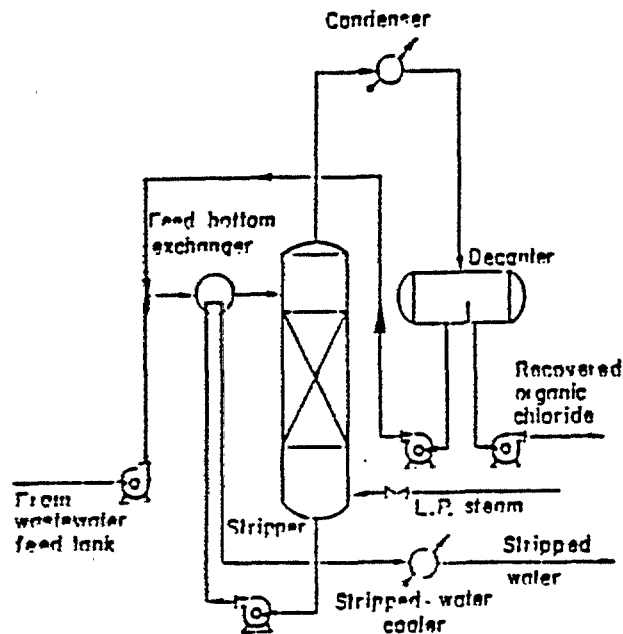


Figure 5.3 Stripping processes: useful for removing the lighter organic chloride (Nathan,1978)

In real systems it is difficult to distinguish the relative influence of the last four listed types of responses, since each results in the disappearance of the subject compound from the soluble phase of the wastewater. An additional mechanism which can dominate over others for many of the volatile organic priority pollutant during biological treatment is volatilization (Patterson, 1985).

In addition, the role of sorption removal may be quite significant. Convery (1973) reported that DDT, dieldrin, and lindane tend to concentrate in the primary sludge. DDT is also bioconverted to DDE and DDD. Other organic pollutants reported by Convery to concentrate in either the primary or secondary sludge are chlordane and PCB.

Data on the occurrence and removal of organic priority pollutants in full-scale biological treatment systems are limited. However, in general, biological treatment is known as an effective technology for removal of many of the toxic organics from wastewaters (Patterson, 1985).

Nathan (1978) reported that, for organic chlorides to be successfully removed in a biological oxidation system, the microbial population of that system must contain components capable of withstanding and of degrading the toxic organic chlorides. The rate at which these organisms develop, in relation to other organisms and to the total amount of

food available, will determine their relative concentration in the biomass. On the other hand, mutant bacteria can be added daily to a conventional activated sludge system in order to enable the system to handle the organic chlorides. A sufficient concentration of mutant bacteria must be maintained to destroy the organics. The amount of such bacteria required for any given waste system must be determined via laboratory tests (Nathan, 1978).

In a recent study, Melcer and Bedford (1988) studied the fate of pentachlorophenol (PCP), when co-mixed with municipal wastewater. The results indicated that PCP concentrations of 0.1 to 12 mg/L can be degraded to less than 10 µg/L, in the 10 to 20 day solids retention time.

5.5.4 Incineration

Another widely adopted technique for the disposal of organo-halogen compounds is incineration (See section 1.4.1.2). In general, the typical operating temperature is 750-1000°C with minimum residence times of 0.3-0.5 seconds. However, better oxidation can be achieved at higher temperatures. For example, for the disposal of PCBs, high efficiency incinerators are suggested (McCoy, 1989). US EPA approves high-efficiency incinerators to destroy PCBs at concentrations greater than 50 ppm. Incinerators burning PCB liquids must meet the following criteria: 2 s dwell time at 1600±100°C and 3 per cent excess oxygen; or 1.5 s dwell time at 1600±100°C and 2 per cent excess oxygen in the stack gas. In either case, the combustion efficiency of these incinerators must be at least 99.9 per cent.

5.5.5 Landfilling

Although there are some restrictions for some of the compounds, one of the disposal alternatives for organohalogen wastes is landfilling. For example, in United States landfilling of wastes with PCB levels of less than 50 ppm is not currently regulated-these wastes can be disposed in landfills permitted under the Resource Conservation and Recovery Act (RCRA) or even solid-waste landfills. However, because of potential future liability, this latter option is not recommended. In order to accept wastes having PCB concentrations between 50 and 500 ppm, special technical requirements must be met (McCoy, 1989):

- a. The facility must have a linear or underlying soil with a permeability of less than 10^{-7} cm/s.
- b. The bottom of the landfill must be at least 15.2 m above the historical high groundwater table.
- c. The site must have monitoring wells and a leachate-collection system.
- d. Specific operating and record-keeping requirements must be met.

5.5.6 Alternative Disposal Methods (McCoy, 1989)

One of the accepted disposal alternative for some of the organohalogen compounds, for example for PCBs, is chemical detoxification. PCBs are chemically destroyed in dielectric fluids, and depending on the specific process being used, PCB concentrations of 1000 to 10000 ppm can be accommodated.

In general, the chemical detoxification processes attack the PCB molecules at the chlorine-carbon bond. Under the mild reaction conditions involved, chlorine is stripped from the biphenyl molecules, and the biphenyls then polymerize to form insoluble sludge. These sludges are subsequently filtered from the dielectric fluid.

The dechlorination reagents used by different companies are proprietary, but generally utilize metallic sodium and solvents to form an organosodium complex. This reagent reacts with the PCBs to form sodium chloride and polyphenylene polymer.

Other components of the dielectric fluid, such as inhibitors, acids, thiols, and chlorides, also react with the sodium reagent to form insoluble sludges. After the reaction step has been completed, a small amount of water may be added to destroy excess sodium reagent through the formation of sodium hydroxide.

6. ORGANOPHOSPHORUS COMPOUNDS

6.1 General Properties of Organophosphorus Compounds

Organophosphorus compounds are organic chemical compounds containing the element phosphorus in any form (UNEP/WHO, 1987). There are roughly 250 organophosphorus compounds manufactured all over the world, and approximately 140 of these compounds are pesticides, the remainder being mainly industrial chemicals used as flame retardants, plasticizers and industrial hydraulic fluids and solvents (FAO/UNEP/IAEA/WHO, 1989). Table 6.1 lists some organophosphorus compounds currently manufactured and used in various countries. Pesticides are used to a varying extent in agriculture or animal husbandry for crop protection or for elimination of ectoparasites and insects. Non-pesticide organophosphorus compounds comprise 4 classes of phosphate esters: triarylphosphates, aryl/alkyl phosphates, trialkylphosphates, and trihaloalkylphosphates.

The basic compound for the synthesis of organophosphorus compounds is phosphine (PH_3), which is alkylated or arylated to R_2PH or R_3P . Following the oxidation of phosphines and the conversion of the C-P bond to C-O-P, phosphinate esters, $\text{R}_2(\text{RO})\text{P}(\text{O})$, phosphonite esters, $\text{R}(\text{RO})_2\text{P}(\text{O})$, and phosphate esters, $(\text{RO})_3\text{P}(\text{O})$ are formed. Within the large groups of organophosphorus compounds esters, especially phosphate esters, are the greatest importance (UNEP/FAO/WHO/IAEA, 1990).

According to use, organophosphorus compounds and their derivatives can be divided into the following categories (UNEP/FAO/WHO/IAEA, 1990):

- a. Industrial use (flame retardants, plasticizers, solvents, antifoaming agents, industrial hydraulic fluids, lubricants, dispersants, detergents);
- b. pesticides (insecticides, acaricides, nematocides, anthelmintic agents, fungicides, herbicides).

In most of the phosphate esters manufactured for industrial use the organic radicals fall into the following categories (UNEP/FAO/WHO/IAEA, 1990):

- a. triaryl phosphates - either three identical aryl groups or two phenyl and one other aryl group;
- b. aryl-alkyl phosphates - either two alkyl and one phenyl or one alkyl and two aryl groups;
- c. trialkyl phosphates - three identical alkyl groups;
- d. trihaloalkyl phosphates - three identical halogenated alkyl groups.

Organophosphorus compounds are ecologically preferred alternatives to organochlorinated compounds because of their rapid breakdown in water and their low environmental persistence (FAO/UNEP/IAEA/WHO, 1989). However, their wide usage has resulted in high contamination in water bodies ranging from 10-20 ng/l up to 127 ng/l (FAO/UNEP/IAEA/WHO, 1989).

The molecular weights of pesticides range from 213 to 466, and from 140 to 698 for non-pesticides (Persoone and Barcelo, 1989). The vapor pressures of the non-pesticides change from less than 0.02 to 127 mm Hg; however, the vapor pressures of pesticides are quite similar, and change from 0.01 to 0.1 mm Hg (Persoone and Barcelo, 1989).

The solubility of organophosphorus compounds in water show great variation. Industrial alkylphosphate esters are soluble while tricresylphosphates are practically insoluble in water. The water solubility of organophosphorus pesticides at room temperature varies from 0.4 to 4000 mg/L (de Bruin, 1989). The water solubilities of non-pesticide organophosphorus compounds are quite similar, and changes from 0.36 to 7000 mg/L (Persoone and Barcelo, 1989).

6.2 Sources and Inputs into the Mediterranean

The types of marine areas at risk from contamination by organophosphorus discharges are, in order of decreasing importance (UNEP/FAO/WHO/IAEA, 1990):

- a. river mouths and estuaries
- b. lagoons
- c. shallow waters
- d. marshes.

The largest input of organophosphorus compounds in the marine environment is via surface waters. Industrial effluents bearing organophosphorus compounds may also be directly discharged into coastal waters from on-shore plants.

Another source of organophosphorus bearing discharges in the marine environment is the spraying of crops with organophosphorus pesticides on fields nearby the sea and last but not least aerial transportation of both non-pesticide and pesticide organophosphorus compounds from various point or non-point sources may eventually also add to the pollution of coastal waters, lagoons and marshes (UNEP/FAO/WHO/IAEA, 1990).

The available figures on production and use of both organophosphorus pesticides and non-pesticides is scarce and fragmentary at the national as well as at the international level. In addition, different figures are reported by different sources and this indicates the difficulties in obtaining accurate and reliable data (UNEP/FAO/WHO/IAEA, 1990). It is known that 21000 tons of organochlorine and organophosphorus pesticides were used in Italy in 1983, of which approximately 19000 tons were organophosphorus insecticides (UNEP/FAO/WHO/IAEA, 1990). Cyprus, Greece, Malta and Turkey reported consumption data on organophosphorus compounds to the Coordinating Unit for MAP (UNEP/FAO/WHO/IAEA, 1990). According to these data Cyprus imported 313 and 389 tons of organophosphorus pesticides in 1987 and 1988 respectively. Similarly, Malta imported in 1986, 45 tons of organophosphorus pesticides. Turkey imported in 1985, 130 tons of pesticide and non-pesticide organophosphorus compounds while this figure in 1986 was reduced to 67 tons. Greece reported the following consumption figures (in tons) for 1988: azinphos-ethyl 80, azinphos-methyl 15, fenitrothion 5, fenthion 130, malathion 50, parathion 30, parathion-methyl 100 and dichlorvos 10.

Table 6.1

Organophosphorus Compounds Currently Manufactured and Used
(Persoone and Barcelo, 1989)

<p>Pesticides:</p> <ul style="list-style-type: none"> acephate amidithion aziphos-ethyl bromophos bromophos-ethyl carbophenothion chlorpyrifos chlorfenvinphos chlorthion coumaphos demeton demeton-S-methyl demeton-S-methylsulfon dialifor diazinon dichlorvos dicrotopos dimethoate dioxathion disulfoton ethion fensulfothion fenthion fenitrothion fonofos formothion leptophos trichlorfon 	<ul style="list-style-type: none"> malathion methamidophos methidathion nevinphos monocrotopos naled omethoate oxydemeton-methyl parathion-ethyl parathion-methyl phenkapton phorate phosalone phosmet phosphamidon phoxim pirimiphos-ethyl pirimiphos-methyl prothoate pyrazophos ronnel sulfotepp temephos tetrachlorvinphos triamiphos triazophos zinophos vamidothion
<p>Non-Pesticides:</p> <ul style="list-style-type: none"> tributyl phosphate cresyl diphenyl phosphate isopropylphenyldiphenylphosphate triphenyl phosphate dibutyl phenyl phosphate isodecyl diphenyl phosphate tris (2-chloropropyl) phosphate tris (1,3-dichloropropyl) phosphate tris (2-chloroethyl) phosphate tris(2-ethylhexyl) phosphate cumylphenyl diphenyl phosphate tricresyl phosphate 2-ethylhexyl phosphate 	

Information on both the sources and inputs of organophosphorus compounds into the Mediterranean is scarce. Most of the information available reports contamination levels in surface waters in Western Europe, especially in Italy. Additional information is available related to the surface waters in France, Spain, and Greece.

In France, 2 and 4 ppb concentrations had been reported for ethyl-parathion and malathion in the river Saone in 1968 (Mestres *et al.*, 1969). In the lake Albufera in Spain, Carrasco *et al.*, (1987) reported a fenitrothion concentration of 0.1-2.0 ppb for the period 1983-1985; these values were reported to decrease each time to non-detectable levels (below 0.05 ppb) within two weeks. In Italy, 0.02-0.03 ppb and 0.04-0.13 ppb tributyl phosphate have been reported in the rivers Po and Turin, respectively (Galassi *et al.*, 1986).

In Greece, organophosphorus pesticides (diazinon, azinphos-methyl and parathion-methyl) were detected in the Ioannina lake and in the Kalamas river. For the period 1984-1985, diazinon concentrations varied from 0 to about 35 ng/l in both the Kalamas river and in the lake of Ioannina. However, the concentrations of the other two organophosphorus compounds, azinphos-methyl and parathion-methyl varied from 0 to about 13 ng/l in the Kalamas river, whereas the concentration ranges for these compounds are 0 to about 13 ng/l in the Ioannina lake (Albanis *et al.*, 1986).

As organophosphorus compounds released into the marine environment are not persistent in water or biota they would not present a hazard to human health through the marine food chain at the concentrations reported in the pilot study which is organized in the framework of the Long-term Programme for Pollution Monitoring and Research in the Mediterranean (maximum concentration in biota, 306 ng/g F.W. for fenitrothion (FAO/UNEP/IAEA/WHO, 1989).

6.3 Principal Industries

6.3.1 Organophosphorus Compounds from Pesticide Production

6.3.1.1 Type and Size of the Industry

The industry produces some 30000 tons per year using organic synthesis technique (FAO/WHO/IAEA, 1990).

6.3.1.2 Type of Wastes

The wastes originate in the various synthesis steps. These include decanter units, distillation towers, hydrolyzing, and product and equipment washing. The wastes may be characterized by BOD, TSS, COD, TOC and phosphates.

6.3.1.3 Form of Wastes

The wastes are aqueous solutions containing small amounts of raw materials, as well as intermediate products and finished goods. For example, the wastes originating from the production of the well known organophosphorus, parathion are acidic and contain alcohol, phosphorus, sulfur, chlorine, soda ash, acetone, paranitrophenol, and some intermediate products (Coley and Stutz, 1966).

6.3.1.4 Total Amounts

Chemical pesticide production plants produce some 2000 m³/d of wastes of which 100 M³/d is from organophosphorus pesticide production. Organophosphorus concentrations in the process waste and in the plant waste are 1000 mg/L and 50 mg/L respectively. Hence some 100 kg per day or 10 tons per year are produced (UNEP/WHO, 1986).

6.4 Treatment

There is only one regulation in the Mediterranean area for organo-phosphorus bearing discharges. In Italy, total concentrations of organophosphorus compounds in the effluents can not be higher than 0.1 mg/L. The other regulations available for organophosphorus compounds mainly refer to surface waters, foodstuff, and crops; and are not for the Mediterranean area. In the USSR, the maximum allowable concentrations of parathion, malathion, and fenitrothion in surface waters are 3, 50, and 250 µg/L respectively. In the United States of America, Environmental Protection Agency has set the water quality criteria for parathion and malathion, for the protection of freshwater and marine aquatic biota at 0.04 µg/L and 0.1 µg/L. Although it has been suggested that many of the toxic organics are subject to treatment by conventional treatment technologies, there is in actuality scant reliable treatment data from full-scale systems (Patterson, 1985). Most of the full-scale data involve performance of systems not specifically designed or operated for removal of the toxic organics, and thus represent incidental performance (Patterson, 1985).

Treatment systems including biological treatment and/or precipitation and sedimentation with chemical addition can be used for the treatment of organophosphorus compounds. The biodegradable nature of most of organophosphorus compounds such as parathion and malathion (Coley and Stutz, 1966) makes biological treatment possible. However, effluent qualities approaching zero can be attained via activated carbon adsorption (UNEP/WHO, 1986).

7. EFFLUENTS CONTAINING RADIOISOTOPES

7.1 Introduction

Radiation may be of natural and anthropogenic origin.

The natural radionuclides in the environment are of two general classes. Cosmogenic nuclides have their origin from the interaction of cosmic rays with atoms present in the atmosphere and in the radioactive decay of radioisotopes produced during the formation of the solar system.

Anthropogenic sources of ionizing radiation are the processes involved in the production of energy with the fission fuel cycle, fallout from nuclear weapon tests, use of radioisotopes in researches, industry and medical applications and consumers goods.

With regards to a release of radioactive effluents into the marine environment the sources of concern are wastes produced during the nuclear fuel cycle and (to a lesser extent) wastes from industrial research and medical applications.

7.2 Sources and inputs into the Mediterranean

Radioactive effluent discharges into the Mediterranean Sea originate from nuclear power plants, fuel reprocessing plants, research reactors and other point sources. Since many nuclear installations in the Mediterranean region are located along major rivers, artificial radionuclides discharged from these installations enter into the Mediterranean Sea by this route. While travelling along the rivers, these discharged radionuclides are subjected to various geochemical processes, such as hydrolysis, precipitation, sorption, ion-exchange, etc. so that the concentrations of the radionuclides entering the marine environment tend to be reduced in the rivers as compared with the original levels at which they were released.

As point sources for radionuclide discharge into the environment, nuclear fuel reprocessing plants are known to be the largest contributors among various types of installations in the nuclear industry. Although some fuel reprocessing activities are conducted in the Mediterranean basin (in France and Italy), the sizes of these reprocessing facilities are relatively small. In addition, these facilities are located along the major rivers in the Mediterranean basin, the Rhone and the Po, and discharge their waste effluents into these rivers. Detailed data have not been published regarding the quantity of radionuclides released into the rivers in question.

Estimates published by IAEA in 1988 demonstrate that nuclear power stations are operational in only four Mediterranean countries: France, Italy, Spain and Slovenia. Estimates for December 1987 show a total of 29 Units in operation, with a combined net capacity of 24,554 MWe, and a further four units with a combined net capacity of 2,989 MWe under construction (UNEP/IAEA, 1991).

The presence of research reactors in Mediterranean countries is more widespread than that of nuclear power reactors. IAEA estimates for December 1987 show a combined total of 25, spread over nine countries. The total discharge rate of radionuclides from research reactors in operation in the Mediterranean region has been estimated at less than 1 GBq a^{-1} (10^9 Bq a^{-1}) in terms of Cs-137 discharge. (UNEP/IAEA, 1991).

Hospitals and scientific laboratories utilizing radioisotopes for medical and scientific purposes may be considered as possible point sources for radionuclide discharges into the Mediterranean marine environment. However, the possibilities of any significant discharges of radionuclides from such establishments are small, due to the fact that the quantities of radionuclides handled are much smaller than in the other types of sources mentioned above.

7.3 Origin and average composition of waste

The nuclear fuel cycle produces wastes along its various steps: mining, milling, feed material preparation, fuel fabrication, energy production by fission in reactors and fuel processing. At each step different type and quantities of wastes are produced. Of the three fuel cycles (uranium, thorium and uranium/plutonium) only the uranium and the uranium/plutonium cycles are used in the Mediterranean countries.

Although all artificial radioactivity is produced in the nuclear reactors by far the greatest amount of these wastes arise in the fuel processing plant. 99.9 percent of these wastes are permanently stored.

In accordance with national requirements of radiation safety, only minor amounts are released into the environment.

Airborne release will only marginally influence the marine environment. Liquid releases may reach the sea indirectly or directly. As will be shown in this section on effects the release into the marine environment of the same quantities results in much lower dose to human than a release into fresh water environment.

Mining, milling, feed material preparation and fuel fabrication produce low level effluents containing uranium, plutonium and thorium and its decay products (daughters). At present no sites are known which discharge into a river and thence into the sea.

The radioisotope composition and the amounts in the effluents released into the environment depend on the reactor type and on the waste processing system used. Therefore, even the composition and amount of the effluents released from the same reactor type may vary widely. In general older reactors release larger amounts of radioactive effluents than recent ones.

The amount of radioactive effluents produced is related to the amount of electric energy produced and the quantities released are normalized into curies per MW(e) y electricity produced.

7.4 Form of waste

Reactors produce airborne and liquid effluents and solid wastes. The main radioisotopes in airborne effluents are the noble fission gases krypton and xenon, the activation gases ⁴¹Ar, ¹⁴C, ¹⁶N, ³⁵S and tritium, radioactive halogens and particulates.

Liquid effluents contain, besides various fission products (FPs), activation products (APs). The average composition of liquid effluents is given in Table 7.1. All values are normalized per MW of electric energy produced. It should be noted, however, that even within the same category of reactors the amounts and the isotopic composition vary widely. With the possible exception of France, spent fuel elements are stored or processed outside the Mediterranean basin. The release of radioactive materials from the fuel reprocessing plant depends upon the type of fuel, irradiation history, cooling time and the specific waste processing systems of the reprocessing installation.

7.5 Total amounts discharged

Approximate release can be estimated from the normalized release and the amount of MW(e) y produced. Future release from nuclear installations may be estimated from the installed power assuming an utilization factor of 0.7. These release will be lower since waste treatment technology will improve. Solid low level wastes are sometimes dumped at sea (but so far no solid wastes have been dumped in the Mediterranean). Wastes from other civilian nuclear uses are often sealed sources, which are not dispersed in the environment. The isotopic composition of non-nuclear wastes to be discharged into the environment is difficult to estimate. Production and import data may be consulted.

7.6 Discharge pattern

Airborne effluents are discharged more or less continuously from BWRs. The amount and relative isotopic composition depend on the hold up times of the gases before

release. In older reactors the hold up time is short (20 to 30 min.). In modern BWRs hold-up times of two hours and more allow short living isotopes to decay. Since in PWRs the primary loop is rarely opened the release is two orders of magnitude less than that from BWRs. The low temperature Magnox reactors discharge insignificant amounts of airborne effluents.

The frequency of release of liquid wastes varies considerably with reactor type and waste treatment plant. Leakage of the primary system to the secondary system and to the auxiliary building means that the amount of floor drainage wastes, from laundry decontamination, wash-down, etc. are important parameters. Then number and capacity of collector tanks and treatment of these wastes and those from the spent fuel pits are other parameters.

7.7 Physical, chemical and biochemical properties

The nuclides may be in ionic form, complexed with organic ligands, particulated and colloidal. According to their form they will follow a different distribution pattern in the marine environment and also different pathways to man. In general ionic radioisotopes are more readily taken up than complexed forms by components of the marine environment. On the other hand particulate and colloidal forms are preferentially accumulated by the so-called filter-feeders, e.g. shellfish.

7.8 Treatment

Except in accidents, radioactive wastes will never be discharged directly into the environment without some treatment which separates the hazardous radioisotopes from the bulk of the waste volume. In fact the scope of waste treatment consists in separating those constituents of the waste which possess a low activity and hence may be safely discharged into the environment (radioactive effluents) from radioactive components too dangerous to discharge (radioactive wastes). These wastes are, in general, concentrated to a small volume prior to permanent storage.

Gaseous wastes are filtered and bubbled through washing solutions in order to retain the fission products and radioactive particles. The retaining of the noble and hence non-reactive gases krypton and xenon is much more difficult and, therefore, in the long run the long-life ^{85}Kr will become one of the most critical gaseous radioisotopes.

Liquid wastes may be treated in various ways in order to separate the radioactive material from the non-active or very low level solutions.

Coagulation and sedimentation is used in many instances. As coagulants clay, alum, iron salts, and calcium may be used. Coagulation is effective for the removal of Sc, Y, Zr/Nb, PO_4 and the rare earths Pr, Ce, Pm, Sm, etc (Figure 7.1). However, different physical-chemical forms can change the effectiveness of the removal process considerably, as the often wide ranges in removal efficiencies indicate.

Clay addition increases the removal efficiency in the cases where the ion exchange capacity of the clay may be utilized. Caesium and strontium are not easily removed under these conditions. The removal can be increased by the addition of iron and by raising the pH to 11.

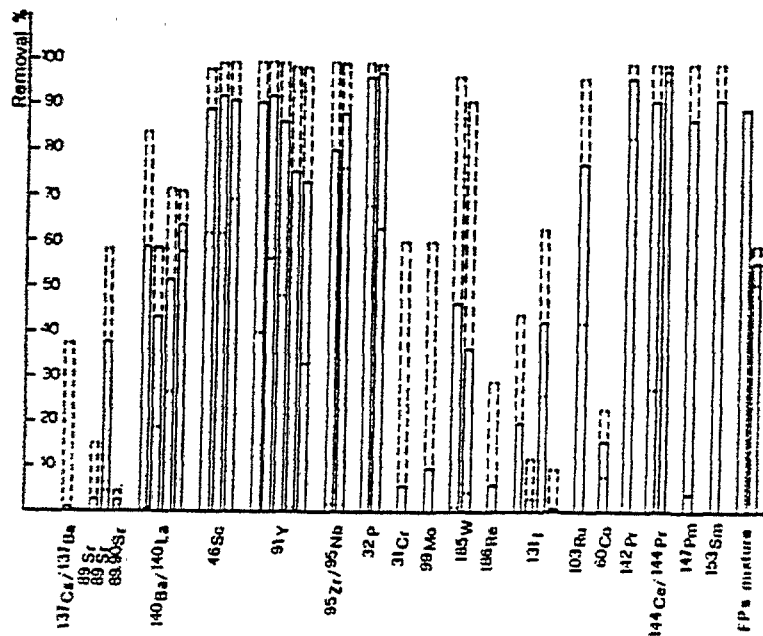


Figure 7.1 Removal of soluble radioactivity by chemical coagulation (Solid column corresponds to average value, intermitted column indicates the range)

Sand filtration removes radioisotopes which are present in the particulate form or which are adsorbed to particles. If slow sand filters are used the first to appear in the effluent is ruthenium, followed by the 90-Sr, 131-I, 239-Pu and 144 Ce. Cerium is retained most effectively, since after 14 days only 8% of the initial activity leaves the filter.

PO₄ may be about 86% removed by either settling, or filtration. A combination of both settling and filtration may achieve 97% PO₄ removal.

Iodine is removed to only a small extent. Here again the physico-chemical state plays an important role, since under certain conditions less than 0.4% may be removed, while in another 11 to 25% can be eliminated.

In Figures 7.2 and 7.3 the data obtained from two different wastes containing fission products (FPs) are given. Although the overall decontamination is practically identical, the individual isotopes are removed by different methods to different extends from the solutions.

Lime and soda-ash softening was reasonably successful in eliminating up to 90% of 140-Ba/La, 89-Sr, 115-Cd, 46-Sc, 91-Y and 95-Zr/Nb, using relatively small quantities of lime (up to 0.2 g/L) and soda (up to 0.15 g/L). High concentrations (up to 0.34 g/L) may remove 95% of 89-Sr, 91Y and 95-Zr/95-Nb. Probably the most important result is the removal of strontium. The efficiency of strontium removal varied from 60 to 90%.

Combined processes are often used for waste treatment. An example is a scavenging-precipitation-ion exchange process in which the ion exchange eluate is recycled to the precipitation system. In this way the sludge from the precipitation step contains practically all the radioisotopes which were removed from the waste.

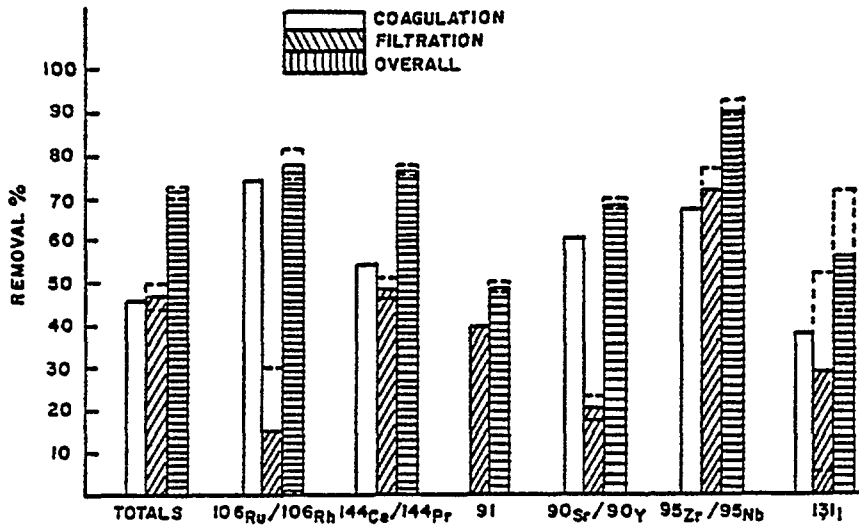


Figure 7.2 Removal of mixed fission products by conventional water treatment processes

Table 7.1 shows the decontamination factors (DF) achieved by the single processes and for the overall treatment. The lowest DFs are obtained for ruthenium and cobalt, which are about 10 to 1000 times less than the DFs for the rare earths, strontium and caesium.

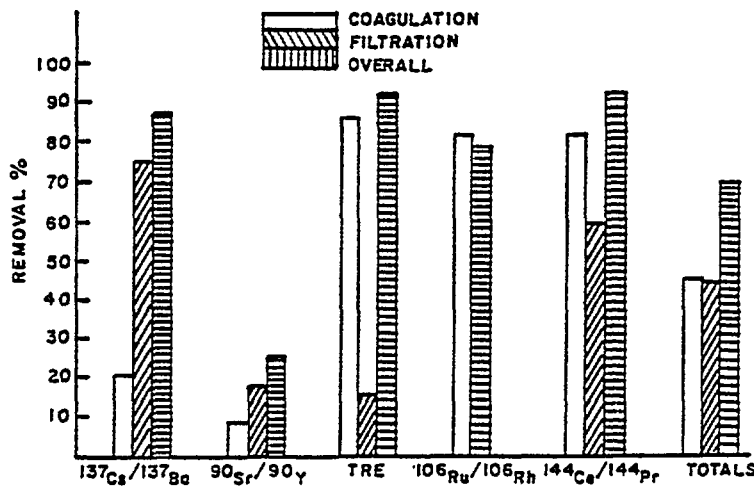


Figure 7.3 Removal of fission-product activity by coagulation, settling and filtration, Initial concentration of radioactive material 22 500 counts/(min)(mL).
TRE= Trivalent rare earths other than cerium

Future nuclear plants may prefer to recycle water in order to economize on fresh water consumption and to minimize discharge of radioactive effluents (Table 7.2). A clarification with alum and activated silica removed principally colloids, ion-exchanger anions and cations and the activated carbon step removed mainly cobalt and organic materials. The overall decontamination factors for individual ions was from 160 to 12,000.

Especially interesting are the DFs obtained for ruthenium, since both acidic and alkaline ruthenium wastes has been added to the original wastes in order to obtain higher counting rates and provide a variety of different physico-chemical states of ruthenium.

Foam separation may be considered in future, since it offers the following advantages: low cost chemicals (air and detergents) and equipment (simple air-sparge column). The process allows the separation of colloids by flotation and an enrichment of cations in the foam of anionic surfactants such as dodecylbenzenesulphonate, Alipal LO 436, Naccol 40 FX etc. The foam separation process may be preceded by a scavenging precipitation.

The DFs for the single processes and for the overall decontamination are smallest for cobalt and ruthenium followed by caesium and zirconium/niobium. Strontium decontamination is highest of all (Table 7.3).

A further example of decontamination is given by the waste of the condensate from alkaline high-level waste-storage.

This waste from a Purex fuel processing is characterized by containing only ammonia and FPs in addition to residues from the solvent extraction methods employed (Table 7.4). Since ion exchange treatment was unsuccessful, this waste was treated by a process combining (i) stream stripping, to remove the ammonia and the organic matter, with (ii) filtration for clarification and (iii) ion exchange. Also here ruthenium had by far the lowest DF, furthermore, the two runs gave quite different results (Table 7.5). The authors attribute the lower DFs in either runs to effects of biological growth which had occurred in the condensate collection tanks, and assumed that the following DFs should be considered.

Ruthenium and other isotopes which may exist in different physico-chemical states (e.g. cobalt, zinc, cerium, etc.) present special problems for decontamination.

Sr	280
Cs	380
Ru	42

¹⁰⁶-Ru especially is very important because of its relatively high fission yield and the many different physico-chemical states in which it may occur.

Electrodialysis (ion transport through permeable membranes caused by an electrical field) may achieve high DFs, (12), and is economically competitive with ion exchange resins and the evaporation processes (Table 7.6).

Table 7.1

Average contamination factors (DFs) for pilot-plant tests of the recycle scavenging precipitation, ion-exchange process

Run	Gross Beta	Gross Gamma earths	Total rare	90-Sr	137-Cs	106-Ru	95-Zr/Nb	69-Co
HR - 17								
Feed (2000 resin-bed volumes, (dpm/mL)	29 ^a	7 ^a	11.5 ^a	49	7.2	0.45	2.7	1.4
Recycled eluate, (dpm/mL)								
DF of scavenging-precipitation	4.3	2.3	7.2	4.9	1.41			
DF of ion exchange	2.6	≈3	≈53.3	≈250	> 510			
DF of over-all	11.2	≈7	≈383.3	≈1225	> 720			
HR - 18								
Feed (2000 resin-bed volumes, (dpm/mL)	42 ^a	5 ^a		42	5.9	0.42	1.4	1.7
Recycled eluate, (dpm/mL)	5.12 ^a	1.25 ^a	12 ^a					
DF of scavenging-precipitation				11.16	6.56	0.01		2.67
DF of ion exchange	1.8	2.08	2.09 ^a		2.71	1.9		6.2
DF of over-all	1.18	6		3.54	230	1.2		1.2
(DF using anion exchange, 300 bed volumes)	2.14	12.5	4.27	500	623	2.1		7.3
(DF over-all using anion exchange)			165	1772		(5) ^c		(1.5) _d
			705			(14) ^c		(11) ^d
HR - 19								
Feed (2000 resin-bed volumes, (dpm/mL)	18.6 ^a	3 ^a	8 ^a	29	4.6	0.4	0.9	
Recycled eluate, ^b (dpm/mL)	10.68 ^a	1.13 ^a	5.14 ^a	13.2	5.93	0.008	0.01	1.3
DF of scavenging-precipitation	4.35	2.1	5.3	3.8	2.5			0.08
DF of ion exchange	5.0	6.7	125	367	840			
DF of over-all	22.5	13.8	657	1407	2106			

a cpm/l
 b calculated from eluate analysis - no recycle during HR 17
 c Anion exchange DF = 1.5 at 1500 bed volumes
 d Anion exchange DF = 1.0 at 1500 bed volumes

Table 7.2
Over-all decontamination factors for the water-recycle process

	144-Ce	69-Co	137-Cs	131-I	106-Ru	125-Sb	99-Sr	95-Zr/Nb	Total rare earths	Gross gamma	Gross beta	Bulk ions specific conductance
Raw-waste analysis dpm or cpm/mL	10.1	70.9	23.6	126.2	44.2	3.5	52.0	0.4	32.0	52	85	290 ^a
Decontamination factors	330	12000	2600	430	610	300	6300	160	11000	140	1100	500
Over-all	1.4	1.4	1.0	1.0	2.0	1.0	1.0	2.1	1.1	1.3	1.1	-
Clarification step	85	72	510	270	440	100	6300	8.6	6000	110	240	-
Ion-exchange step	2.8	120	5.0	1.6	1.4	3.0	1.0	8.6	1.7	1.0	4.3	-
Activated-carbon step												

^a In mho/cm

Table 7.3
Typical decontamination factors for the
scavenging-precipitation-foam separation process

	Foam height		V/LD ^d (cm ⁻¹)	Grundite clay (1b/1000 gal)	Time (h)		
Conditions :							
- Laboratory	22 in.		202	0.5	10		
- Pilot plant	8 ft.		140	0.7	91		
Liquid flow (gal ft ⁻² h ⁻¹)	Scavenging- precipitation Laboratory ppc		Foam column Laboratory ppc		Over-all Laboratory ppc		
	12	24	39	15			
			Decontamination factors				
	Ca	50	60	≈2	-	≈ 100	-
	Sr	16	10	220	36	>3500 ^a	1080 ^b
Cs	21	8	1	1	18	8.0	
Co	2.3	-	1	-	2	1	
Ru	1.8	-	4	-	>7 ^a	4.2 ^a	
Ce	24	-	4	-	100	>20 ^a	
Zr/Nb	-	-	-	-	-	>50 ^a	

- a Close to lower limit of analytical determination
- b Includes a decontamination factor of 3.0 obtained in foam recovery columns
- c Pilot-plant
- d V/LD: V and L are gas and liquid flow-rates and D is the effective bubble diameter

Table 7.4

Average composition of alkaline and acidic condensates
from Purex wastes at Hanford

Waste constituents or property	Alkaline condensate (μCi/mL)	Acid condensate (μCi/mL)
C 8 144-Pr	10 ⁻³	10 ⁻³
98-Sr	10 ⁻⁴	10 ⁻⁷
106-Ru	10 ⁻³	10 ⁻²
137-Cs	10 ⁻²	10 ⁻⁴
95-Zr/Nb	10 ⁻³	10 ⁻²
Butyl phosphate	30-200 mg/L	-
Hydrocarbons	10-70 mg/L	-
NH ₄ ⁺	35-200 mg/L	-
Na	1-2 mg/L	-
NO ₃ ⁻	1-5 mg/L	-
NO ₂ ⁻	5-10 mg/L	-
HNO ₃	-	1-3*10 ⁻² M
pH	9-10	2

Table 7.5

Average decontamination factors for pilot plant.
Tests for the stripping - Ion exchange process

	Decontamination factors				
	137-Cs	90-Sr	106-Ru	95-/Zr/Nb	144-Ce/Pr
<u>Run No. 1^a</u>					
Filter	1.0	1.2	1.1	2.7	2.4
Anion column ^c	-	1.0	3.0	2.2	2.0
Cation column ^d	130	550	1.7	15	7.7
Over-all	130	875	5.7	85	37
<u>Run No. 2^b</u>					
Filter	49	8.9	2.8	2.9	3.8
Anion column ^c	-	-	4.1	3.3	3.2
Cation column ^d	7.8	32	3.6	>23	>27
Over-all	380	280	42	>230	>330

- a With diatomaceous earth filter aid
- b With diatomaceous earth and clinoptilolite filter aid
- c Strong base IRA - 900 (Antrachite)
- d Strong acid IR - 200 (antrachite)

Table 7.6

Electrodialysis cell comparison

Seven-cell unit		Twenty-cell pair unit	
Total effective membrane :110 cm ²		Total effective membrane :4400 cm ²	
Cell cross-section : 36.67 cm ²		Cell cross-section : 220 cm ²	
Cell width : 1.9 cm		Cell width : 0.16 cm	
% Removed		% Removed	
Nitrate	Ruthenium	Nitrate	Ruthenium
30	13	30	12
50	23	50	22
70	37	70	34
90	58	90	56

PART II

ANNEX II SUBSTANCES

8. INORGANIC POLLUTION

8.1 Zinc

8.1.1 Introduction

Zinc is usually found in nature as the sulphide; it is often associated with sulphides of other metals, especially lead, copper, cadmium and iron. It also occurs as a silicate complex and carbonate. Furthermore, zinc is an essential constituent of many metallo-enzymes, proteins and structural cellular components (Bowen, 1966). High concentrations of zinc in the sea may result from the discharge of industrial wastes from mining, electroplating and synthetic fibre production (Bryan, 1971). A slow but continual process of mobilization occurs as a result of metal complexing and certain other microbiological processes.

In seawater zinc can exist in several different stable or meta-stable forms. One of these forms has been called the "complexed" fraction, which appears to be relatively stable and can only be broken down at low pH. In addition, this fraction resists recombination with the ionic and "particulate" fraction. (Fowler and Heyraud, 1974).

8.1.2 Sources and inputs into the Mediterranean

Anthropogenic activities such as mining, the industrial processing of ores and metals and the use and disposal of metals and metal compounds have resulted in increased inputs of zinc into the oceans. Other sources including combustion of fossil fuels, waste incineration and smelting, release zinc into the atmosphere which is subsequently transported by various pathways to the sea.

Industrial processes which give rise to zinc in their waste solutions include zinc and brass metal works, zinc and brass plating, basic steel works, steel galvanization, silver and stainless steel tableware manufacture, viscose, rayon, yarn and fibre production, battery production, paint and dye manufacturing, anti-corrosion in cooling towers, organic chemical thermoplastic products, fertilizers, petroleum refining, as well as pulp and paper manufacture and production of newspapers and magazines.

Elevated concentrations of zinc are present in the suspended solids of wastewaters and sewage sludges as a result of industrial waste inputs and corrosion within the urban water supply network, and in urban runoff containing metals derived mainly from the surface of streets and highways (Forstner and Wittmann, 1983; UNEP/FAO, 1986a).

Rivers transport zinc from inland industries or urban centres, from increased erosion due to mining, and from agriculture.

There is no accurate information available as to the amounts of zinc discharged into the Mediterranean through effluents.

8.1.3 Zinc-bearing wastes

Processes which give rise to zinc in their waste solutions include zinc and brass metal works, zinc and brass plating, steel galvanization, silver and stainless steel tableware manufacture, viscose rayon yarn and fibre production, battery production, paint and dye

manufacturing, anticorrosion in cooling towers (together with chromium), as well as pulp and paper manufacture.

Zinc is mainly found in the rinse solution of plating and metal processing industries (galvanization). Separation of zinc through treatment is very difficult due to its association with other metals in waste streams. It is not economical to separate and recover zinc.

8.1.4 Principal industries

8.1.4.1 Metal plating industry

Type and size of industry

Zinc is used in the electroplating process (for zinc plating) in cyanide solutions. Zinc may also be used in metal coloring process plants. Zinc is used in the anodizing plants and also zinc plated steel may be treated with phosphoric acid. Industry sizes vary from small electroplating shops with a few tons per week capacity to major metal works with platings of tens of thousands tons of finished product per year.

Types of wastes

The origin of zinc bearing wastes is mostly electroplating dipping baths. In most cases the bath solution is alkaline and it contains zinc-cyanide, NaOH, Na₂CO₃, Na₂SO₄, NaCN and Rochell salt.

Following electroplating, most zinc compounds appear in the wastes in the form of Zn(CN)₂ and some in the form of Zn₂Fe(CN)₆.

As with other plating wastes, zinc concentrations will vary according to plant management. Average concentration of zinc in general electroplating wastes is 5 to 8 mg/L. Concentrations may vary from 11 mg/L in silverware plants, to 110 mg/L in cyanide bearing wastes from automobile manufacture. Plating solution may contain as much as 34,000 mg/L of zinc.

Form of wastes

Zinc bearing wastes are of a similar type to other plating wastes, they are in a clear liquid form and most zinc is soluble in alkaline solution of pH above 9. Sometimes zinc compounds form a suspension with white grey milky form. Most wastes are generally cyanide bearing and may include aluminium, lead and copper depending on the other process steps. Solutions may include both insoluble zinc and dissolved zinc as well as floating scum and oil.

Total Amounts

Zinc plating of one ton of product usually discharges 0.4 kg of zinc with a flow of approximately 8 m³ of total liquid wastes. Bath water including cleansing and rinsing amount to 60 litres of wastes per 1 m² of plated surface in water-saving plant.

Discharge Pattern

Zinc coating and silverware processing are both batch processes leading to semi-continuous discharges of wastes. Most plants operate one or two shifts per day. Weekly cleaning of baths may result in peak flow on a certain day of the week. There may also be peak discharges due to accidental or unintentional spills and dumpings.

8.1.4.2 Steel galvanizing plants

Type and size of industry

Steel galvanizing industry, specifically galvanized pipes, is usually large, as far as individual plants are concerned. Plants with capacity of 5,000 to 50,000 tons per year are in existence. Most plants use the Hot Dip Galvanization technique which is in many aspects similar in principle to the zinc electroplating but the industry is more mechanized and processes are more continuous and are usually with automatic control.

Type of wastes

Two forms of steel galvanization exist, namely: (1) galvanization in alkaline solution, usually with the presence of cyanides, and (2) galvanization with acidic solution with the presence of zinc sulphate. The galvanization in alkaline solution is almost similar to the zinc electroplating technique described in the preceding paragraph.

The acidic galvanization wastes originate mostly from the process of fluxing which in large galvanization plants is continuous and wastes contain zinc sulphate together with other salts.

Form of wastes

Wastes are in a clear or slightly coloured liquid solution with pH levels of between 2 and 3. Wastes contain zinc and iron ions as well as sulphate and chloride anions.

When pH levels are raised, a milky suspension is formed which finally yields a slurry type sediment.

Total amounts

Large galvanization plants produce approximately 5 to 15 m³ of total plant wastes per ton of galvanized steel capacity. Approximately 5 to 10 percent of these wastes are galvanization fluxing wastes i.e. approximately 1 m³ of process wastes per ton of plant production capacity.

Discharge patterns

In small plants with batch operation discharge is semi-continuous (depending on number of batches per day). In larger plants discharge is continuous for at least 12 hours per day. For a plant to become economical at least two-shift operation is required.

8.1.4.3 Viscose rayon production

Zinc is discharged from the viscose rayon production process. General rayon wastes may contain from 250-1000 mg/L of zinc. Ion exchange recovery of zinc may reduce concentrations to 20 mg/L.

8.1.4.4 Groundwood pulp production and newsprint production

Little information is available as to the concentrations of zinc in wastewaters from these processes. It has been noted that a large groundwood pulp mill used 6 tons of zinc per day.

8.1.4.5 Cooling water

The use of a commercial process 'Cathodic Treatment' leads to zinc being discharged in the blow down of circulating water systems. Zinc concentrations of 6 mg/L have been found.

8.1.4.6 Paint production

Zinc has been found in the wastes from the paint industry in concentrations ranging from 0.3-10 mg/L.

8.1.5 Treatment

Treatment processes employed for wastewater zinc removal involves precipitation and disposal of resulting sludge solids, or recovery processes such as ion exchange, evaporative recovery, and reverse osmosis.

8.1.5.1 Chemical Precipitation

Among the above mentioned methods, the standard treatment method for zinc involves its chemical precipitation as the relatively insoluble zinc hydroxide after pH adjustment to a highly alkaline range, usually achieved by lime addition. Lime is especially used for economic reasons, even if, in the presence of high sulphate levels, it can cause a considerable precipitation of calcium sulphate which will result in a considerable increase in total sludge volume.

According to the theoretical considerations, the optimum pH for zinc hydroxide precipitation is about 10 (Figure 8.1), with a minimum solubility of 1.1 mg/L in pure water (Lanouette, 1977); and, zinc hydroxide undergoes resolubilization at higher pH values. However, results obtained from actual treatment systems indicate that treatment efficiency increases with further increase in operating pH. For example, in testing actual zinc plating rinse wastewaters containing alkaline cleaning compounds, Yost and Scarfi (1979) reported that optimum zinc precipitation treatment is achieved at pH 11 and above. They also reported that the effluent zinc concentration and treatment pH are also influenced by initial zinc concentration.

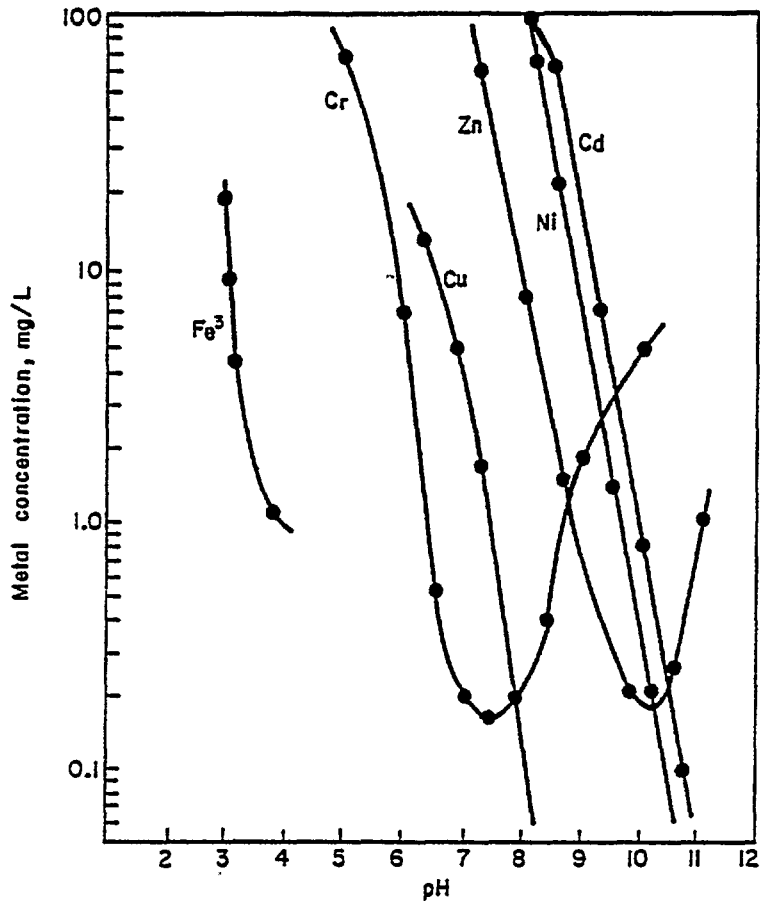


Figure 8.1 Precipitation of heavy metals as hydroxides (Lanouette, 1977).

In the plating industry, the presence of zinc is generally associated with that of cyanide and chromate. Cyanides must be previously removed by oxidation; an incomplete cyanide removal may adversely affect the efficiency of the subsequent zinc hydroxide precipitation, because of formation of complexes. Similarly, if chromate is also present in the waste, as frequently occurs in zinc and brass plating, chromate reduction must precede metal hydroxide precipitation.

Separation of precipitated hydroxide is carried out by sedimentation which, to be satisfactory, must avoid floc carry-over into the effluent; should this occur, the effluent quality would deteriorate considerably. Better results and in particular greater operating safety may be achieved by carrying out a final sand filtration. This stage is seldom applied because it is expensive and causes operating difficulties. With careful adjustment of pH, followed by sand filtration, the zinc concentration in the effluent can be lowered below 1 mg/L. Table 8.1 is a representative summary of published treatment results for hydroxide precipitation.

Zinc recovery from sludge by acid regeneration is economically profitable only when the element is highly concentrated and other metals are absent, as is sometimes the case in rayon production. An alternative method of recovery involves the use of ion exchange resins.

Table 8.1

Summary of Hydroxide Precipitation Treatment Results for Zinc Wastewater

Industrial source	Zinc conc., mg/L		Comments	Reference
	Initial	Final		
Galvanizing	-	0.2-6.0	Sand filtration	Chalmers, 1970
Brass wire mill	36-374	0.08-1.60	Integrated treatment for copper recovery	Leslie & Forbes, 1971
Viscose rayon	20-120	0.9-1.5		Enka Am.Co., 1971
Metal fabrication	-	0.5-1.2	Sedimentation	Stone, 1967
	-	0.1-0.5	Sand filtration	

8.1.5.2 Ion Exchange

Ion exchange process may be either used as a polishing process following chemical precipitation, or as a means for water recovery and reuse. One application for a plating wastewater, achieved an effluent zinc level below 0.05 mg/L (Yeast, 1977). However, unless associated with other materials, or a requirement for water reuse, zinc treatment by ion exchange for recovery of the metal alone is not usually economical, except at high zinc concentrations (Patterson, 1985).

Successful zinc removal by ion exchange for viscose rayon manufacturing wastes was reported, since the wastewaters are highly concentrated and other metals are absent (Patterson, 1985). In the electroplating industry, zinc is generally associated with other metals; the use of ion exchange resins may thus be foreseen for water re-use and for the concentration of the pollutant into small volumes. These must be later subjected to a conventional precipitation process, which may be thus carried out on a much reduced scale, generally as batch treatment, which is easier to control and requires simpler instrumentation. This also offers the advantage of a decrease in the chemical reagent consumption and in the over-all amount of discharged zinc and other metals.

The recovery of the zinc in wash waters (from plating baths and pickling processes) is also possible by concentration obtained by evaporation, provided that the flow rates to be treated are limited by the adaptation of appropriate rinsing techniques. Concentrations may thus be re-used for bath topping up, while condensates have zinc contents that are low enough to allow their discharge without any further treatment.

However, the economic convenience of such systems always depends on the rationalization of the production cycles and usually only exists in large scale operations, even then varying widely with location, nature of product and the concern for eventual re-circulation of the waters.

8.2 Copper

8.2.1 Introduction

Copper is a widely distributed trace element but, because most copper minerals are relatively insoluble and because copper is sorbed to solid phases, only low concentrations are normally present in natural waters. The presence of higher concentrations of copper in seawater can usually be attributed to industrial wastes.

8.2.2 Sources and inputs into the Mediterranean

Anthropogenic activities such as mining, the industrial processing of ores and metals and the use and disposal of metals and metal compounds have resulted in increased inputs of copper into the oceans. Other sources including combustion of fossil fuels, waste incineration and smelting, release copper into the atmosphere which are subsequently transported by various pathways to the sea.

Copper is also used in various industrial processes, in alloys, as a chemical catalyst, and in antifouling paints as an algicide and in wood preservatives.

Metallic copper is used in industry and for jewellery and ornamental purposes. Copper bearing solutions arise from metal plating operations in the subsequent rinse water, while jewellery processing also involves plating of or on copper. Copper is also a major component in the electrical wiring industry. Electroplating and etching of printed circuits in the electronic industry produce copper containing wastes. It is also used in agriculture.

Elevated concentrations of copper are present in the suspended solids of wastewaters and sewage sludges as a result of industrial waste inputs and corrosion within the urban water supply network. (UNEP/FAO, 1986a).

Rivers transport copper from inland industries or urban centres, from increased erosion due to mining, and from agriculture.

The amounts of copper discharged into the Mediterranean Sea through domestic and industrial effluents have been estimated 2.3 and 6.0 tonnes $\times 10^3$ per annum respectively (UNEP/FAO, 1986a).

8.2.3 Copper-bearing wastes

Copper metal is used both in industry and for jewellery and ornamental industry. Copper bearing solutions arise in the metal plating bathing operations with subsequent rinses while jewellery processing also involves plating of or on copper. Copper is also a major component in the electrical wiring industry. Electroplating and etching of printed circuits in the electronic industry also products copper bearing wastes.

8.2.4 Principal industries

8.2.4.1 Metal processing and plating

Type and size of industry

Industrial copper utilization occurs in large industrial complexes involving copper mills, and appliance manufacturing. The production of electrical cables and automobile radiators is another major use of copper. Electroplating also involves copper waste flows. Size of plants vary from small shops processing a few tons of copper per year to large industries processing hundreds of tons of copper and brass products per year.

Type of wastes

Copper is electroplated using four types of baths, alkaline cyanide, acid sulphate, pyrophosphate and fluoborate - all made using the copper salts. Copper is electroplated where a thick coat is required.

Chromates are often coated on to copper. Immersion plating is used to put a copper coat on steel, gold on copper and tin on copper.

Plating process wastes may contain up to 120 mg/L of copper, brass mill wastes may be up to 400 mg/L, while other processes may lead to waste concentrations up to 50 mg/L generally. Exceptions are copper wire mills (800 mg/L average) 1000 mg/L in silver plating.

Total plants wastes usually contain 20 to 80 mg/L of copper according to amounts of rinse waters. Continuous rinsing (following dipping) and stationary rinsing contain between 5 to 20 mg/L of copper.

Two major types of copper plating processes exist, namely: the alkaline cyanide process and the acid sulphate process. Both processes produce respectively different types of wastes.

The alkaline cyanide copper plating involves electroplating in baths containing 15,000 to 60,000 mg/L Na_2CO_3 , 5000 mg/L to 10,000 mg/L NaCN or KCN and 20,000-40,000 mg/L $\text{Ca}(\text{CN})_2$. pH levels are maintained at 11-12.5.

Plating baths wastes contains small monocline crystals of CuCN and dissolved $\text{CuK}_3(\text{CN})_4$ as well as KCN , NaCN and other salts and heavy metals. Wastes are strongly alkaline with pH between 11 and 12.

The acid sulphate copper plating involves electroplating in baths containing 50 gr/litre sulphuric acid and 200 gr/litre copper sulphate. In many cases thiourea-dextrin molasses are added. All the bath substances appear in the bath wastes and in the various rinsing operations.

Form of wastes

Alkaline cyanide process wastes are turbid with dark colour and they contain suspended matter and small crystals in suspended and sludge form. They have a typical copper cyanide odour and should be kept in their alkaline form to prevent the emission of

HCN. Wastes can contain oils and other metals. Acid sulphate wastes are clear with the typical light blue colour of copper sulphate.

Total amounts

Alkaline cyanide processes produce 30 to 40 m³ of wastes per ton of plant product. Acid sulphate processes produce 20 to 30 m³ of wastes per ton of plant product.

Discharge patterns

Small plants produce frequent batches when baths are being emptied after plating (dipping) which produce extremely concentrated wastes. Stationary (fixed) rinsing, following plating, produce medium concentrated wastes and continuous or semi-continuous rinsing produces wastes with decreasing concentrations.

Large plants produce the wastes virtually continuously. In a very well-managed waste handling plant the concentrated (hot) wastes from plating and stationary rinsing are segregated from the concentrated sequential rinsing. In a few plants, an attempt to recover some of the chemical substances from the "hot" wastes was made. The economics of such recovery is still controversial.

8.2.4.2 Electric wire treatment

Type and size of industry

Electric wire plants can vary from 500 to 2000 tons of wires produced per year with a few exceptions of larger plants.

Type of wastes

When wires are drawn from the melted copper they are pickled with sulphuric acid to remove layers of copper oxides. Sodium carbonate is used for neutralization. Wastes contain copper sulphate and copper carbonate together with sodium sulphate.

Form of wastes

Turbid solution containing dissolved copper sulphate and suspended and sludge of copper carbonate with orange colour.

Total amounts

Approximately 2 to 5 m³ of wastes are produced per ton of wires processed. Flow reduction, which is advisable for metal recovery, can bring down the amount to between 1.5 to 2.5 m³ per ton of wires. Plant raw wastes contain 50-100 mg/L of copper sulphate and 50-100 mg/L of copper carbonate.

Discharge patterns

In smaller plants operation is intermittent and discharge is for a few hours per day or on certain days per week. Larger plants have a continuous or semi-continuous flow.

8.2.4.3 Copper ornamental industry

Type and size of industry

Copper ornaments, jewellery and souvenirs are "blackened" in small shops or larger copper ornament industries.

The industry is limited in size but is a significant waste producer because it is difficult to control.

Type of wastes

Following coating of copper products they are washed with sulphuric acid and sulfide-containing substances such as $K_2S_2O_3$, K_2S etc. Copper oxides and copper sulphate are produced in the wastes together with oils, detergents and salts.

Concentrated bath wastes can contain between 100 and 300 mg/L of copper while sequential rinse waters will contain between 5 to 20 mg/L.

Wastes are very acidic and most copper is in solution.

Form of wastes

Turbid acid solution containing suspended matter and greyish sludge.

Total amounts

Approximately 5 m³ of wastes per ton of copper products.

Discharge patterns

Usually intermittent batches of concentrated bath wastes and rinse waters.

8.2.4.4 Electronics printed circuit industry

Type and size of industry

This is a developing industry usually of medium and small size establishment producing 1000 to 6000 m² of printed circuit per year. A few major electronics firms have opened large printed circuit factories with capacities of 10,000 m² of printed circuits per year and more. It should be noted that the trend is to reduce the size and increase the sophistication of printed circuits, thus measuring surface area is not adequate for plant capacity nor for its waste discharge.

Type of wastes

Wastes contain mainly copper associated with other metals such as chromium, tin, zinc, nickel and cadmium. Pickling of copper components by chromic acid forms an especially problematic waste containing $Cu_3(CrO_4)_2$, and H_3CrO_4 . Process wastes from plating baths and stationary rinsing contain 80,000 to 150,000 mg/L of copper while total plant wastes can contain 100 to 250 mg/L copper.

Form of wastes

Clear bluish acid solution.

Total amounts

15 to 30 m³ of wastes are produced per square meter of printed circuits produced. Copper discharge in wastes might reach 2 to 4 kg per m² of printed circuits.

Discharge patterns

Batch in small establishments followed by intermittent rinsing. Virtually continuous in large establishments with occasional peaks in concentration due to spills, emptying and cleaning.

8.2.4.5 Other industries with wastes containing copper

Copper wastes may also originate from the following processes: wood preserving, pulp and paper mills, paper and paper board mills, fertilizer manufacture and petroleum refining.

8.2.5 Treatment

As with most heavy metals the treatment commonly adopted involves its precipitation as hydroxide and disposal of resulting sludge solids, or recovery processes such as ion exchange, evaporation, and electrolysis.

8.2.5.1 Precipitation

Copper can be removed as the relatively insoluble copper hydroxide Cu(OH)₂, after pH adjustment to a highly alkaline range, or occasionally as the sulphide; to this purpose, lime is especially used for economic reasons, even if, in the presence of high sulphate concentrations, it can cause a considerable precipitation of calcium sulphate. This is an inconvenience when metal recovery from sludges is desired, but it may be obviated by the use of other alkalizing agents, e.g. sodium hydroxide.

The minimum solubility of copper oxide which forms copper hydroxide occurs in the pH range 9 and 10.3. Under this condition, theoretically, very low copper concentrations can be obtained (even to 0.01 mg/L) (Stumm and Morgan, 1970). In actual practice the results are decidedly worse because of the difficulty of controlling reactions (slow reaction rates, pH fluctuations), the influence of other ions in solution and the carry-overs in the sedimentation phase. Data presented in Table 8.2 is a summary of treatment levels achieved by precipitation in full-scale industrial treatment operations.

Hannah *et al.* (1977) studied the removal of copper together with other trace metals by physical-chemical treatment system consisting of chemical clarification, filtration and carbon adsorption. Alum treatment followed by activated carbon adsorption was found to be effective in removing copper from wastewater. Alum treatment removed 70 percent of the copper and activated carbon increased the cumulative removal to 97 to 98 percent.

A significant problem associated with copper treatment in achieving low residual concentrations is the presence of complexing agents in wastewater. Patterson (1985)

pointed out that the removal of complexing agents is essential for good copper removal. Copper cyanide wastewaters can be treated by first destroying the cyanide, followed by conventional copper treatment. Similarly, wastewaters containing excess carbonate should also be pretreated. One possible approach would be pH reduction to a near-neutral value plus air stripping, followed by pH readjustment for copper precipitation.

An alternative precipitation process involves the use, along with sodium hydroxide, of a reducing agent such as hydrazine, which allows the separation of the metal in the cuprous, rather than cupric, form (such a system may be operated at a pH 7-8); hence the advantage offered is of obtaining a much denser sludge, which may be more conveniently subjected to recovery processes. Precipitation as sulphide has sometimes has been adopted, principally on mining and ore extraction wastes.

Table 8.2

Summary of Effluent Copper Concentration After Precipitation Treatment

Source (treatment)	Copper concentration, mg/L		Reference
	Initial	Final	
Nonferrous metal processing (lime)	200-400	0.2-2.3	Stone, 1972
Metal Processing (lime)	204-385	0.5	Nyquist and Carroll, 1959
Brass mill (Hydrazine+caustic)	75-124	0.25-0.85	Leslie and Forbes, 1971
Electroplating (lime)	6-15.5	n.d-1.2	Talmange, 1965
Integrated circuit manufacture (lime)	0.23	0.05	Hango <i>et al.</i> , 1973
Acid mine drainage (lime)	3.6-30.4	0.1	Huck and LeClair, 1975

The above precipitation processes may be applied to fairly low copper concentrations that are typical, for example, of rinse waters from the pickling and electroplating industries. However, because of the high commercial value of copper, it is advisable to adopt other recovery systems, especially from concentrated baths.

Costs associated with precipitation treatment systems depends on precipitating agent used and the presence of other interfering agents such as cyanide. A printed circuit board waste treatment plant which includes pretreatment for a chelated/ammoniated copper rinsewater was reported to have an operating cost of \$2.8/1 m³ treated, not including sludge disposal. The capital cost for this plant was reported to be \$3.68/liter per day treatment capacity (Jashnani and Green, 1979).

8.2.5.2 Evaporative Recovery

Recovery by evaporation is also feasible for copper due to its high value. Use of evaporation has also been practiced to obtain water suitable for re-use in the plating bath. However, progressive increase of impurities limits this method of direct recovery. As the impurities which are added with plating chemicals and those formed by decomposition of additives build up, defective plating may result.

8.2.5.3 Ion Exchange

The use of ion exchange resins in the case of effluents with a low initial copper concentration, leads to excellent removal efficiencies, often to an undetectable level, but it is only economically justified by the subsequent recovery of the metal. It is necessary, however, that the regeneration of the resin is carried out with small quantities of regenerant in order to recover a concentrated copper solution. To this end, counter-current processes of regeneration are also available to yield concentrated eluate. The process may also be applied in the case of cuprous-ammoniacal wastes, and allows the removal of both copper and ammonia.

Other processes that can be applied for the treatment of copper wastes are cementation, electrodialysis, reverse osmosis, and activated carbon. Cementation is applicable for both dilute and concentrated copper wastewaters, with the recovery of pure metal. One pilot plant cementation application has been reported to reduce the influent copper level of 80 mg/L down to 0.33 mg/L. Electrodialysis has been cited as economically feasible for copper wastes. The major operational problem associated with electrodialysis was reported to be membrane fouling. Successful activated carbon adsorption and reverse osmosis were also cited for copper wastes. In the treatment of copper cyanide wastes, activated carbon treatment has been reported to give a total removal greater than 98 %. Although some problems and limitations arise connected with the membrane selection, reverse osmosis has also been reported to be successful for copper pyrophosphate, acid copper, and copper-cyanide plating-bath rinsewaters (Patterson, 1985).

8.3 Nickel

8.3.1 Introduction

Nickel compounds are found in many ores and minerals and, as most nickel salts are quite soluble, they may contribute to water pollution through municipal waste discharges.

8.3.2 Sources and inputs into the Mediterranean

There is no accurate information available regarding the amounts of nickel discharged into the Mediterranean Sea through industrial effluents.

8.3.3 Nickel-bearing wastes

Nickel is found in the wastes from metal processing and plating industries. These include tableware plating, and metal finishing plants. Copper and brass plating plants produce wastes which contain little or no nickel (< 1 mg/L).

8.3.4 Principal industries

8.3.4.1 Metal processing

Type and size of industry

Types of industry are tableware plating, metal finishing, appliances and business machine manufacture, and general plating plants. The size of plants varies.

Type of wastes

Typically the wastes arise from plating and pickling processes as well as rinsing. Nickel plating is performed using a sulphate boric acid - chloride solution as well as baths of the nickel salts of sulfonate, chloride and fluoborate. Baths for nickel plating contain approximately 300 gr/litre of NiSO_4 , 40 gr/litre of NiCl_2 , together with 40 gr/litre of H_3BO_3 .

For thick metal coatings, nickel is used as a primary coating of complex objects. Nickel is usually in an acidic bath. Nickel is also coated on steel using immersion baths. Nickel may be in concentrations in the range of 10-130 mg/L for tableware plating plants, 2-50 mg/L for metal finishing plants, 10-40 mg/L for business machines and appliances manufacturing, and up to 100 mg/L for general plating.

Wastes are acidic and contain besides NiSO_4 and NiCl_2 , H_2SO_4 and H_3BO_3 . Spent plating baths, stationary rinsing and primary dipping contain high concentrations of nickel. If the concentrated wastes are segregated, rinsing water contains between 5 to 20 mg/L nickel.

It is associated with other metals used in the general metal processing industry.

Form of wastes

Wastes appear as acid green solutions.

Total amounts

Between 20 to 50 m³ of liquid wastes are produced per ton of processed products.

Discharge patterns

Discharge of rinse waters and process associated occasional spills, will give rise to a continuous discharge with peaks in concentrations.

8.3.5 Treatment

The primary sources of nickel wastes are the plating and metal-processing industries. Therefore, the nickel-bearing wastes are frequently polluted with the other contaminants, and the nickel treatment is combined with treatment for other contaminants.

The commonly adopted techniques for the removal of nickel include precipitation, ion exchange, evaporative recovery and reverse osmosis. The application of electrodialysis has also been reported for nickel wastes.

Regardless of the type of treatment employed for nickel, the level of treatment required and associated costs can often be reduced by good housekeeping practices to reduce accidental loss, spillage, or leaks of plating or pickling solutions containing nickel (Patterson, 1985).

8.3.5.1 Precipitation

As for other heavy metals the treatment commonly adopted involves its precipitation as hydroxide after pH adjustment to a highly alkaline range by lime addition. The nickel

hydroxide has a minimum theoretical solubility of 0.01 mg/L at pH 10; little benefit is gained by operating at higher pH values. In actual practice, nickel concentration in the treated effluent can be expected to be in the range of 0.5-1 mg/L. Patterson (1985) has reviewed the nickel treatability data and reported that the most effective treatment occurs at a pH above 11, and treatment efficiency achievable depends also on the presence of other constituents in the wastewater.

In the precipitation of nickel, pH control can be achieved either by the addition of lime or sodium hydroxide. The selection depends on the economics and the size of treatment plant. Although its cost is relatively higher, liquid sodium hydroxide is usually preferred in small installations due to easy storage and handling properties (Patterson, 1985). In the treatment of copper and nickel sulphate-manufacturing wastewaters treatments, the results obtained have indicated that, both clarifier and filter effluent nickel is higher when caustic is used for the pH control (USEPA, 1980). The reason for this dissimilarity remained unexplored.

The process removal efficiency is considerably affected by the physical treatment for precipitate separation; as a general rule, sedimentation is enough, especially when improved by the addition of coagulant aids. More complete removals may be achieved by a final sand filtration; the presence of complexing agents, such as cyanides, hinders the hydroxide precipitation and may cause a considerable decrease in the removal efficiency. Patel and Pearson (1977) report that continuous solids separation results in much better clarifier performance than batch solids precipitation of nickel hydroxide. Continuous treatment with gravity clarification has been claimed to yield residual total effluent nickel concentrations below 2 mg/L, with lower values possible by polymer addition. The data in Table 8.3 is a comparison for the results obtained from different physical treatment processes.

Table 8.3

Average Effluent Nickel Concentrations from Alternative Solids Removal Processes (USEPA, 1979)

Process	Effluent Nickel, mg/L	
	Avg	Range
Precipitation and settling	1.4	0.1-12.5
Direct filtration	0.75	0.3-1.3
Precipitation, settling and filtration	0.63	0.1-1.1

A possible alternative, though seldom adopted, consists of the precipitation of insoluble sulphides by the addition of sodium sulphide. The advantage of sulphide precipitation over hydroxide precipitation is effective treatment at more near-neutral pH values. In one study, nickel concentration of gold-ore extraction wastewater with an initial nickel content of 6.5 mg/L, was reduced to 2.1 mg/L at pH 7 (Rosehart and Lee, 1972).

8.3.5.2 Ion Exchange

Satisfactory results may also be obtained using ion-exchange resin; nickel may be recovered from eluates by precipitation. However, recovery is not economical when nickel is mixed with other metals in the effluent. Thus, waste stream segregation is required in the presence of other constituents, particularly in the presence of cyanide. Nickel-cyanide permanently contaminates ion-exchange resins (Patterson, 1985).

Complete nickel removal was reported for nickel sulphate plating bath rinsewaters containing 870 mg/L nickel (Reents and Stromquist, 1952). The reclaimed wastewater was acceptable for use in the rinse tank. Chemical costs of ion exchange treatment plus regeneration was reported to be \$1.15/kg nickel recovered, for another plating plant (Heidorn and Keller, 1958). However, ion exchange treatment was reported to be more than twice as costly as chemical precipitation, since recovery is not economical (Ross, 1968).

8.3.5.3 Evaporative Recovery

Recovery by evaporation is also feasible, though it requires a rational use of water leading to decreased consumptions. Hence, it might be convenient to perform a further concentration by evaporation of washing waters with recovery of a concentrated phase to be directly used for topping up the baths; condensates may possibly be re-circulated to the rinse water system.

The spent plating bath solutions containing nickel (and other heavy metals like copper), can also be treated directly by the Lancy process, without dilution by rinse water (Figure 8.2). The plated metal, with dragout adhering to it, after a static rinsing, is directly submerged in a vat containing a concentrated solution of lime - or other alkalizing agent - used to precipitate the nickel. This solution is continuously recycled to a reservoir where sedimentation of metal hydroxides occurs and where make-up chemicals are added in proportion to the amount of precipitate formed.

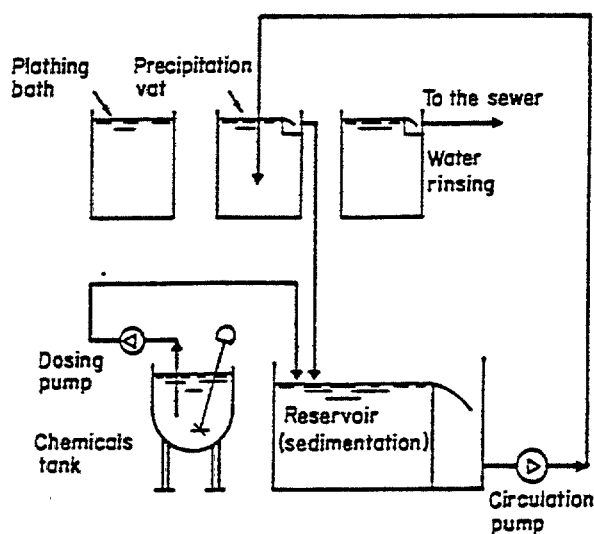


Figure 8.2 The Lancy Process in metal plating industry.

A final rinse with water eliminates the last traces of hydroxide from the plated metal. Because most of the pollutants have been removed in the precipitation vat, the rinse water does not need treatment, except possibly sedimentation or filtration to eliminate the small amounts of precipitate still present.

8.3.5.4 Reverse Osmosis

Reverse osmosis plants seem interesting because, in addition to water recirculation, it offers the possibility of nickel recovery. Reverse osmosis is especially suited for handling the near-neutral nickel solutions, and the economics are favourable for recovery and reuse of expensive nickel chemicals (Patterson, 1985). Table 8.4 is a summary for the reverse osmosis treatment of nickel wastewaters.

Table 8.4

Application of Reverse Osmosis to Nickel Wastewaters
(Crampton and Wilmoth, 1982)

Membrane type	Bath type	Overall Performance	Comments
Polyamide	Nickel sulfamate	Good	pH must be above 2.5 pH must be above 2.5
	Nickel fluoroborate	Moderate	
	Watts nickel	Good	
Cellulose acetate	Nickel sulfamate	Good	
	Nickel fluoroborate	Good	

8.4 Chromium

8.4.1 Introduction

Chromium (Cr) is an abundant element in the earth's crust, and occurs in oxidation states ranging from Cr⁺² to Cr⁺⁶. The most common form in nature is Cr⁺³, which is also the valence which is considered essential as a trace element in humans (EPA, 1976).

Marine organisms are able to concentrate Cr to various degrees, and a wide range of toxic effects have been noted for chromium in the hexavalent state, the stable form in seawater (EPA/ORNL, 1978).

8.4.2 Sources and inputs into the Mediterranean

Large amounts of Cr are used by industry, and sources to the environment include fossil fuel combustion, metal plating, ore refining, the leather industry, etc. In the Mediterranean, the Liguro-Provencal region receives the highest Cr load from land-based sources, mostly due to river run off (UNEP, 1977b).

There is no accurate information available regarding the amounts of chromium discharged into the Mediterranean Sea through industrial and domestic effluents. Earlier estimates (UNEP, 1984) were 250 and 950 tonnes per annum from domestic and industrial discharges respectively, originating in the coastal zone, with a further 1,200 tonnes per annum reaching the Mediterranean Sea through rivers.

8.4.3 Chromium-bearing wastes

Chromium compounds are ubiquitous in industries and in their wastewater, Chromium appears in many alloys and plated metals and as an anti-corrosion inhibitor, used in cooling water to protect pumps and heat exchangers. Thus, it can be found in a multitude of wastewaters.

Chromium is used in the electroplating and alloy industry, chromium compounds are used in dyes including some of the common textile dyes and chromium oxides, specifically Cr_2O_6 is used as an effective oxidant, and softener, especially in tannery wastes.

Due to its ubiquitousness in many products and emission from small industries and laboratories, chromium concentration in general municipal wastes can reach 5 to 10 mg/L while their most common concentrations are below 1.0 mg/L.

8.4.4 Principal industries

8.4.4.1 Tannery industry

Type and size of industry

Tanneries can vary from very small at village level, processing less than 10 tons of hides per year, to major tanneries producing between 5000 and 20000 tons of hides per year.

The type of wastes depends on the degree of processing of the hides to leather, form of hides (raw, cleaned, with or without hair, etc.).

Type of wastes

Raw hides are passed through about 30 stages of hide pickling, cleaning (using oxidants) and softening. Chromate salts are used at various stages, particularly in the tannin-oxidizing and in the pulp chrome finish stages usually in a strong acidic solution with the aid of sulphuric acid.

Hexavalent and trivalent chromates are used but during the processes almost all hexavalent chromium is reduced to trivalent, particularly due to the presence of sulfides. Besides chromium compounds, tannery wastes contain sodium chloride, ammonia, enzymes, detergents, suspended and floatable organic matter, greases, lanolines, dyes and dissolved organic matter.

Chromium dosages are in the form of $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2CrO_4 but following reduction trivalent $\text{Cr}_2(\text{SO}_4)_3$ is formed. Sequential processes involve the use of strong alkaline solutions where $\text{Cr}(\text{OH})_3$ is formed.

BOD and COD concentrations of 5,000 to 20,000 mg/L respectively, are common in some of the tannery processes waste streams while BOD levels of about 1000 mg/L are common in the overall tannery wastes stream. In tanneries where water-saving measures were adopted, chromium concentrations in the total raw tannery wastes can vary between 2000 and 1500 mg/L as chromium, while approximately 500 mg/L chromium should be regarded as average. Other tanneries discharge between 50 to 200 mg/L chromium in the total effluent, usually after some precipitation has occurred in the waste holding basins.

Form of wastes

Tannery wastes are very turbid, coloured (usually red) frothy and malodorous. The wastes are usually alkaline with pH of between 9.5 to 12. Most chromium appears in the form of $\text{Cr}(\text{OH})_3$ which forms a greenish precipitate at higher pH levels. At neutral and acidic pH levels and progressing part of the chromium solubilized.

Total amounts

Tannery wastes amount to between 20 to 100 m³ per ton of hides processed, depending on type of process and on degree of water-saving measures which are taken within the plant. Consumption of chromium salts can reach 10 to 40 kg per ton of hides processed with discharge of 5 to 15 kg chromium per ton of processed hides. Thus, a 2,000 tons per year tannery can discharge between 40,000 to 160,000 m³ of wastes per year containing chromium wastes amounting to 25-35 percent of total plant wastes (20-25 m³ per ton of hides). They can be treated separately.

Discharge pattern

Hide soaking, pickling and polishing is usually done in tanks, baths and basins, which are filled and emptied in batches. In large tanneries this will form a semi-continuous flow (such as daily batches, or a few batches per day), while in small plants, batches are discharged every few days or few weeks. Where earth basins are used, discharge is infrequent and even seasonal when basins are emptied to allow the evaporation, drying and disposal of the tannery sludges.

8.4.4.2 Electroplating and alloy industries

Type and size of industry

The industry may vary in size from small 'shop' levels to large highly-developed industrial complexes. Metal profile coating and anodizing industries with capacity of 10,000 tons per year and more of product are in existence. Car and automotive industries maintain chromecoating and plating production facilities with capacities of tens of thousands of tons of chromium-coated parts per year. The type of industry may be electroplating of common metals, precious metals or specialty metals. There are finishing processes, such as anodizing, coating as well as chemical etching and milling.

Type of wastes

Wastes may vary from innocuous and non-toxic wastes, to highly lethal and toxic wastes. The former are the result of good plant management and the latter may be due to intentional or unintentional spills of concentrated process solutions. For typical plating operations the chromium concentrations may vary from 100 mg/L for car grill manufacture,

to 50 mg/L for a metal fastener plant. Total plant wastes including both plating and rinsing wastes usually contain 10 to 30 mg/L of chromium. Associated with the chromium may be compounds such as zinc, iron, lead, aluminium and cyanide, and sometime fluorides. Chromium is introduced in the form of CrO_3 together with sulphuric acid to form H_2CrO_4 acid solution.

The wastes usually are generated in the rinsing of processed items after removal from baths. However, the intermittent dumping of spent process solution will also cause major peaks in concentrations.

In the alloy industries, the electrolytic chromium gives rise to the highest concentrations of chromium. While other processes may give rise to concentrations less than 10 mg/L, in the electrolytic process the concentration may be as high as 2000 mg/L. The waste will have a low pH and high concentrations of ammonia, iron and manganese.

Form of wastes

The wastes are usually coloured with floating scum, oil and metal particles. There will be both suspended and dissolved solids. In typical acidic wastes most chromium is in soluble form, mostly as CrO_4 salts. Colour of wastes is clear, greenish or reddish according to the type of the process and the pH.

Total amounts

Chromium electroplating plants produce between 20 to 100 m^3 total plant wastes per ton of plated product. In well managed plants the total plant wastes will be between 30 to 40 m^3 per ton. Raw waste levels of chromium may be up to 1 kg/ton processed with a pH ranging from 2-13 depending on the process. If the pH is high the chrome will be an insoluble green precipitate which is soluble at low pH. Galvanizing process may use up to 2500 gallons/ton.

Discharge patterns

The process wastes are discharged continuously because they usually are the result of a series of batch processes. The discharge of spent bath solutions will be intermittent if there is no flow equalization or re-use of the solutions.

8.4.4.3 Textile and wool dyeing

Type and size of industry

Textile and wool dyeing processes are quite common in most countries. Size of factories will vary from small dyeing and re-dyeing establishments to large dyeing plants within a textile and wool plant or as a separate plant. Size of plant can reach 50,000 tons of fabric dyed per year.

Type of wastes

A significant number of textile and wool dyes contain, or are based on, chrome-acid and metachrome substances. Textile and wool plants contain several streams from various processes among them alkaline wastes, chlorine wastes, acidic wastes, detergent wastes and fibrous suspended matter wastes. Dyeing facilities wastes are usually separated from the

wastes of the entire plant and they contain between 20 and 70 mg/L of chromium both in hexavalent and in trivalent forms.

Form of wastes

Liquid coloured wastes with some suspended matter, pH vary according to the combination of dyes.

Total amounts

Dyeing process wastes can amount to between 20 to 60 m³ per ton of fabric dyed.

Discharge patterns

Dyeing, soaking and rinsing are done in batches which in large plants form a continuous or semi-continuous flow.

8.4.4.4 Use of chromate as a corrosion inhibitor

Type and size of waste source

Chromate salts are added to closed cycle cooling system, usually those which are based on cooling towers. The addition of zinc salts and/or dispersants can reduce the concentration of chromates.

Closed cycle water cooling systems are very common in many industries such as refineries, petrochemical industry, thermal combustion industry, chemical industry, ceramic and glass industry, metal industry, freezing works, large air conditioning facilities and small and medium scale power generation plants. Closed cycle cooling systems are used when open flow through systems are not feasible due to shortage of natural cooling waters or when measures to prevent thermal pollution have been taken.

Type of wastes

Water cooling wastes are usually in the form of spent bleed-off or renewals of the cooling system waters. Chromate salts are added with various salts containing $\text{CrO}_4^{=}$, usually in the form of $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Na}_2\text{Cr}_2\text{O}_7$.

Cooling water spent bleed-off contains, beside chromates (hexa-valent chromium), also zinc, dispersants, dust, algae, slimes and dissolved solids of the natural water origin but in two to three-fold concentration.

Form of wastes

Clear water, occasionally with some colour and turbidity and some dust or grit.

Total amounts

Amounts depend on size of plant, climate, shortage of water, composition of water, presence of scale-forming substances such as calcium, magnesium, iron and manganese, type of heat exchanger and cooling towers, corrosiveness of piping etc. A common medium

to large size refinery, for example, requires approximately 10 million m³ per year of cooling water of which between two to four millions are spent bleed-off.

Discharge patterns

In small cooling systems, bleed-off water is spent intermittently while in large systems continuously or semi-continuously with occasional complete renewal of the cooling system which is usually coupled with cleaning of the entire system plus removal of scale, rust and slime.

8.4.4.5 Other industries with wastes containing chromium

Chromium has also been found in the wastes originating from the production of paint pigments and plastics.

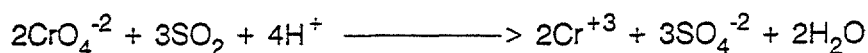
8.4.5 Treatment

The usual chromium limits for most effluents are less than 0.05 mg/L for hexavalent chromium and 0.5 mg/L for trivalent chromium (Lanouette, 1978). However, for domestic water suppliers, the US EPA, and The WHO limits both are 50 µg/L (McKee and Wolf, 1963).

Treatment of chromium is widely performed through chemical precipitation which is a two stage process: the reduction is of hexavalent chromium to trivalent form and removal of trivalent chromium by precipitation. For this reason, chromium-bearing waste streams of the industries are segregated from the other waste streams; hexavalent chromium is reduced to trivalent form and then blended with other streams. However, due to increasingly stringent effluent standards, the use of other removal methods such as ion exchange, evaporative recovery etc. have become common.

8.4.5.1 Precipitation

As it was mentioned earlier, chromium removal is achieved by chemical precipitation by simple alkalinization. However, if chromium is at hexavalent state then chromium is reduced to trivalent state by the use of a reducing agent (usually sulphur dioxide) at pH below 3. The reduction reaction taking place is:



At reaction pH which is usually achieved by dosing sulphuric acid, chromium is in the form of insoluble trivalent chromium hydroxide. Instead of sulphur dioxide other reducing agents such as sodium bisulphite, meta-sulphite or hydrosulfite, or even ferrous sulphate might be used. The reduction of hexavalent to trivalent is not completely effective, and the amount of residual nonreduced hexavalent chromium depends upon the allowed time of reaction, pH of the reaction mixture, and concentration and type of reducing agent employed (Patterson, 1985). As it is shown in Figure 8.3, the reduction reaction is almost instantaneous at a pH 2, and it takes about 30 minutes at a pH 3 (Lanouette, 1986). After the pH is adjusted, the reducing agent is added. The amount added is controlled based on oxidation-reduction potential (ORP) readings. Typical relationships between ORP and Cr(VI) (Lanouette, 1977) is:

<u>ORP</u>	<u>Cr(VI).mg/L</u>
590	40
570	10
540	5
330	1
300	0

Then the pH of the system should be increased in order to initiate precipitation (Fig. 8.4).

Once the precipitation of chromium hydroxide has been completed, wastewaters flow to a settling basin where precipitates are separated from the wastewaters (Figure 8.5). The supernatant then neutralized with sulphuric acid before discharged.

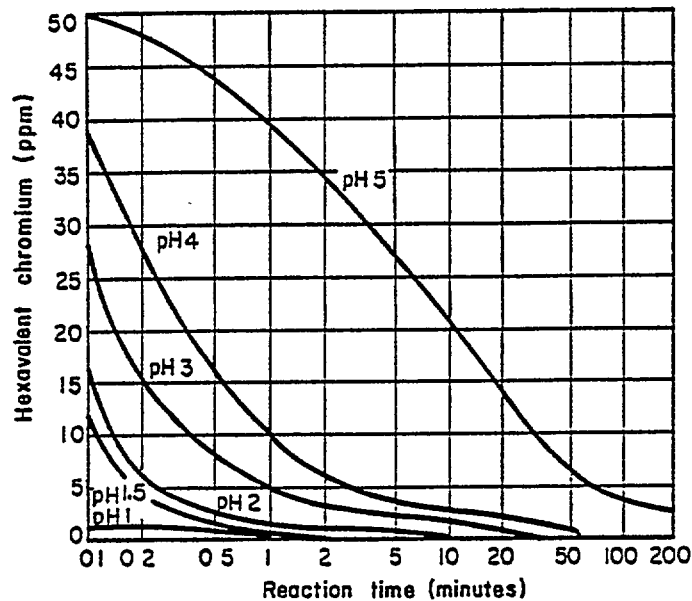


Figure 8.3 Reduction of hexavalent chromium with SO₂, as a function of the pH and the reaction time.

The underflow which is hydroxide chromium sludge is large in quantity, and it can be either concentrated or dewatered. The amount of sludge produced when ferrous sulphate used as the hexavalent chromium reducing agent is about four times the sludge encountered with the use of other reductants (Kralijik, 1975). Typically these sludges settle but do not compact well, and the water content is reported as 2-3 % (Patterson, 1985). Table 8.5 presents the typical disposal techniques of heavy metal hydroxide sludges. The filtrate from sludge dewatering is normally recirculated back to the sedimentation basin.

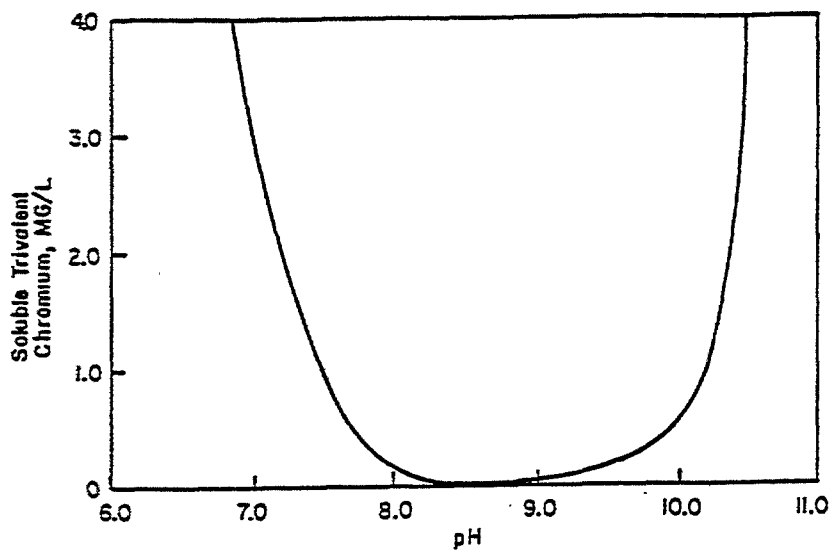


Figure 8.4 Effect of pH on solubility of trivalent chromium (Patterson, 1985).

Table 8.5

Metal hydroxide sludge concentration and disposal techniques
 (Anderson, 1971)

Method	Comments
Lagooning	Requires large areas of land. Might contaminate groundwaters unless properly lined
Vacuum filtration	Equipment and operating costs high. Discharge cake dry enough for haulage
Pressure filtration	Equipment and operating costs high. Requires proper conditioning of sludge. Dry cake
Centrifugation	Equipment costs high. Method of solids removal for large volumes and large particles

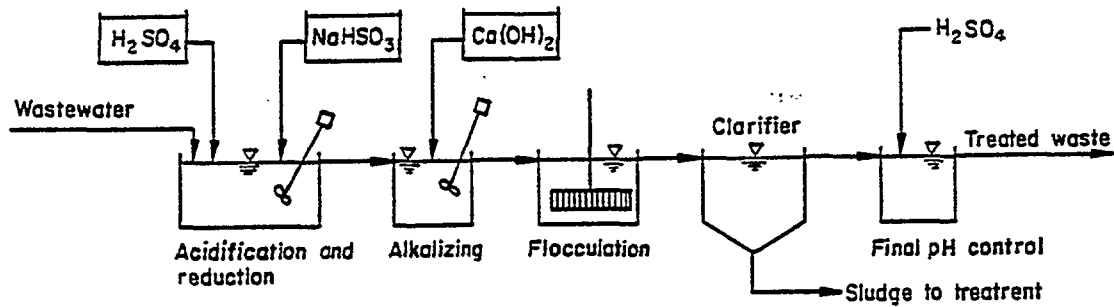


Figure 8.5 Chemical treatment of wastewater polluted by hexavalent chromium

Other means of removing chromium from wastewater are ion exchange, activated carbon adsorption, biological treatment and evaporative recovery. Ion exchange systems are widely used in those instances where chrome is being recovered, and in turn water to be recirculated.

8.4.5.2 Ion Exchange

In ion exchange plants, cation exchange process is employed for the removal of trivalent chromium and anion exchange process for the removal of chromate and dichromate, since trivalent chromium has positive charge, and hexavalent chromium in its usual form of chromate or dichromate has negative charge. When the anion exchange resin is exhausted it is regenerated usually with sodium hydroxide, and sodium chromate is eluted from the ion exchange resin. Purified chromic acid is then recovered by passing the eluted sodium chromate through a cation exchange resin. The effluent of ion exchange plants exhibits characteristics that make it fit for recycling to industrial processes. Obviously the method is effective when effluents do not contain other anions. Figure 8.6 shows the scheme of a classic ionic exchange plant for the treatment of wastes containing chromium.

In the ion exchange systems, wastewater pH is a critical factor. At pH below 4, the oxidizing power of chromic acid begins to attack the resin, and at pH above 6, the ratio of chromate to dichromate in solution increases. Most anion exchange resins are less selective for dichromate. The highest chromate removal is reported to occur at pH 4.5-5 (Patterson, 1985). One typical use of ion exchange treatment for chromium wastes is the treatment of chromate-contaminated blowdown from cooling-water systems. It is reported that chromate can be effectively removed at a pH of 4.0-5.0, even in the presence of several hundred mg/L sulphate and chloride (Anderson, 1974).

Ion exchange treatment was also reported to be efficient in the treatment of metal finishing wastewaters, to meet a chromate effluent standard of 0.05 mg/L (Rothstein, 1958). Table 8.6 presents data on ion exchange performance in chromate removal.

Table 8.6

Ion exchange performance in chromate removal (Patterson, 1985)

Wastewater source	Chromium, mg/L	
	Influent	Effluent
Cooling-tower blowdown	17.9	1.8
▪ ▪ ▪	-	0.1
▪ ▪ ▪	10.0	1.0
▪ ▪ ▪	7.4-10.3	1.0
▪ ▪ ▪	9.0	0.2
Plating rinsewater	44.8	0.025
▪ ▪	41.6	0.01
Pigment manufacture	1210	<0.5

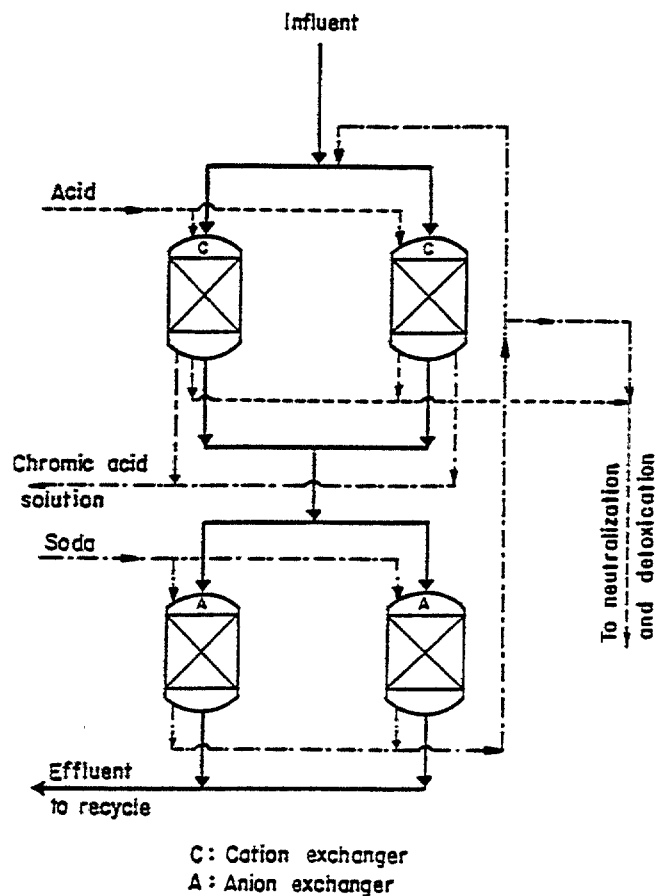
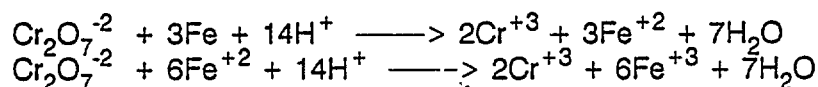


Figure 8.6. Ion exchange process with the partial recovery of chromic acid.

8.4.5.3 Electrochemical reduction

In the electrochemical treatment of chromium wastes, upon the application of electric current to the electrodes, ferrous ions which reduce the Cr(VI) to Cr(III) ions are released into solution:



Jester and Taylor (1973) reported an effluent Cr(III) level of 0.01-1.4 mg/L for the electrochemical treatment of chromium wastes bearing 2.5-52 mg/L Cr(VI). However, USEPA reported a four fold increase in the dry sludge solids upon precipitation of trivalent chromium, as a result of the soluble iron released in the reactions (USEPA, 1979).

8.4.5.4 Evaporative Recovery

In evaporative recovery which can be used on all process rinse water systems, water in the solution is driven off as water vapor, and the chromic acid is concentrated. In this process, all constituents of the wastewater together with the chromic acid are retained in the concentrated product which is the major drawback of the evaporative recovery since the buildup of impurities results in defective plating. Plating-waste rinsewater containing only a few mg/L chromic acid can be concentrated to above 900 mg/L (Patterson, 1985).

8.4.5.5 Activated Carbon Adsorption

Among alternative techniques, mention is made of the activated-carbon adsorption process investigated by USEPA: It has been found that hexavalent chromium is easily adsorbed by passing solutions with chromium concentration of several ppm, to filters of activated carbon in granular form. Removal efficiencies of properly dimensioned columns are higher than 99 %. Regeneration is conveniently carried out with sodium hydroxide, which leads to the formation of a sodium chromate solution which will be subjected to detoxication treatment. Experience has shown, however, that gradual loss of adsorption properties occurs when the number of regeneration cycles is augmented, probably due to the partial reduction of hexavalent chromium on carbon to Cr_2O_3 . After 100 regenerations, the adsorption capacity is noted to be lowered from an initial value of 0.08 kg of hexavalent chrome per kg of activated carbon to the value of 0.04.

In an application of activated carbon adsorption for treatment of hexavalent chromium, influent hexavalent chromium levels of 0.09-0.19 mg/L were reduced to 0.04 mg/L or less. However, activated carbon appeared to be less effective at higher influent chromate levels; effluent levels of 0.05-195 mg/L have been given on initial concentrations of 100-820 mg/L (Maruyama *et al.*, 1975).

8.5 Lead

8.5.1 Introduction

The main sources leading to environmental contamination by lead arise from the industrial and other technological uses of lead by man. Though lead, as an element, occurs naturally in all phases of the environment, inputs from natural sources to the marine environment are insignificant compared to atmospheric washout, river input and industrial effluents which result from man's activities.

Lead serves no known biological function. The ability of many marine organisms to accumulate lead presents a potential hazard to humans through ingestion of contaminated marine produce. The toxic effects of lead in humans have been well documented, as lead has been used extensively by man for thousands of years.

8.5.2 Sources and inputs into the Mediterranean

Anthropogenic activities such as agriculture, mining, industrial processing of ores and metals as well as the use of metals and metal components have resulted in increased inputs of heavy metals into the oceans. Other sources including combustion of fossil fuels, smelting and the use of lead gasoline release heavy metals into the atmosphere which are subsequently transported to the oceans (Förstner and Wittmann, 1983).

Sources of Pb include mining and smelting of ores such as galena, cerusite and anglesite and industrial processes involving the manufacture of batteries, pigments, alloys, and tetraethyl leads.

Heavy metal sources into the marine environment include surface runoff, domestic and industrial effluents disposed through outfalls, dumping of sewage and industrial sludges and the atmosphere. Metals are appreciably enriched in the suspended load of wastewaters and in sewage sludges as a result of industrial wastes, corrosion within the urban water supply network and urban runoff transporting metals such as Pb and Zn from the surface of streets and highways (Zafiropoulos, 1976, Förstner and Wittmann, 1983).

The amounts of lead discharged into the Mediterranean Sea through domestic and industrial effluents have been estimated at 200 and 1400 tonnes per year respectively. These figures apply to discharges from the coastal zone, and do not include river inputs (UNEP/FAO, 1986a).

8.5.3 Lead-bearing wastes

Lead was formerly used in many of the original water piping installations in many countries. Hence, in older areas, used water coming from houses was found to contain lead. This lead was found in both untreated and treated sewage. Industrially, lead is used in a number of industries. The major ones being metal electroplating, battery production and paint production.

Lead has also been the subject of much investigation because it is an additive to petrol (gasoline) and hence is an air pollutant. Lead from the combustion of petrol will also find its way into drainage and sewage through spills, washing out by rain and sedimentation onto the roads.

8.5.4 Principal industries

8.5.4.1 Battery production industry

Type and size of industry

The production of batteries requires the use of lead for the plates used within the batteries. The plates may be either newly made or produced from used batteries.

Type of wastes

The wastes are generated in the plate forming areas and also where the batteries are cleaned and filled. The wastes will be acid and highly corrosive due to the use of sulphuric acid.

Form of wastes

The wastes will be $PbSO_4$ in the ionic form. The wastes will be white in colour, and turbid. There may be some particulate lead from the plate forming areas.

Total amount

Wastes from the plate forming areas will contain 1-50 mg/L lead. The wastes from the cleaning and filling areas will be about 10-12 mg/L lead. The volume of wastes are 4-5 litres/battery.

Discharge patterns

Continuous due to continuous plating operation.

8.5.4.2 Metal plating industry

Type and size of industry

The electroplating of lead is a process sometimes used. The lead may come from anodizing baths. Electronic printed circuit production involves lead plating and welding, usually in combination with tin and copper plating.

Type of wastes

The wastes will arise from rinsing of plates after processing and spills of process bath solutions. Plating baths are highly concentrated and initially contain 900 g/litre of lead fluoroborate $Pb(BF_4)_2$, 30-40 g/litre H_3BO_3 , 10 g/litre HBF_4 as well as metallic lead and sulphuric acid. Wastes might contain also other metals such as tin, copper, zinc and nickel.

Form of wastes

The wastes could contain insoluble lead and will be grey-white containing suspended $PbSO_4$. There will be both floating and settleable material. However, when the wastes are strongly acid, the lead will be mostly soluble.

Total amount

The lead-bearing wastes in the form of either lead or lead sulphate will be produced at a rate of 8 m³/ton of processed metal. The concentrations of lead will be about 8-10 mg/L in total plant wastes.

Discharge patterns

The discharge of waste will be continuous with peak concentrations associated with spills.

8.5.4.3 Petroleum additives

The production of tetraethyl lead as a petroleum additive gives rise to lead waste. Additionally after the fuel is burnt the lead may be found in the air or on road surfaces. Hence, rainfall, and the resulting urban runoff will also be lead-bearing wastes. The production wastes may contain lead in the range of 100-200 mg/L as organic and inorganic lead.

8.5.4.4 Other industries with wastes containing lead

Lead may also be found in the waste from printing, pigment, fuel, photographic, match and explosive industries. In the paint and pigment industry 1.0-10.0 mg/L lead has been found in waste waters.

8.5.5 Treatment

8.5.5.1 Chemical precipitation

Soluble lead removal is generally carried out by chemical precipitation, in the form of either carbonate or hydroxide. The form precipitated depends upon the treatment pH and the amount of carbonate available in water. At intermediate pH values, lead carbonate is normally more insoluble than is lead hydroxide (Patterson, 1985). In addition, lead carbonate sludge is more readily settleable and dewaterable than lead hydroxide sludge.

For hydroxide precipitation, a treatment with lime is generally preferred at highly alkaline pH values (pH 9-10), although literature reports processes carried out at lower pH. For Example, Dean *et al.* (1972) reported that most effective precipitation occurs at pH of 6.0. In contrary, a pH range of 8.7-9.3 has been suggested for metal plating wastewaters, in another instance (Anonymous, 1971). However, as shown in Figure 8.1, solubility data for lead indicate that most effective precipitation occurs at pH near 10. As parallel to this theoretical information, there are some information in the literature suggesting that the optimum pH for lead precipitation is near 10 (Day *et al.*, 1974).

In the precipitation of lead in the form of carbonate, there are two important factors controlling the process: pH of the treatment and the carbonate level. Optimum pH range and optimum carbonate level for lead carbonate precipitation were reported to be 7.5-9.0 (Rohrer, 1975) and at 200 mg/L as equivalent calcium carbonate (Naylor and Dague, 1975), respectively.

In lead precipitation systems there are two important factors controlling the efficiency of the treatment. These are (a) lead solubility, and (b) lead precipitate settleability, where effluent filtration is not applied (Patterson, 1985).

A particular problem in the treatment of wastewaters containing several metals each having a different optima is the adjustment of optimum pH. Noncompatible pH optima among metals contained in a multimetal waste often requires use of a compromise, nonoptimal treatment pH, or operation of the system at the pH for which best results are achieved for the metal representing the most stringent effluent limitation (Patterson, 1985).

An alternative precipitation consists of the use of ortho phosphoric acid to form lead phosphate which has a very low solubility at pH values close to 7. The use of sodium phosphate has also been reported to precipitate lead as lead phosphate. Treatment of a

battery waste with sodium phosphate at a pH of 7.2-7.4, has been reported to be effective in achieving a total lead concentration of 0.2-0.6 mg/L (Randall and Ondenber, 1974). However, the requirement of a large excess of the phosphoric acid, or sodium phosphate could create possible problems of excessive phosphate content in the effluent.

Table 8.7

Typical operating conditions (Maruyama *et al.*, 1975)

Plant	System	Coagulant	pH
1	Iron	Ferric sulphate, 45 mg/L Fe	6.0
2	Low lime	Lime, 260 mg/L Ferric sulphate, 20 mg/L	10.0
3	High lime	Lime, 600 mg/L	11.5

Different possibilities are open in the use of sodium sulphide as a precipitation agent, with the formation of lead sulphide which is black and insoluble. The toxicity of this product, however, makes rigid control of the process necessary in order to avoid carry-over which can also be caused by the bad settling characteristics of the precipitate; it is therefore advisable to provide filtration downstream of the sedimentation which can effect an adequate removal of the suspended material.

8.5.5.2 Coagulation

Maruyama *et al.* (1975) operated three physical-chemical pilot plants using different coagulant systems consisting of coagulation, flocculation, settling followed by a dual-media filter, and activated carbon columns. Excellent lead removals were reported for all three processes which are reported in Table 8.7. Precipitation, settling and filtration accounted for approximately 99 percent of the removal; activated carbon increased removal to as high as 99.6 percent.

The use of coagulation for tetraethyl lead-manufacturing was proposed by Nozaki and Hatotani (1967). Effective coagulation treatment by the use of ferric and ferrous sulphate, following pre-settling was reported. However, the process was not so effective in treating the waste containing both organic and inorganic lead compounds.

8.5.5.3 Ion Exchange

As to the removal of both organic (in particular of lead tetraethyl) and inorganic lead compounds, satisfactory results may be obtained by ion exchange, with the use of acid cationic resins. In the treatment of an ammunition industry wastes, an effluent level of 0.01 mg/L was achieved by ion exchange treatment with a phosphoric acid resin at a pH of 5.0-5.2 (Shannon, 1973). The eluates containing high lead concentrations may be subjected to an oxidation process for organic lead mineralization; this may be removed by the physico-chemical treatment already described.

8.6 Arsenic

8.6.1 Introduction

Arsenic and its compounds are ubiquitous in nature, and display both metallic and non-metallic properties. The trivalent and pentavalent cations are the most common oxidation states, though elemental arsenic also occurs. Trivalent arsenic is much more toxic to both mammals and aquatic organisms, and industrially produced arsenic is in the toxic trivalent (inorganic) state (Schroeder and Balassa, 1966).

Although arsenic itself is insoluble, many of its compounds are soluble in water, leading to average seawater concentrations of 2.0-3.0 ug/l. Marine organisms especially invertebrates, are able to concentrate arsenic from seawater to high levels. Most of the arsenic is in the organic form in marine organisms, which is much less toxic than the trivalent inorganic compounds (Bernhard, 1978).

8.6.2 Sources and inputs into the Mediterranean

Arsenic is released into the environment as a component of pesticides, as the result of smelting or roasting sulphide minerals, combustion of fossil fuels, leaching of exposed wastes from mining activity, and accelerated erosion of land. Its release from anthropogenic sources seems to exceed those from natural processes (MacKenzie *et al.*, 1979).

There is no accurate information available as to the amounts of arsenic reaching the Mediterranean Sea through domestic and industrial effluents.

8.6.3 Arsenic-bearing wastes

Arsenic and its associated compounds have been found in the wastes of the following industries: metallurgical, glassware and ceramic, tannery, dye and pesticides. However, as the inorganic pesticide industry is on the decline it is thought that this waste source will also diminish. Concentrations of As_2O_3 in raw inorganic pesticides industries were found to be between 100 and 500 mg/L.

8.6.4 Treatment

Treatment methods commonly employed for arsenic-wastewater treatment are lime or sulphide precipitation or co-precipitation with iron or aluminum hydroxide, plus adsorption onto coagulant floc, with enmeshment of particulate arsenic. Other processes employed for arsenic include adsorption onto activated carbon or alumina, and ion exchange.

8.6.4.1 Precipitation

Effluent arsenic levels of 0.05 mg/L are obtainable by precipitation of arsenic as sulphide, with the addition of sodium or hydrogen sulfide at pH 6-7 recommended. Although sulfide precipitation is effective in treating arsenate form of arsenic, it is completely ineffective in treating arsenite form (Rosehart and Lee, 1972). In the latter case, a preliminary chemical oxidation is generally advisable, which may be carried out by chlorination. Rosehart and Lee reported that best treatment by sulfide precipitation occurs at pH 7. In that study, sulfide precipitation process was found to reduce an initial arsenate level of 132 mg/L down to approximately 26.4 mg/L, at an optional sulfide/arsenic dosage ratio of 0.5. The other precipitation chemicals which might be used for arsenic are lime, caustic, ferric sulphate,

ferric chloride and alum. Lime precipitation yielded equal or better treatment results than other chemicals, at lower cost. Optimal pH for lime precipitation is reported to be 12, both for arsenite and arsenate forms, with equal removal efficiencies. Optimum treatment pH required for other coagulants are 10 with caustic, 8 with ferric sulphate, and 7-8 with alum (Rosehart and Lee, 1972).

8.6.4.2 Co-precipitation

Arsenic is an industrial waste which contains heavy metals in solution can be concurrently co-precipitated upon precipitation of the heavy metals. Coagulation process with polyvalent metals (especially iron and aluminium) can remove arsenic, even in the soluble form. This is a consequence of complexation with metals and of a subsequent co-precipitation with hydroxide flocs which form under convenient pH. A simultaneous adsorption onto the flocs may also occur. The same flocculents commonly used for the treatment of primary waters and effluents can be used, in particular ferric sulphate and chloride as well as aluminum sulphate.

Flocculent addition is no longer required for arsenic removal from waste waters that contain heavy metals; in fact complexation takes place with the metal ions already present in the wastewaters to be treated. It is therefore enough to adjust the pH according to the technique commonly used for metal hydroxide precipitation. The high removal levels sometimes achieved by using lime alone may probably be attributed to the described phenomenon; in the absence of heavy metals, lime addition generally leads to poor results.

Therefore the treatment to be adopted does not differ from the usual physico-chemical processes for the removal of suspended matter from waters, i.e.: coagulation-flocculation, sedimentation; filtration on sand; if arsenites are present, pre-chlorination is required. If a particularly high removal is necessary, an additional adsorption treatment may be provided using activated carbon. Lime is generally used for pH adjustment.

Pilot plant studies on physical-chemical removal processes involving coagulation, flocculation, settling, dual media filtration, and carbon adsorption, indicated that arsenic can be effectively removed from municipal waste (Maruyama *et al.*, 1975). Treatment results for an initial arsenic concentration of 5 mg/L are reported in Table 8.8.

A difficulty associated with arsenic treatment by co-precipitation is the sludge management. Formation of a fine precipitate with poor settling properties was reported for lime plus ferric chloride precipitation.

8.7 Barium

8.7.1 Introduction

Despite its fairly common occurrence geologically as a sulphate or a carbonate, barium is found in only minor concentrations in natural waters.

8.7.2 Sources and inputs into the Mediterranean

There is no accurate information available regarding the amounts of barium discharged into the Mediterranean Sea through effluents.

Table 8.8

Pilot Plant Arsenic Removal (Maruyama *et al.*, 1975)

System	Cumulative percent removal			Effluent Concentration (mg/L)
	Settling +	Filtration +	Carbon	
Iron (ferric sulphate at 45 mg/L Fe)	90	89	96-98	0.06
Low-lime (lime at 260 mg/L ferric sulphate at 20 mg/L Fe)	79	79	82-84	0.92
High lime (lime at 600 mg/L)	73	75	84-88	0.77

8.7.3 Barium-bearing wastes

Barium as barium sulphate is used in the production of white paint. Barium is also found in the following processes: metallurgy, glass, ceramics and dyes and rubber vulcanization. Little information is available on waste concentrations.

8.7.4 Treatment

The common methods for the treatment of barium wastes are precipitation and ion exchange. However, based upon the relative economic, the precipitation method of barium removal is suggested to be the method of choice (Patterson, 1985).

8.7.4.1 Precipitation

Barium removal is generally carried out by chemical precipitation as barium sulphate upon addition of ferric, aluminum, or sodium sulphate; or precipitation as barium carbonate with lime used for pH adjustment.

Owing to the low solubility of the barium sulphate produced, one of the most widely adopted treatment techniques is the addition of excess sulphate ions to wastewaters. Barium sulphate is relatively insoluble, having a minimum theoretical solubility of approximately 1.4 mg/L as barium at stoichiometric concentrations of barium and sulphate. However, the solubility level of barium can be altered by the addition of excess sulphate (Patterson, 1985).

Extensive pilot plant studies on physical-chemical removal processes for barium in municipal waste involved addition of a coagulant, followed by flocculation and settling, mixed media filtration, and carbon adsorption (Maruyama *et al.*, 1975; Hannah *et al.*, 1977). Types and levels of coagulants employed and the treatment results for the indicated barium concentrations are reported in Table 8.9. Treatment levels of 90 % or greater were found for the iron, low lime and alum treatment systems, while the high-lime process was much less efficient.

Barium may even be precipitated as a carbonate in sufficiently alkaline waters, by operating at pH 10.5. At a higher pH, reduction of purification efficiency is observed, because of the preferential formation of the more soluble barium hydroxide.

8.7.4.2 Ion Exchange

Although the ion exchange process leads to better final results in terms of residual barium content, direct chemical precipitation is preferred from the economic point of view. In any case, both processes allow residual barium concentrations below 0.5-1 ppm to be obtained. Table 8.10 is a summary of treatment level reported for barium wastes. Chemical precipitation has always been adopted for barium removal from regeneration eluates.

Table 8.9

Pilot Plant Barium Removal (Maruyama *et al.*, 1975;
Hannah *et al.*, 1977)

System	Cumulative percent removal			Effluent Concentration (mg/L)
	Settling +	Filtration +	Carbon	
Iron (ferric sulphate at 45 mg/L Fe)	97	95	95	0.27 ^a
Low-lime (lime at 260 mg/L ferric sulphate at 20 mg/L Fe)	99	99	99	0.03 ^a
High lime (lime at 600 mg/L)	80	78	81	0.94 ^a
Alum (aluminum sulphate at 200 mg/L)	87	79	93	0.04 ^b

^a Initial barium concentration = 5 mg/L

^b Initial barium concentration = 0.5 mg/L

Table 8.10

Summary of Barium Treatment Methods

Method	pH	Barium Concentration, mg/L		Removal	Reference
		Initial	Final		
Precipitation Sulphate	6.0	5.0	0.27	95	Maruyama <i>et al.</i> , 1975
	6.4	0.5	0.04	93	Hannah <i>et al.</i> , 1977
	7.5-8.5	7.0-8.5	2.1-2.6	70	Logsdon <i>et al.</i> , 1974
Carbonate	10.5	7.0-8.0	0.15	98	Logsdon <i>et al.</i> , 1974
Hydroxide	11.5	5.0	0.94	81	Sigworth and Smith, 1972
Ion exchange	-	11.7	0.17	98	Logsdon <i>et al.</i> , 1973

8.8 Boron

8.8.1 Introduction

Boron is a metal used in a number of industries. However, not a great deal is known about concentrations in processes wastes and final effluents. This is because boron is generally discharged together with heavy metals which are often of greater interest.

8.8.2 Sources and inputs into the Mediterranean

There is no accurate information available regarding the amounts of boron discharged into the Mediterranean Sea through industrial or domestic effluents.

8.8.3 Boron-bearing wastes

Boron is found in the process bath waters in the metal finishing industry. Boron is also used in the fruit packing industry and as a chemical in the photographic industry.

8.8.4 Principal industries

8.8.4.1 Metal processing

Type and size of industry

Hydroboric acid is a component in the process bath water for many metals such as lead, nickel, copper and tin. The boric acid is particularly important in the nickel treatment industry.

Type of wastes

In the metal plating industry the major processes are metal preparation, metal coating and finishing. All these processes use rinse waters. The source of wastes are process solution spills and disposal as well as rinse water disposal. As mentioned in the above sections, the wastes contain the heavy metals themselves, plus borate, fluoride, possibly cyanide. There will also be sulphates and chlorides and they will be acidic.

Form of wastes

In the case of nickel the wastes are a green acid solution containing many other ions apart from dissociated and undissociated boric acid (H_3BO_4). The wastes may be warm. The boric acid is in the dissolved state.

Total amounts

The concentrations of boron are of the order of 1-2 mg/L in both process and plant wastes. Waste flows are of the order of 20-50 m³ per ton of processed metal.

Discharge patterns

The discharge of waste will be intermittent.

8.8.4.2 Fruit canning and packing

Type and size of industry

In the washing of fruit, which is the first stage of processing and packing of fruit, boron is used. Hence boron is discharged primarily during the fruit canning season. The fresh citrus exporting industry use boric acid and sodium borate to clean the fruit before waxing. This is a major source in Mediterranean countries which are citrus exporters.

Types of wastes

The wastes originate in the washing process and are likely to be mixed with other process wastes. Those from the peeling, canning, cooking etc. process. In this first washing section the fruit is washed with water, then dipped in a NaBO_3 solution and then washed again. Hence the borate will appear through the second rinse and spills and disposal of the NaBO_3 solution.

Form of wastes

The process wastes are an aqueous solution of NaBO_3 in water. It has no colour or odour. The waste is dissolved. However, this waste stream when mixed with other wastes will be similar to that described in section 3.2.3.2 (a).

Total amounts

Waste flows amount to 3 m^3 per ton of fruit processed. The concentration of the boron in both the plant and process wastes is of the order of 2-3 mg/L.

Discharge patterns

The wastes will be discharged continuously.

8.8.4.3 Detergent production

Sodium perborate is used as a bleach in household washing powder. Hence it has been found in raw sewage in appreciable amounts as well as in detergent manufacturing wastes. Sodium perborate is also used in laundries and cleansing facilities due to its degreasing properties.

Boron concentrations in raw municipal sewage can amount to between 2 and 6 mg/L. In countries where reclaimed effluents are used extensively, for agricultural irrigation, strict measures should be applied to restrict the use of sodium perborate in order to reduce boron concentrations in the effluent. This is due to the sensitivity of many agricultural crops to boron.

8.8.5 Treatment

It is usually found in wastewaters as borate ion. Although it is extensively used in industry and in the formulation of commercial detergents, the information available on its presence in wastewater is scarce. The experience acquired so far concerning its removal are also few and not very convincing.

For boron removal, the conventional biological treatment and chemical coagulation with lime and ferrous and aluminium salts proved to be ineffective.

Results of some interest have been obtained by distillation and ion exchange on selective resins, by means of which boron contents below 1 ppm may be obtained. An ion exchange resin, Amberlite IRA-943 is claimed to be highly selective for removal of boron as borate and boric acid (Kunin, 1973). In the treatment of waste water, for an influent level of 10 mg/L, effluent levels down to 1 mg/L were achieved.

Experimental studies on reverse osmosis and on extraction with chemical reagents have been published. Cruver (1973) indicated that boron removal by cellulose acetate membrane reverse osmosis treatment of a brackish ground water initially containing borate at 0.35 mg/L as boron, reverse osmosis achieved a boron level of 0.14 mg/L in the permeate and 0.4 mg/L in the concentrate. Kunin (1973) has claimed that ion-exchange resin, Amberlite IRA-943 is highly selective for removal of boron as borate and boric acid.

8.9 Silver

8.9.1 Introduction

Silver occurs naturally in the elemental state as well as in ores in which it is combined with chlorine, sulphur and antimony. Silver ions may be leached into surface and ground waters, but the insolubility of most silver salts as well as of the free metal limits its concentration to low levels.

8.9.2 Sources and inputs into the Mediterranean

There is no accurate information available regarding the amounts of silver discharged into the Mediterranean Sea through industrial or domestic effluents.

8.9.3 Silver-bearing wastes

Silver plating is used for cutlery and jewellery. It is an age old process. A newer process is the development of photographic films. This process also involved the use of silver. Because of its high value, the recovery of silver is most desirable, thus the elimination of silver from the waste stream can become an economically profitable operation.

8.9.4 Principal industries

8.9.4.1 Silver plating

Type and size of industry

The industries are silver plating of cutlery, jewellery and ornaments. Apart from a few rather large cutlery plating plants most industries are small town silversmith shops.

Types of wastes

Little particulate silver and suspended silver oxides are found in the wastes as well as some dissolved silver. The bath solutions are made of silver cyanide, potassium cyanide, potassium carbonate, metallic silver and free cyanide. Bath spills contain high concentrations of silver while rinse waters contain 2-5 mg/L of silver.

Form of wastes

The wastes are mainly soluble AgCN. Associated chemical pollutants are Ag, K_2CO_3 and KCN. The wastes are alkaline, sometimes slightly turbid and without colour.

Total amounts

Approximately 8 m³ of waste are produced per ton of treated metal.

Discharge patterns

Discharges are continuous with peak concentrations due to spills and dumping of process solutions. Due to the value of silver intentional dumping is unlikely.

8.9.4.2 Photographic industry

Type and size of industry

The developing of photographic and x-ray film utilizes silver solutions. This is usually a small size industry, except for major film development centres.

Type of waste

The development process involves the conversions of AgBr to Ag₂S which is on the negative. The films are rinsed in a number of solutions at various stages.

Form of wastes

The silver is in the ionic form and is associated with $K_4 [Fe(CN)_6]$, KBr, K_2S , $Na_2S_2O_3$ and Na_2SO_3 . The wastes are all soluble and will have a light white colour.

Amount of wastes

The concentrations of silver are of the order of 1-2 mg/L up to 8 mg/L in x-ray film developing.

Discharge patterns

The wastes are discharged intermittently. Due to the smallness and vast distribution of film and x-ray development establishments, control and surveillance is extremely difficult. On the other hand, due to the high value of silver recovery, contractors are seeking the collection of concentrated wastes.

8.9.4.3 Various industries with wastes containing silver

Silver metal is used in the food and beverage processing industries. Silver nitrate is used in porcelain and ink manufacturing industries. Insufficient information is available on silver concentration in such wastes.

8.9.5 Treatment

The major treatment methods applied for silver include precipitation, ion exchange, reductive exchange, and electrolytic recovery. Less commonly adopted methods for silver are electro dialysis and reverse osmosis.

8.9.5.1 Precipitation

In contrast to the other heavy metals, silver forms an extremely insoluble chloride salt that will dissolve in water to a maximum concentration of approximately 1.4 mg/L silver ion (Butler, 1964).

For this purpose, it is made to react with hydrogen chloride or with chloride, to precipitate silver chloride. This product, originally white, turns violet on light exposure and decomposes into chlorine and silver. Excess chlorides must be controlled in order to avoid the formation of silver chloride soluble complexes. In the hypothesis of a simultaneous precipitation of the hydroxides of other metals, silver recovery from mixed sludge may be carried out by acidification which, by redissolving the hydroxides, leaves the insoluble silver chloride unaltered.

In the case of presence of cyanides in the effluent, as in the case plating wastewaters, cyanide interferes with the described precipitation process; that is why previous removal of this anion is strictly necessary. Oxidation with chloride or related derivatives not only removes cyanides, but also supplies those chloride ions that are necessary for silver chloride precipitation.

Bench-scale studies on silver waste treatment consisted of addition of chlorine in the ratio of 3.5 mg/mg cyanide, a 30 min reaction time yielded 90-99 % silver recovery in the wastewater (Walker *et al.*, 1954). The results obtained from this study are presented in Table 8.11.

Table 8.11

Results of Bench-scale Experiments on Silver Removal by Chlorination
(Walker *et al.*, 1954)

Experiment	Cyanide, mg/L		Silver, mg/L	
	Initial	Final	Initial	Final
1	102	0	105	3.5
4	208	0	250	2.8
10	156	0	150	1.0

The effluent quality may be improved by addition of flocculation and coagulation agents, as well as by filtration after sedimentation. Hannah *et al.* (1977) have reported that either ferric chloride or alum coagulation, at pH 6.2-6.4, can reduce silver by 95 % from an initial 500 µg/L level.

Chemical precipitation as black silver sulphide is not very suitable as the sludge separation and its subsequent treatment are not very feasible.

8.9.5.2 Ion Exchange

Of some interest is the use of ion exchange systems, which allow the recovery of silver in the cationic phase. Anionic exchangers may conveniently be used to remove complex ions of the $\text{Ag}_2(\text{S}_2\text{O}_3)$ type, which are present in the effluents from photographic and radiographic industries. The economic feasibility of the ion exchange process depends on the concentration of the other ions present in solution in the effluent.

8.9.5.3 Other Processes

Electrolytic recovery with cathodic deposition of the silver, present in particularly concentrated baths is another possibility. If sufficient metallic ions are in the waste such an operation is feasible. Electrolytic recovery usually begins at 5000 mg/L, and reduces bath silver concentration to 500 mg/L (Patterson, 1985).

Both electrodialysis and reverse osmosis have also been reported for removal of silver from wastewaters, and both of them appeared to be feasible.

8.10 Other Elements

(Tin, Cobalt, Antimony, Titanium, Vanadium, Thallium, Tellurium, Beryllium, Molybdenum, Uranium, Selenium)

The above elements are seldom found in wastewaters. As a result, the information available concerning their possible treatment is limited. (Patterson, 1985 and UNEP/WHO 1982).

For them, as also for the examined metals, chemical precipitation, co-precipitation, extraction with solvents, ion exchange and adsorption treatment may be foreseen. The last process, together with chemical precipitation is of particular interest from the application point of view. In particular, in addition to the adsorptive capacity of the various chemical precipitates, which differ depending on the element involved, on its concentration and on the concentration of the other elements contained in the sewage, it is also important to stress the interesting results obtained from a number of adsorption tests on activated carbon.

As far as chemical precipitation is concerned, mention is made of the sulphide-aided treatment for the precipitation of tellurium, selenium (reduction of the selenite ion to elementary selenium), molybdenum, antimony, cobalt and tin.

The last three of these elements can also be precipitated as hydroxides, under alkaline conditions. Considering their amphoteric character, antimony and tin are nevertheless soluble in an excess of alkalizing reagent. Especially as regards cobalt, the capacity to form complex ions can produce notable interference in the precipitation phenomena. As regards tin, the application is also known of an ion exchange process to recover the element present in the waste as stannate ion. The process consists of the exhaustion of a weak anionic resin having chloride as a functional group which is exchanged with the stannate ion. On regeneration with sodium hydroxide, an eluate rich in sodium stannate is obtained which may be reused in electrolytic baths.

Molybdenum may be removed by using iron and aluminium salts, through the possible co-precipitation and adsorption mechanisms. The process takes place in a weakly acid solution. Vanadium may be removed by precipitation with ferrous sulphate under neutral pH or weakly alkaline conditions. The precipitates consist of $\text{Fe}(\text{VO}_3)_2$ and FeV_4O_9 in respect of the vanadium present in the penta- and tetra-valent forms. With quantities of iron ten times as large as the stoichiometric one, values of 1-2 ppm may be obtained with regard to the pentavalent form and of 5 ppm for the tetravalent one.

9. BIOCIDES AND THEIR DERIVATIVES

(other than organo-halogenated and organo-phosphorus compounds)

Biocides comprise a large series of chemical compounds generally used for example as insecticides, algacides, herbicides, fungicides, and water and sewage disinfectants.

The nature of such compounds can be organic or inorganic and their origin can be natural or synthetic. Examples of inorganic biocides are given by some compounds of lead, arsenic, mercury, copper, zinc, chromium, chlorine and their derivatives. Examples of organic biocides are several organophosphorus compounds, such as Demeton, Diazinon, EPN, Methyl Parathion, Malathion, Parathion, Phenoxyalkanoic compounds, Triazines, Carbamates, Phenoxyalkanoic acids, Urea substituted compounds, Amine compounds.

It is practically impossible to describe all feasible treatments and their relative results concerning each type of biocide. Therefore a survey is given of the general applicability of a series of techniques which may constitute a useful basis for a further examination of details. A preliminary consideration concerns the possibility of minimizing pollution from biocide factories, by setting up techniques to reduce the leakage of raw materials, finished products and solvents. To this purpose, automatic monitoring systems fitted with alarms may be situated along the sewerage system, these are capable of bringing to evidence highly polluted flows, of diverting them to dumping systems and simultaneously of indicating which plant is responsible for the polluted effluents. Another device consists of isolating the areas where biocide production is carried out, so that highly polluted waters may be collected separately. In other cases, the dry collection of powders has been carried out by systems under vacuum and also by systems involving separation with cyclones.

Effluents from biocide-producing factories are generally acid. Hence neutralization, generally with lime and sometimes with limestone or dolomite beds, takes place frequently. The use of this reagent almost always involves the precipitation of chemical compounds.

Inorganic biocides may be removed through the treatment systems already considered for different elements, copper, lead, arsenic, zinc, etc.

For organic biocides the possibility exists of detoxication of some compounds by alkalization with soda or lime at high pH. The treatment leads to the hydrolytic decomposition of biocides, generally favored by temperature. On the other hand, alkaline decomposition has been ascertained for IPC compounds (Isopropyl-Phenylcarbamate), for some Phenoxy herbicides and carbaryl. The hydrolysis rate may be considerably increased by the use of catalysts, such as iron chloride.

A number of methods are known of chemical oxidation with chlorine, chlorine dioxide, potassium permanganate, peroxides and ozone. The results obtained differ considerably from case to case. Chlorine and peroxides generally exhibit a quite poor effect.

Ozone in particularly large doses gives the best results. Oxidation with ozone is more effective on unsaturated compounds than on the saturated ones.

Chemical coagulation with the classical aluminium and iron salts does not have any significant effects on biocide removal; therefore it is of little interest for such applications.

The treatments based on adsorption phenomena are among the most effective ones. For the purpose, the use of bentonite, saturated clay, hydrous aluminium silicate, activated carbon and other substances is known. Activated carbon is however of the most interesting from the point of view of application. Such a treatment, suitably dimensioned, generally allows particularly high removal levels and the achievement of low residual concentrations.

Biological treatment may often be applied provided that microorganisms are protected against shock load, rapid pH variations and accidental biocide leakages from the production departments. The results obtained by biological treatment are not only a function of the selected process and of its dimensioning, but they are also connected with the biodegradability characteristics of biocides. Some compounds, such as tertiary aliphatic alcohols, ethers, benzene, halogenated aromatic compounds, are not very biodegradable.

Some satisfactory examples have been achieved using activated sludge treatments, percolating beds and oxidation ponds. These last are considered of particular interest both as a direct treatment and for polishing. In order to function correctly, the discharge of highly coloured effluents and emulsions which make the water turbid, should be limited so as to avoid negative effects on algal growth, a factor of major importance for such a treatment. Much care must be taken with regard to sulphides; actually, at high concentrations, they cause the growth of dark bacterial colonies which can hinder light transmission through the water.

One of the most widely adopted techniques is incineration. The operating temperature for an efficient combustion of organic compounds is 750-1000°C with minimum residence times of 0.3-0.5 seconds. At higher temperatures, oxidation is better guaranteed, but some problems arise, concerning the thermal resistance of the materials, and the greater facility with which flue gases are formed of nitrogen oxides and of aerosols containing sodium chloride and phosphorus pentoxide which can produce persistent white fogs when atmospheric humidity is high.

The use of scrubbers for flue gas purification is almost always required. In any case, particular care must be taken for the control of atmospheric pollution derived from sulphur dioxide, hydrogen chloride, heavy metals and organic by-products. Heavy metals can be found following the combustion of biocides containing such elements in their chemical formulation; the serious environmental pollution that may occur in such cases discourages the adoption of this technique.

Further treatments that may be evaluated at an experimental scale are photochemical degradation, liquid-liquid extraction and foam fractionation.

For inorganic biocides having the characteristics of chemical oxidizers, such as chlorine and its derivatives, potassium permanganate and peroxides, removal from water is carried out by reduction, using inorganic compounds, such as sodium bisulphite, sodium meta-bisulphite and sulphur dioxide to quote the more frequently employed reagents. Water dechlorination is often carried out by activated carbon treatment; its action is not exactly an

adsorption mechanism, but rather a catalytic activity of reduction to chloride. Activated carbon exhibits an analogous action toward chloramines.

In the case of potassium permanganate reduction, the violet colour changes to brown because of the precipitation of tetravalent manganese hydroxide which, in its turn - by excess of the reducing agent - may be reduced to divalent manganous hydroxide, which is white and more soluble.

10. CRUDE OIL AND PETROLEUM-DERIVED HYDROCARBONS

10.1 Introduction

As is known, this class of pollutants includes numerous chemical compounds of substantially different structural characteristics. In any case, they are hydrocarbon compounds (light and heavy hydrocarbons, lubricant oils, fats) which may be singled out by chemical analysis according to common methods, by organic solvent extraction.

10.2 Sources and inputs into the Mediterranean

The input of petroleum hydrocarbons from land-based industrial discharges into the Mediterranean has been conservatively estimated at 20,000 tonnes per year (Rouit, 1975). The overall input of oil from different industrial sources is estimated at 110,000 tonnes.

Urban inputs can be computed by using the estimates of Eganhouse and Kaplan (1981) of 1,014 per year per person for urban populations and 398 per year per person for rural areas. Taking into account the Mediterranean population distribution given by Henry (1977) the total input is of the order of 160,000 tonnes of oil per year.

10.3 Oil-bearing wastes

Tabakin *et al.*, (1978) have proposed five categories to describe the physical forms of oil in wastewater:

1. Free oil. That which rises rapidly to the surface under quiescent conditions.
2. Mechanical dispersions. Fine droplets ranging in size from microns to a few millimeters in diameter, which are stabilized by electrical charges or other forces but not through the influence of surface active agents.
3. Chemically stabilized emulsions. Oil droplets similar to mechanical dispersions but with enhanced stability resulting from surface active agents at the oil-water interface.
4. Dissolved oil. Truly soluble species in the chemical sense plus very finely divided oil droplets (typically less than 5 μ diameter). This form generally defies removal by normal physical means.
5. Oil-wet solids. Oil adhered to the surface of particulate material in the wastewater.

The above distinction acquires a particular meaning in view of the selection of the possible treatment for the removal of such pollutants from wastewater.

10.4 Principal industries

10.4.1 Mineral oils from garages and car washes

Type and size of industry

There are many garages and car washes to be found throughout the cities and country. Each of these establishments will give rise to waste mineral oils either directly through oil changes or accidentally through spills and leakage.

Type of wastes

The wastes will be a mixture of oil, water, petrol, some heavy metals and detergents. The wastes may be segregated or combined depending on the reuse possibilities entertained.

Form of wastes

The wastes will be aqueous with foam. They will be dirty, black with floating and dissolved oils. They can be characterized by BOD, TSS, COD, pH, oil and grease, and some heavy metals.

Total amounts

The amount of oils used will vary with engine size. However, an average car uses 150 litres/year while buses use 300 litres/year. This may give rise to oil concentrations of 50-60 mg/L.

Discharge

Discharge may be continuous during part of the day for car washes. For garages discharges will be intermittent.

10.4.2 Iso-amyl alcohol

Type and size of industry

The chemical iso-amyl alcohol is used in the production of both phosphoric acid and potassium nitrate. The industry produces some 12,000 tons per year of phosphoric acid.

Type of wastes

The iso-amyl alcohol is used to separate hydrochloric acid from potassium nitrate and also for the separation of phosphoric acid from the process solutions. Hence the chemical will be found in wastes from the reaction stages as well as purification and recovery stages.

Form of wastes

The chemical formula of iso-amyl alcohol is $(\text{CH}_3)_2\text{CH CH}_2\text{CH}_2\text{OH}$. The other components in the waste streams will be Ca, P, Cl^- , Fe, Mg, K, F, $\text{PO}_4^{=}$. The wastes will mostly dissolve and will have a distinctive odour. The specific gravity of the chemical is 0.812.

Total amounts

Plant wastes are about $1000 \text{ m}^3/\text{d}$ while the wasted chemical will be about 100-200 mg/L in concentrations. This will give rise to about 150 kg/day.

Discharge patterns

As this is a large continuous plant the waste streams will be continuous also.

10.4.3 Oils from meat processing

Type and size of industry

The meat cooking and processing industry is quite large. One plant produces about 1000 tons per year.

Type of wastes

Wastes are produced in all phases of production. Oils are produced in the cutting section, rendering sections and the cooking and packing sections.

Form of wastes

Wastes are aqueous mixtures of blood, waste, meat, oils etc. They may be characterized through the concentrations of BOD, SS, DS, COD, colour, pH, grease, P, N, Cl etc. In general, the wastes are coloured with soluble and insoluble components. There will also be odors arising from the waste flows. The oils will be organic in nature.

Total amounts

There are about $150\text{-}200 \text{ m}^3/\text{day}$ of waste flows with all these flows originating from oil bearing processes. Oil will be at about 100-180 mg/L or about 20 kg/day.

Discharge patterns

As the plant operates continuously, with care for hygienic conditions and cleanliness there will be continuous waste streams.

10.4.4 Organics and oils from palm processing

Type and size of industry

The industry gives rise to about 16,500 tons/year of palm oil.

Type of wastes

The wastes are generated in three esterification and purification steps of oil production. Also washing down of plant floors gives rise to wastes. The process involved is



Form of wastes

The wastes are aqueous solutions with oils, mainly dissolved but with some separation of phases. The wastes will be odorous and will be warm, 20-100° C. There are also constituents such as sulphuric acid, sodium sulphate and sodium chloride.

Total amounts

The process and washing down produces about 10 m³/d of wastes, with 1/2 actually process wastes. There will be 1200 mg/L oils and waste COD is about 16,500 mg/L. There is about 0.1 m³ of waste/ton of product.

Discharge patterns

The batch process is operated twice per day throughout the year. Hence wastes are discontinuous.

10.4.5 Fruit processing

Type and size of industry

The fruit canning and juicing industry uses many organic compounds such as fructose and other sugars. The fruits include oranges, apples, lemons, grapefruit, grapes.

Type of wastes

The main processes are washing, peeling, concentrating, filtering and product packaging. All the processes give rise to waste streams including washing water, wash down water, spills and disposal of excess material.

Form of wastes

The wastes contain many organic compounds such as C₆H₁₂O₆.

There will be some colour and possibly some odour. There will be floating and dissolved materials.

Total amounts

About 4 m³ of wastes are produced from each ton of fruit. The organics in process wastes are at about 3200 mg/L but fall to 1280 mg/L in plant wastes.

Discharge patterns

The wastes are discharged continuously during the season which lasts from September to May.

10.5 Treatment

The simplest separation technique consists of gravity separators which form a primary level of treatment. The treatment process normally involves retaining the oily waste in a holding tank and allowing gravity separation of the oily material, which is then skimmed from the wastewater surface. Hence it is a process of natural flotation and therefore it is aimed at free fraction removal only. In theory, the separation process in gravity separators can be predicted by Stoke's law, but turbulence and short circuiting are common. Thus, in practice, the effectiveness of a gravity separator depends upon proper hydraulic design, and design period of wastewater retention. Longer retention times allow better separation of the floatable oils from the water. The influence of retention time on separator efficiency for a refinery wastewater is indicated in Figure 10.1. Gravity separators are equally effective in removing both greases and nonemulsified oils. The standard unit in refinery waste treatment is the API separator, based upon design standard published by the American Petroleum Institute. Two other gravity separators, both referred to as plate separators, are the corrugated plate interceptor (CPI) and the parallel plate interceptor (PPI). These units differ from the API separator in the placement of inclined plates in the separation chamber effectively decreases the vertical rise of the oil globule. Table 10.1 presents the efficiencies of several oil separation processes, including the API separator.

Secondary level of treatment involves the processes directed toward breaking the oil-water emulsion which has passed through the primary separator, and separating the demulsified oil from the water phase. Breaking up of emulsion may be achieved by chemical, physical, electrical or thermal methods.

Table 10.1

Efficiencies of oil separation processes

Treatment	Source of Influent	% Removal	
		Free oil	Emulsified oil
API separator	Raw waste	60-99	NA
Air flotation, without chemicals	API effluent	70-95	10-40
Air flotation, with chemicals	API effluent	75-95	50-90
Chemical coagulation and sedimentation	API effluent	60-95	50-90

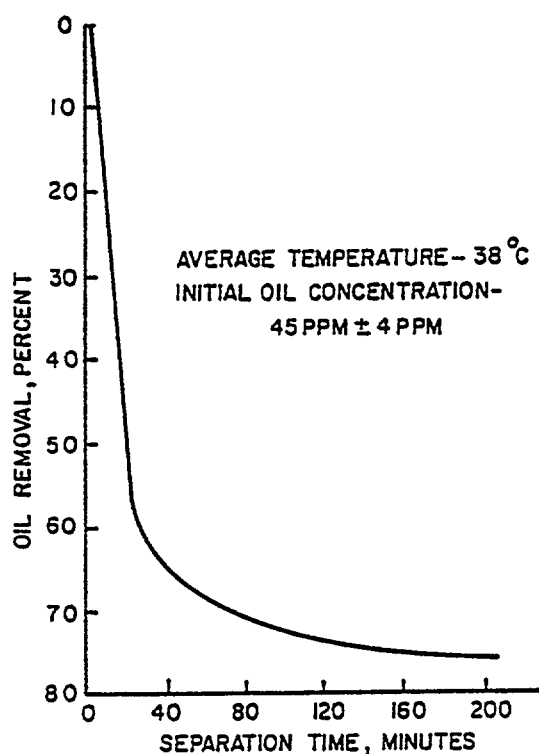


Figure 10.1. Effect of detention time on oil removal by gravity separation (Wallace *et al.*, 1965)

The chemical methods, which are most widely used, consist of adding to the wastewater the classical coagulants (iron or aluminium salts, polyelectrolytes). The chemical sludge, enriched with destabilized oily compounds, may be separated from the water either by sedimentation or by flotation. Acidification may also be effective in breaking an oil-water emulsion. Alternative chemical demulsifying processes include (Mentens, 1967):

- . adding of coagulating salts
- . adding of acids
- . adding of salts and heating the emulsion
- . adding of salts and treatment by electricity
- . adding of acids plus organic cleaving agents

Coagulation with aluminum or iron salts is generally effective for demulsifying oily wastes (Barker *et al.*, 1970). However, the aluminum or iron precipitate hydroxide sludges, which may provide difficult to dewater. Also, the salting out of emulsified oil by adding large quantities of an inorganic salt may create additional problems by significantly increasing the dissolved solids in the effluent. Organic demulgators are extremely effective demulsifying agents, but due their high cost they are considered impractical at high rinse water flow rates and low oil concentrations (Barker *et al.*, 1970). Acids generally cleave emulsions more effectively than do coagulant salts, but are more expensive, and the resultant acidic wastewater must be neutralized after oil water separation. The pH required for acid demulsification depends upon the nature of the waste.

Following chemical stabilization of an oily emulsion, air flotation is commonly employed as an alternative to sedimentation, to separate the oil and water. Air flotation consists either of saturating a portion of the wastewater with dissolved air under high

pressure (dissolved air flotation, DAF) or of dispersing air bubbles by a rotor-dispenser mechanism (induced air flotation, IAF). In DAF the pressure is then abruptly released, resulting in the formation of thousands of microscopic air bubbles which attach to oil droplets and float them to the surface. In IAF a rotor forces the liquid through the dispenser orifice, creating a negative pressure that draws air down into the liquid, generating the desired small air bubbles. IAF normally represents a lower capital investment and smaller space requirements than does DAF.

Destabilization techniques that are mainly adopted for highly concentrated oil emulsion consist of heating or of the application of a strong electric field. Electroflotation and electrocoagulation are the two processes utilizing electricity for the destabilization of oil in wastewater. The former technology is an alternative to air flotation to induce small gas bubble formation through the electrolysis of water to oxygen and hydrogen gas. The recent development of lead dioxide electrodes has improved the economics of the electroflotation process. The electrocoagulation process utilizes consumable electrodes such as scrap iron. Voltage applied to the system oxidizes the electrode to release a metallic coagulant such as the ferrous ion.

Physical emulsion-breaking methods include centrifugation, pre-coat filtration, filtration on coalescing beds. Centrifugation breaks oil emulsions by separating the oil and water phases under the influence of centrifugal force. Centrifugation is best applied to oily sludges and it is generally not used in treatment of the typical dilute oily waste stream, unless the volume is small. Oil removal by filtration involves a combination of two mechanisms: direct removal based on droplet size, and induced coalescence (Ford and Elton, 1977). Factors affecting performance are many and include the character of the oily waste, concentration of oil and droplet size, waste solid content, and hydraulic variation (Ford and Elton, 1977; Tabakin et al, 1978). Operational problems include "poisoning" of the media, which may necessitate high unit replacement and maintenance costs.

Nanofiltration is a filtration process which is effective down to molecular dimensions (10-100 angstroms). The membranes used are truly porous, and separation is a physical process requiring elevated pressure to achieve passage of fluid through the filter. Essentially, the water molecules (and other low molecular-weight solutes) pass through the membrane pores while larger molecules or aggregates such as oil micels are rejected. Actual performance is a function of variables such as membrane composition, structure and thickness, applied pressure, temperature, and waste concentration (Klinkowski, 1978). Table 10.2 presents pilot-scale ultrafiltration performance data on several industrial wastewaters.

Another membrane process, reverse osmosis, can selectively reject solutes (molecules and ions) of the same size order as water molecules (Klinkowski, 1978).

Bench scale ultrafiltration/reverse osmosis tests on a synthetic rubber waste reduced influent oil levels of 5-11 mg/L to an average effluent level below 5 mg/L (Cawley, 1980; Kleper and Turner, 1978). Pretreatment requirements for application of reverse osmosis to oil removal are much more critical than for ultrafiltration.

No generalization is possible as to the results expected from the treatments considered, the quality of the effluents polluted by such substances being extremely variable. As an indication, the results obtained from several full-scale and experimental treatments suggest that, after the examined treatments including emulsion break-up, the residual oil content is of the order of 10-30 ppm, and that this is due to both dissolved and emulsified residual fractions.

Table 10.2

Pilot Scale Performance of Ultrafiltration in oil and Grease Removal (Cawley, 1980)

Industry	Oil and Grease (mg/L)		% Removal
	Influent	Effluent	
Adhesive and sealants	113	131	(-16)
	522	162	69
	478	184	62
Commercial laundries	600	<9	98
	749	28	96
	795	10	99
	7,890	38	99
Synthetic rubber manufacture	12	5	58
	28	11	61
Timber products processing	2,160	55	97

Biological treatment may be adopted either as an alternative or integrated with the above processes. As a matter of fact, activated sludge plants, percolating beds, and in particular oxidation ponds have been widely applied for the treatment of oily discharges.

When choosing a treatment for such discharges, particular attention must be paid to the variability of composition in relation to the result obtained. However, among those organic compounds most commonly found are various hydrocarbons, their oxidation products (alcohol and aldehydes), phenolic compounds, esters and oily impurities. Biological systems can remove oils and mineral fats from wastewaters because of adsorption on bacterial flocs and biodegradation. This last phenomenon, and consequently the overall purification efficiency, is particularly related to the biodegradability of hydrocarbons. Table 10.3 presents data on activated sludge and aerated lagoon treatment of oily wastes.

With regard to the feasibility of biological treatment, apart from biodegradability, the initial concentration of the substance itself plays an important role. As a matter of fact, because of the known interferences with bacterial activity and the oxygen transfer process in aerobic treatment, in the case of high initial concentrations it is generally advisable to perform biological treatments after the previously discussed physico-chemical ones or to use mutant bacterial inoculums into an industrial activated sludge plant to enhance oil and grease removal.

Table 10.3

Biological System Performance for Control of Oil and Grease
(Cawley 1980)

Type of System	Industry	Oil and Grease (mg/L)		% Removal
		Influent	Effluent	
AS ^a	By-product coke manufacture	240	5	98
AS	Leather tanning and finishing	171	91	47
		247	35	86
AL ^b	Leather tanning and finishing	553	17	97
AS	Textile mill	413	25	94
		720	17	97
		324	303	6

^a Activated sludge

^b Aerated lagoon

The preliminary treatments are aimed at the removal of other inhibiting compounds such as, sulphides and sulphur-based organic compounds. To this end oxidation processes are normally used or, in the case of sulphides, precipitation of iron sulphide.

Figure 10.2 is a schematic diagram giving an example of a chemical-biological plant for the treatment of the discharges from the petrol-chemistry. The plant consists of an homogenization basin for the balancing of the pollution load, of a stage for the separation of the oily contents by means of pressurized flotation, and the addition of demulsifying reagents, and finally a 2-stage biological treatment with activated sludge.

The dissolved fraction may be removed not only by the biological treatments, but also adsorption processes, amongst which adsorption on activated carbon is certainly the most interesting. Obviously, for this treatment too, the degree of reliability is different and depends on the quality and concentration of the oily and fatty fractions present in the effluent. However, the wide experimentation done proves the great importance of the applications of activated carbon in this particular field. Two types of consideration must be taken into account when considering the possibility of using the above process: one concerns the final quality of the purified effluent, the other is strictly connected with the economic aspect of the treatment. Adsorption on activated carbon is profitably applied when particular quality characteristics are required or whenever sound reasons against the application of biological treatments exist. Due to its operating costs, the process is especially applied as a finishing treatment downstream of the purification methods previously considered.

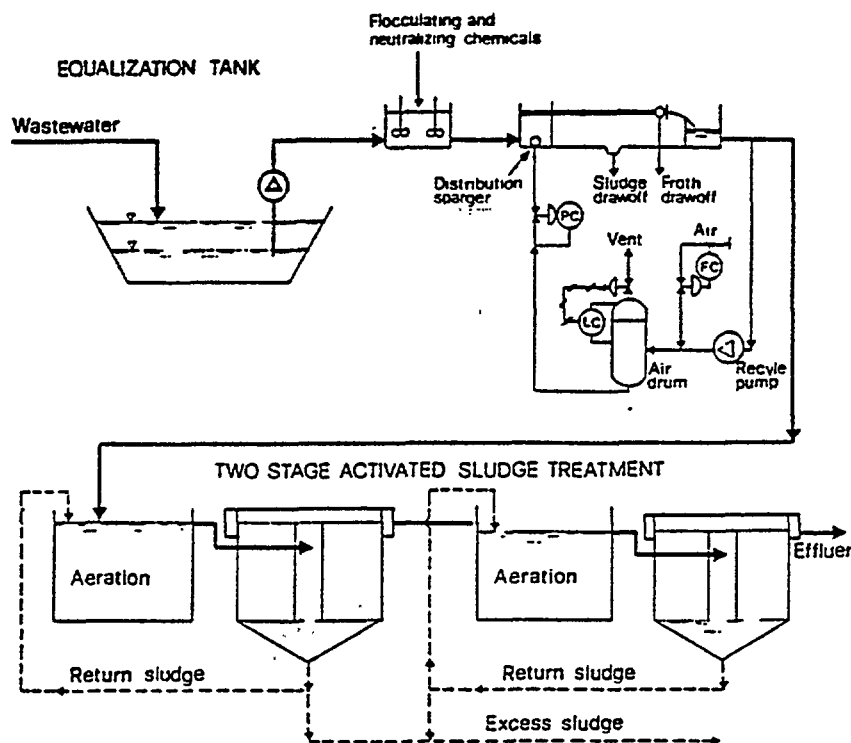


Figure 10.2. Chemical-biological treatment of wastewaters from the petrochemical industry.

11. CYANIDES

11.1 Introduction

Cyanides are widely used in industry. In addition to the simple cyanidric acid, HCN, the alkali metal salts such as sodium cyanide, NaCN, and potassium cyanide, KCN, are commonly-occurring forms and sources of cyanide. These salts are readily dissolved in water. The extent of HCN formation is pH-dependent; at 25°C, the acid dissociation constant has a value of 4.8×10^{-10} . Cyanide ion combines with numerous heavy metal ions to form cyanometallic complexes. These anions have various degrees of stability. The cyanide complexes of zinc, cadmium and lead dissociate readily. The copper complex dissociates less easily and the complexes of silver, gold, nickel and cobalt are even more stable. No measurable dissociation of the cyanide complexes of iron takes place except in the presence of sunlight.

11.2 Sources and inputs into the Mediterranean

There is no accurate information available regarding the discharge of cyanides into the Mediterranean Sea through industrial or domestic effluents.

11.3 Cyanide-bearing wastes

Cyanide wastes arise from a number of different industries. In the aquatic environment they are highly toxic to plant and animal alike. Pollution of water sources of recreational areas causes a situation of extreme danger to human beings. Industries which

discharge cyanides are metal processing industries, organic chemical industries and petrochemical industries.

11.4 Principal industries

11.4.1 Metal processing industries

Type and size of industry

Zinc plating is conducted in cyanide baths as is silver and gold. In general cyanide baths are also used in copper production. Industries can vary from small shops to large metal processing plants. Sometimes smaller establishments are more problematic than larger plants because of difficulties of surveillance and control.

Type of wastes

Wastes are generated in the cyanide bathing processes. Cyanide is generally associated with many other heavy metals such as zinc, copper, iron, nickel, aluminium. Mixed wastes contain on the average 50 to 70 mg/L CN^- while typical total plant wastes contain an average of 15-30 mg/L CN^- . Concentrations of cyanides from general process wastes are 200-1500 mg/L for electronic hardware, 70 mg/L for silver-ware and up to 130 mg/L in general plating wastes. The wastes are generated by the rinsing of plates and occasional spills.

Form of waste

Most cyanides appear in alkaline bath solutions since acidic environment can produce highly toxic HCN vapor.

The wastes are aqueous turbid solutions with dissolved CN^- ion, associated are coils and detergents as well as suspended floating and dissolved metals. They may be warm and coloured.

Total amounts

Quantities of cyanides will depend on the particular bathing process being used. Quantities of wastes per ton of product are given in the sections on respective metals. Primary plating baths may contain between 30 to 50 g/L of cyanide salts. Approximately 10 to 30 kg of cyanides are used per ton of plated products.

Discharge patterns

In small shops or plants discharge is intermittent or semi-continuous. In larger plants discharge is continuous with peaks depending on spills and dumping of process solutions.

11.4.2 Petrochemical industry

Type and size of industry

The petrochemical industry can be subdivided into a number of production categories namely: crude oil distillation, cracking, petrochemical production, lubrication oil manufacturing and coke manufacturing. Larger plants are usually integrated to produce

various combinations of the above. Plants may vary in size, but to render the plant economical its production capacity should be at least 50,000 tons per year.

A medium to large size refinery and petrochemical plant processes between 1 and 10 million barrels of oil per year.

Type of wastes

Cyanides are produced in small quantities in all process steps. However, in the cracking process (thermal) up to 10 mg/L of CN^- may be found. In other process wastes concentrations of up to 0.2 mg/L of CN^- are found.

Form of wastes

Cyanides are dissolved ions of CN^- in the waste streams. Wastes vary in each process and they usually contain oils, dissolved organics, sulphates, nitrates and ammonia, and phenols.

Total amounts

Old refineries and petrochemical plants produce enormous quantities of wastes of between 2 to 5 m³ of wastes per ton of crude oil processed. New refinery technology has cut amounts of wastes to approximately 0.2-0.3 m³ per ton of crude.

Approximately 1.0-1.5 kg of cyanide is used per ton of cracking plant input.

Discharge patterns

Discharge is intermittent with varying frequencies according to plant operation.

11.4.3 Other industries with wastes containing cyanides

Cyanide wastes are also found in a number of other industries.

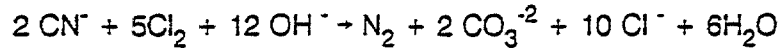
These include the photographic industry where concentrations of 6 mg/L have been found. Cyanides were found in the process wastes of the ferroalloy industry at up to 30 mg/L. Cyanides may also be found in the wastes from the pharmaceutical industry, as well as the rubber and plastics industries.

11.5 Treatment

Common methods employed for cyanide removal includes cyanide destruction by chlorination, electrolytic decomposition, ozone oxidation and evaporative recovery. Other cyanide treatment processes which are less commonly adopted are reverse osmosis, ion exchange, and catalytic and thermal oxidation.

11.5.1 Chlorination

Cyanides present in wastewaters may be removed by chemical oxidation by chlorine which, in an alkaline medium (pH = 10.5-11), causing cyanide conversion to carbon dioxide and nitrogen, according to the reaction:

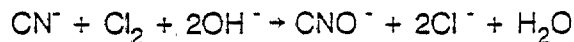


Transformation actually occurs in subsequent steps involving the formation of cyanogen chloride (CNCl), which is later oxidized to cyanate ion (CNO⁻). The alkaline medium in which the reaction occurs, besides favoring the kinetics of the oxidation process, maintains those conditions which prevent volatilization of the poisonous cyanogen chloride.

Figure 11.1 shows the importance of the accurate control of the pH for the conversion of the cyanogen chloride to cyanate. One sees that at a pH lower than 10, reaction times of approximately 30 minutes are sufficient in order to achieve about 90 % decomposition of the cyanogen chloride, whilst at a pH of 9.2 a minimum of two hours is needed; it has been noted that the dosage of chlorine has a certain influence on the rate of decomposition. It must be dosed in excess of the stoichiometric requirements.

Concerning the kinetics of the cyanide oxidation reaction one often finds opposing data in the relative literature. This presumably is due to catalytic action exercised on those ions present in the wastewater. This is particularly valid in the oxidation of the complex cyanides.

The complete oxidation of cyanides, although undoubtedly offering the best guarantee for environmental protection, is not always considered convenient to achieve. In fact, oxidative conversion is sometimes limited to cyanide formation, being a rapid reaction that involves a lower chlorine dose:



Furthermore, the cyanide ion toxicity is one thousandth of that of cyanide ion; hence an oxidation limited to such an intermediate step may be justified.

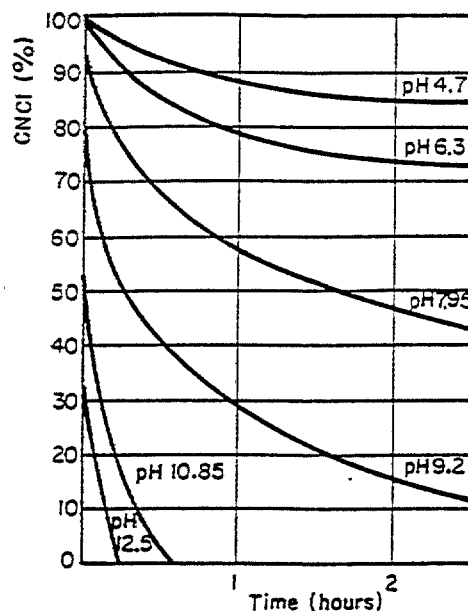


Figure 11.1. Decomposition of the cyanogen chloride with time and pH.

Particular problems can come to light when the oxidation refers to complex cyanides; for example in the cyanide complex of potassium and copper $K_3Cu(CN)_4$, three cyanogenic groups are destroyed very rapidly, whilst the fourth group is very resistant; in the detoxication of the complex cyanides of copper and silver, after the oxidation of some cyanogen groups the insoluble copper cyanide can precipitate the oxidation of which is extremely difficult. Finally, the complex iron cyanides can only be oxidized by extremely high amounts of chlorine at high temperature.

Since cyanide-containing effluents are often polluted by heavy metals too, the oxidation and alkalization process is accompanied by the formation of chemical precipitates which essentially consist of heavy metal hydroxides, of calcium carbonate and sometimes even of calcium sulphate, if hydrated lime is used as an alkalizing compound.

The results obtained with chlorine are comparable with those obtained with chloro-derivatives, e.g. hypochlorites of sodium and calcium. The former, in particular, is extensively used, it being simple to store and dose.

Actually it does not require all the precautions which are rigorously needed for chlorine, which as is known, is extremely toxic. The quoted reagents being basic, the need for the alkalizing agent may be limited and sometimes even obviated. Hence, sodium hypochlorite is used in low- and medium- capacity treatment plants.

Other oxidizing agents such as potassium permanganate, ozone, chlorine dioxide and hydrogen peroxide have rarely been applied. The reason for this is to be found in the higher costs involved in such treatments and in the little information available as to the results which may be obtained under different operating conditions.

In the treatment of metal processing effluents, cyanide baths and rinses are frequently treated together, with the concentrated bath solutions being blended into the more dilute rinsewaters. It is advised to apply batch treatment when average flows do not exceed 0.96 l/sec (15 gallon per minute) (Patterson, 1985).

Treatment of a cyanide waste flow of 2.5-3.2 l/sec (40-50 gpm) by alkaline chlorination to the level of cyanate has been reported by Schink (1968). An effluent cyanide level of 0.1 mg/L reported for the treatment of plating wastewaters. In another study, cyanide was completely oxidized to CO_2 , by applying alkaline chlorination plus acid hydrolysis. The waste was treated to zero cyanide level from the initial 700 mg/L by this treatment process ((Hansen and Zabban, 1959). Table 11.1 presents a summary of the alkaline chlorination treatment of cyanide wastewaters.

Operating and capital costs for alkaline chlorination treatment of cyanide can be approximated by utilizing the cost curves developed by Zievers *et al.* (1968).

Oxidation with atmospheric oxygen, using additional catalysts, is also of a certain interest. Various patented processes are known: one method makes use of the catalytic action of the active powdered carbon, another employs a coal-like product derived from slow distillation of fossil coal.

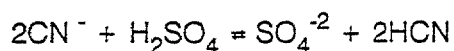
Table 11.1

Alkaline Chlorination Treatment of Cyanide Wastewaters

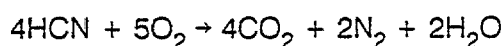
Treatment process	Cyanide concentration, mg/L		
	Initial	Final	Reference
Alkaline chlorination (single stage)	28	2.0	USEPA, 1975
	-	1.7	Coulter, 1970
	-	0.1	Schink, 1968
Alkaline chlorination (two-stage)	-	0.4	O'Neil, 1970
	700	0.0	Hansen and Zabban, 1959
	32.5	0.0	Watson, 1954
	1.3	0.25	Yost and Masarik, 1977
	-	0.6	Yost and Masarik, 1977
Alkaline chlorination (high temperature, high pH)	5.1	0.1	Yagishita, 1973

11.5.2 Stripping

Among the used alternative techniques, mention is made of stripping either with air or air-steam mixtures. Cyanide-polluted effluent is subjected acidification to pH=2-3, to release hydrogen cyanide in the gas phase:



Separation of the hydrogen cyanide is carried out by air or air-steam blowing into the acidified effluent. In order to obtain satisfactory results, the interphase contact occurs in packed columns preferentially operating under vacuum. A further parameter useful for increasing process efficiency is the temperature. As it is impossible to release hydrogen cyanide into the atmosphere, it may be eliminated by combustion in the presence of excess oxygen:



The process may be carried out at relatively low temperature (about 300°C) in the presence of combustion catalysts (Figure 11.2). Instead of combustion, it is also possible to recover cyanide in the gaseous form by adsorption in sodium hydroxide solution producing sodium cyanide solution.

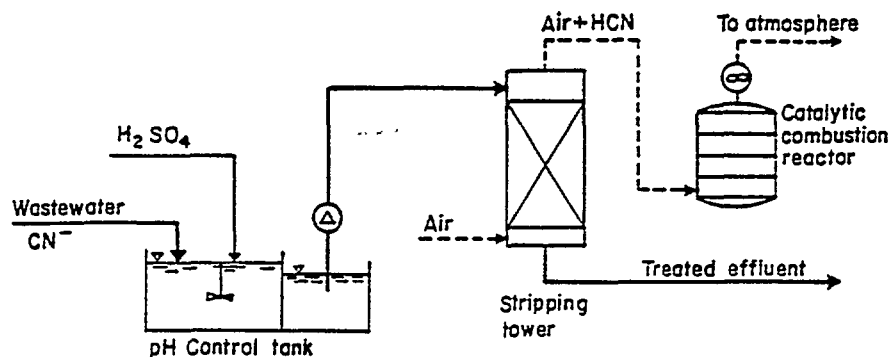


Figure 11.2 Stripping and catalytic combustion process of cyanidric acid

11.5.3 Electrolytic Decomposition

Another method of treatment is made of electrolytic decomposition processes, which may be carried out by different methods; in all cases, they cause the anodic oxidation of cyanides. Wastes containing high concentrations of cyanide are most successfully treated by electrolytic decomposition. However, it has not generally been practical to treat rinsewaters by electrolysis, due to their initial low cyanide concentrations.

It is also reported that it usually not economical to carry the electrolytic decomposition process below a few hundred mg/L residual cyanide. Further cyanide treatment is usually achieved by chlorine oxidation.

In this treatment method, the concentrated cyanide wastes are subjected to anodic electrolysis at high temperature ($50-95^\circ\text{C}$) for periods of several hours to days. During the start of the process, cyanide in the waste is broken down to the gaseous products carbon dioxide, nitrogen, and ammonia. As the process continues, the waste electrolyte becomes less capable of conducting electricity, and the reaction may not go to final completion. Low effluent cyanide levels can be achieved by electrolytic decomposition if sufficient treatment time is provided. Wastes containing several tens of thousands of mg/L of cyanide were treated, over 7 to 18 day periods, down to cyanide levels of less than 0.5 mg/L. One major problem associated with electrolytic decomposition is the presence of sulfates, which causes lower treatment efficiencies (Patterson, 1985).

11.5.4 Ion Exchange

At present, ion exchange plants are also used for treatment and subsequent recirculation of the rinsing waters used for plating processes and generally from surface treatment of metals. Cyanides are fixed, with other anions, on anionic resins and are subsequently recovered from them in the alkaline regeneration phase. The cyanides that are present in regeneration eluates must be subsequently removed by other methods described. However, Patterson (1985) has reported that ion exchange recovery of cyanide is not feasible due to primarily cyanide deterioration of the exchange resin. Another disadvantage with ion exchange treatment of cyanide is the danger of evaluation of highly toxic hydrogen-cyanide gas upon resin regeneration.

11.5.5 Evaporative Recovery

Evaporative recovery has been shown to be practical and economical under proper circumstances due to its high capital and operating cost. However, it is economical to apply this method of treatment for cyanide plating solutions due to the noncorrosive nature of the distillate, The advantage associated with this method is the recovery of the cyanide which overweighs the disadvantages of high capital and operating costs.

Other techniques which can be applied for the treatment of cyanide wastes are ozonation, Kastone process, activated carbon adsorption plus copper-catalyzed oxidation and thermal cracking. Ozonation is an alternative for chlorination which oxidizes cyanide efficiently to cyanate, whereas thermal cracking is an high temperature and high pressure process with the final end products ammonia and formic acid.

12. FLUORIDES

12.1 Introduction

Fluorine is the most electronegative and reactive of all the elements existing naturally in the form of fluoride. It is the 17th most abundant element in the earths crust. Its soluble compounds can produce toxic affects at very low doses. However, the bulk of the element is locked up in relatively insoluble minerals, such as fluorite (CaF_2) and fluoroapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$).

12.2 Sources and inputs into the Mediterranean

Fluoride is produced as a waste product by several industries in the Mediterranean. However, there is no accurate information available regarding amounts discharged through industrial or domestic effluents.

12.3 Fluoride-bearing wastes

Fluorides appear in wastes of numerous industries among them the fertilizers industry, metal processing industry, glass and ceramics industries, in some petrochemical and pesticide industries and in various mining and mineral processing wastes. Only the principal fluoride emitters are described here.

12.4 Principal industries

12.4.1 Phosphate fertilizer and H_3PO_4 industry

Type and size of industry

Phosphate fertilizer industries, as well as producing ortho phosphoric acid for industrial purposes are usually large in size with capacity of at least 5000 tons of H_3PO_4 per year. Major fertilizer plants can reach capacity of 10,000 to 100,000 tons of phosphate (as H_3PO_4). As in other mining and mineral industries, fluoride is present in the raw material (rock) and is emitted into the waste-stream during the recovery and processing of the commercial product being superphosphate fertilizer and ortho phosphoric acid in this example.

Type of wastes

Phosphate rock is treated with hydrochloric acid to produce H_3PO_4 , $CaHPO_4$ and $Ca(H_2PO_4)_2$.

Fluoride ions are dissolved from fluoride salts and complexes in the rock and they appear in the wastes in the form of CaF_2 , HF, NaF and KF. Wastes contain H_3PO_4 , $CaCl_2$, $CaSO_4$, HCl, and other dissolved salts and minerals. When the industry is producing other fertilizers (usually nitrogenous) ammonium and nitrate salts will also be present in the plant waste stream.

Concentrations of fluoride in the phosphate acidification process are between 1000 and 4000 mg/L depending on fluoride content in the raw material (rock) and on the amount of water used in the process. Total fertilizer plant wastes might contain between 200 and 800 mg/L of fluorides.

Ortho phosphoric acid production processes contain 2000-4000 mg/L of fluorides and total plant wastes contain approximately 1000-2000 mg/L of fluorides.

Form of wastes

Waters are in a turbid, milky solution, due mainly to the content of calcium sulphate suspension.

Total amounts

Phosphate fertilizer plants produce approximately 10 m^3 of waste per ton of product. Fluoride discharge can reach 10 to 30 kg per ton of product expressed as H_3PO_4 .

Discharge patterns

Discharge is normally continuous.

12.4.2 Electronic industry

Type and size of industry

Processing of printed electrical circuits and conductors and special plating processes involve the use of fluoride-containing compounds. Industries vary in size and they are usually small with a few exceptions, the major electronics industries.

Type of wastes

HBF_4 is added to plating and processing baths, usually when copper and special alloys are used (sometimes also in zinc, nickel and silver plating).

Process wastes contain 20-30 mg/L of F^- while total plant wastes might contain process copper and other metals.

Form of wastes

Usually clear or slightly coloured solution.

Total amounts

Total plant wastes amount to approximately 10 to 20 m³ per m² of plated or processed surface while process wastes amount to 1-2 m³ per m² of plated or processed surface.

Approximately 20 g of HBF₄ is discharged per m² of processed surface.

Discharge patterns

Intermittent batch production, almost a continuous flow in large plants. Peak concentrations when spills occur.

12.4.3 Glass industry

Type and size of industry

Fluoride is generally found in the wastes generated from glass surface treatment processes. This involves the removal of surface faults such as minute cracks and flaws. It is also used in the production of frosted surfaces such as for frosted glass or light bulbs.

Type of wastes

The wastes from the glass industry include cooling and boiler water, and washwater from plate, float and automotive subcategories.

Hence, the fluoride wastes will be due to the washing of glass after frosting at HF treatment.

Form of wastes

The wastes will be acidic containing mercury, diofluoric acid, sulphuric acid, oils and abrasions and silicon compounds. The wastes may be warm and turbid. There will be associated suspended solids but little BOD.

Amount of waste

The concentrations in the wastes will be

HF	:	1000-3000 mg/L
H ₂ SO ₄	:	500-1200 mg/L
Oils	:	50- 150 mg/L
Abrasions	:	1500-3000 mg/L

About 46,000 l of wastewater/ton of glass processed will be produced.

Suspended solids concentrations may be as high as 15,000 mg/L giving 700 kg/ton of glass.

Discharge patterns

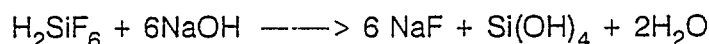
Discharges may be intermittent due to batch processing.

12.5 Treatment

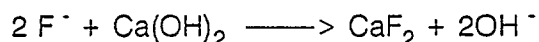
A variety of treatment methods are available for fluoride-bearing waste streams, such as precipitation adsorption and ion exchange. Application of electrochemical process has also been report for fluoride wastewaters.

12.5.1 Precipitation

Fluorides which are generally found in wastewaters either in the form of fluoride ions or hexafluosilicic acid are usually removed from wastewaters by chemical precipitation with calcium compounds. This last, by reaction with alkali, under neutral conditions is transformed into the fluoride ion according to the reaction:



The fluoride anion can be precipitated by adding calcium to the fluoride solution to form a calcium fluoride precipitate which has a theoretical maximum solubility of 8 mg/L fluoride at stoichiometric concentrations of calcium, according to the reaction:



Lime is the most used for fluoride precipitation as calcium fluoride, a white crystalline precipitate. Results obtained at both experimental and full scale prove that, in order to obtain optimum results, 100 % excess calcium over the stoichiometric amount is required. Patterson (1985) reported improved fluoride removal at very high lime dosages. Lime dosing at the 4 g/L level has been reported to reduce fluoride from 200 to 3 mg/L, in 19 h reaction time (Rohrer, 1971). The residual fluoride concentrations found experimentally approached the theoretically predicted values only at high calcium concentrations (F_7/Ca molar ratio = 0.24) for long equilibrium times (Parthasarathy *et al.*, 1986).

In any case, the use of lime produces some problems because of the low solubility of the reagent, and hence the lower availability of the calcium ion in solution. Much better results are obtained by performing the simultaneous acidification of wastewaters to pH of 7-8.

Alternatively the use of calcium chloride can be foreseen, possibly in addition to the lime used as a neutralizing agent. In the treatment television picture tube plant wastewaters, the lime-calcium chloride method of treatment effectively reduced fluorine levels to comparable levels achieved with lime alone (Rohrer, 1974).

A series of laboratory experiments has been conducted for the optimization of fluoride precipitation with calcium salts. It was pointed out that the relationship between acidity and fluoride content of the incoming waste dictates alternative proportion of calcium chloride and calcium hydroxide. Laboratory results indicated that a pH between 8 and 9 gives better results, as in Figure 12.1.

A 2-stage process was also proposed for the reduction of fluorides from 90-135 ppm to 1-2 ppm. The outline of the treatment is shown in Figure 12.2. The wastewaters are treated in the first stage with a high dose of lime to raise the pH to approximately 12, and then settled. The effluent is neutralized by the addition of acid and then undergoes chemical coagulation with alum and polyelectrolyte. In order to obtain good removal efficiency, an excess of lime and accurate control of pH during the coagulation stage (the influence of which is illustrated in the graph in Figure 12.1) are determining factors.

The performance of the fluoride removal by precipitation technique based upon three basic factors: a) sufficient excess calcium to shift the equilibrium of the reaction towards the formation of calcium fluoride, b) maintaining of a highly alkaline pH throughout the precipitation reaction, and c) efficient suspended solids removal in a clarifier. Effluent from a cathode ray tube manufacturing operation, treated by precipitation, approached to a minimum level of 23 mg/L; by using lime (600 mg/L), calcium chloride, and a polymer (4 mg/L).

12.5.2 Adsorption

In addition to chemical precipitation, fluorides may be removed by adsorption. However, the process has seldom been applied at full scale and may be convenient only for very low strength wastewaters. In this sense, it may be considered as a possible integrative treatment to chemical precipitation.

Adsorption treatment of fluoride involves the passage of the wastewater through a contact bed, with fluoride being removed by general or specific ion exchange or chemical reaction with the solid bed matrix (Patterson, 1985). However, these methods are usually appropriate only for low-level fluoride wastes, or polishing process after fluoride reduction by previous treatment to the 10-20 mg/L level. Otherwise, the requirement for frequent bed regeneration makes the process economically unfeasible (Patterson, 1985).

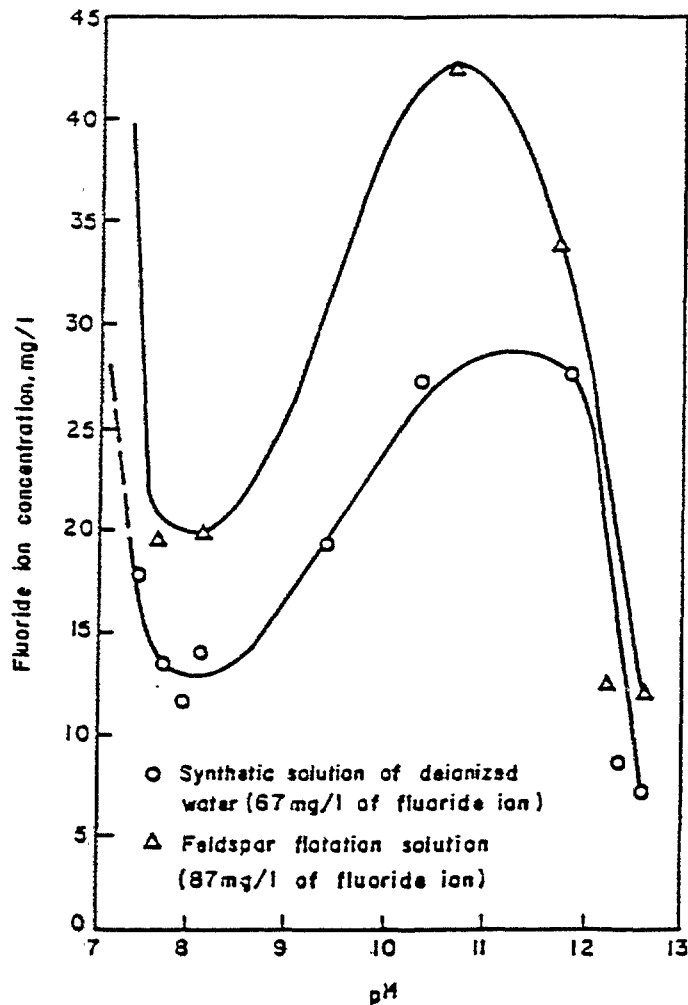


Figure 12.1. Effect of pH level on residual fluoride after lime treatment (Patterson, 1985)

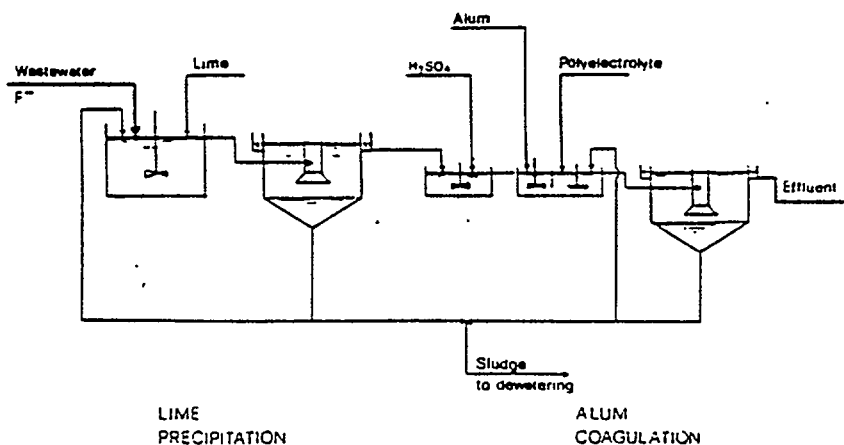


Figure 12.2 2-stage process for chemical precipitation of fluorides.

Type of media that have been used are hydroxyapatite, ion-exchange resins, and activated alumina. Among these, activated alumina is the one which shows the greatest possibilities. It has been used for many years in municipal water treatment plants for removal of fluoride ion. Activated alumina can be regenerated by sodium hydroxide, with subsequent neutralization of the eluate with sulphuric acid. One unit, in Barlett, Texas, has operated successfully and the fluoride level was reduced from 8 mg/L to 1 mg/L, applying caustic for regeneration (Maier, 1953). The exchange capacity of activated alumina for fluoride has been found to be 12 mg/g, while the maximum rate is occurring at pH 5 (Wu and Nitya, 1979).

Natural and synthetic ion exchangers have been reported to be effective for removal of fluoride. Fluoride removal by ion exchangers was attributed to aluminum salts which were used for both pretreatment and regeneration of ion exchangers (Patterson, 1985).

Another type of media that have been used for fluorine treatment is hydroxyapatite. Reduction of fluoride from 10 mg/L to 1.5 mg/L was reported for a pilot plant operation in South Africa (Cillie *et al.*, 1958). However, a significant problem in the treatment is the presence of chlorides. These reduces filter-bed capacity and in turn increases the regeneration chemical requirements.

Natural and synthetic zeolites have been examined and reported to be affected for removal of fluoride.

13. NON BIODEGRADABLE DETERGENTS AND OTHER SURFACE-ACTIVE SUBSTANCES

13.1 Introduction

Detergents which are either non-biodegradable or very slowly biodegradable are normally referred to as hard detergents. They may be anionic, cationic and non-ionic. Some effort has been made in recent years to convert to soft detergents i.e. those that are easily and quickly biodegradable. Slow, hard detergents are still being used, and therefore they are found in the waste streams originating from the production process itself, in laundry wastes,

in car wash wastes, and in the wastes from metal degreasing processes. Hard detergents are also found in urban runoff and in raw sewage.

In many parts of the world the use of non-biodegradable detergents are forbidden because of its persistence in the environment and lack of simplified treatment techniques.

13.2 Sources and outputs into the Mediterranean

Detergents have been detected in wastewaters and in seawater in many parts of the Mediterranean. However, there is no accurate information available as to the amounts discharged in domestic or industrial effluents.

13.3 Principal industries

13.3.1 Hard detergent

Type and size of industry

Hard detergents such as Alkyl benzil sulphonate (ABS) are produced as a by-product of the petrochemical industry. The size of the industry is 5.5×10^6 tons/year.

Type of wastes

Depending on the success of waste segregation there will be larger or smaller amounts of water with the waste products. The wastes originate in all stages of the detergent preparation process.

Form of wastes

The wastes contain ABS as well as NH_4^+ , Na^+ , BOD, COD, SS, fats. As anionic tensides ABS may be characterized by using MBAS (methylene blue active substances).

Total amounts

The plant gives rise to $3000 \text{ m}^3/\text{day}$ of wastes with a concentration of 600 mg/L, hence some 1800 kg/day of product are found in the waste streams. The BOD of the waste streams may be in the range of 60-3500 mg/L, the COD 100-2000 mg/L and MBAS 50-1400 mg/L.

Discharge patterns

The discharges will be intermittent depending on process operation, washing down and production requirements.

13.3.2 Laundries

There are many types of laundry processes including industrial laundries, linen only, auto washes, carpet and upholstery cleaning, laundromats and dry cleaning. Concentrations of 100 mg/L ABS have been found in waste streams.

13.4 Treatment

The above compounds are removed by physicochemical treatments. For effluents containing average concentrations, chemical coagulation with the conventional iron and aluminum salts is extensively used. The treatment efficiency obviously depends upon the effluent characteristics and on the reagent type and dose. Tests carried out on alkyl benzene sulphonate polluted effluents at concentrations above 100 ppm show the possibility of obtaining residual concentrations lower than 20 ppm. The drawback of this method is the high production of sludge containing the removed surfactants.

In order to achieve an improved quality, chemical coagulation may be conveniently integrated with a subsequent adsorption on activated carbon. The surfactants removal is comparable with the adsorption of other organic compounds; in fact, in agreement with theoretical forecasts, surface-active substances are better adsorbed from pure solutions than from effluents containing other pollutants, e.g. as is the case of laundry effluents.

Activated carbon may be used for wastewater treatment in powdered form or in the granular form as a fixed bed. As is known, the latter allows a greater flexibility and the possibility of obtaining lower residual concentrations. The determination of the adsorption isotherms allows an evaluation of the adsorption efficiency of the different activated carbons available on the market. Other useful information for the design of the adsorption system is the relationship between removal efficiency and contact time.

When the detergent concentration is particularly high, foaming may be advisable; this process is carried out by air dispersion in the form of very fine bubbles into the wastewater to be treated. Surfactants accumulate as foams, which are continuously removed from the column, and later disposed of usually by incineration. Like chemical coagulation, foaming seldom allows the achievement of residual concentrations lower than 5-10 ppm. The process efficiency is affected by temperature, pH, air flow-rate, bubble size and obviously by the surfactant characteristics.

The addition of inorganic compounds capable of complexing surface-active substances was found to exert a favorable effect on foaming efficiency. To this end, iron and aluminum hydroxides are suitable for anionic surfactants; for cationic ones, satisfactory results have been obtained with copper and hexacyanoferrates.

The possibility of using surface-active substances of opposite charge to bring about the formation of an insoluble complex is proved by the use of alkyl-dimethyl-benzyl-ammonium chloride for alkyl benzene sulphonate. The precipitate may be removed either by chemical coagulation or by filtration.

Use of the process of ultrafiltration has been experimented with on different effluents containing detergents, in particular laundry wastes polluted by anionic and non-ionic detergents. Cellulose acetate membranes have shown a low grade of rejection of the non-ionic tensides and also of anionic tensides when polyphosphates are present. On the contrary, using PSAL-type membranes (non-cellulosic skin on cellulosic backing), rejection grades of over 90 % have been obtained.

Tests are in progress on other treatments, such as reverse osmosis and the use of adsorption resins.

14. INORGANIC PHOSPHORUS COMPOUNDS

14.1 Introduction

Phosphorus occurring as phosphate is one of the major nutrients required by plants, and is essential for all forms of life. In the elemental form, phosphorus is extremely toxic, and is subject to bioaccumulation in marine organisms. Since virtually all phosphorus in seawater occurs as phosphates (PO_4^{-3}), due to oxidation and hydrolysis reactions, measurements are often given in terms of "total phosphate phosphorus", or "phosphorus as P". Evidence from Placentia Bay, Newfoundland, indicates that elemental P, discharged from a phosphorus production plant, was responsible for a large fish kill there, and that phosphorus in the elemental state shows some degree of persistence in sediments.

14.2 Sources and inputs into the Mediterranean

In spite of its high toxicity in the elemental form, the main problem in the Mediterranean stemming from contamination by phosphorus is probably eutrophication. Nutrient enrichment, as well as sewage effluents containing a high organic matter load, occurs mainly near large coastal cities and near the estuaries of large rivers. Aesthetic degradation and ecosystem alteration are probable results of severe eutrophication along some shores of the Mediterranean.

No comprehensive evaluation of the total inorganic phosphorus entering the Mediterranean Sea has been made. An earlier survey (UNEP, 1984), estimated a total of 22×10^3 and 0.1×10^3 tonnes per annum originating from domestic and industrial sources respectively, discharged from the immediate coastal zone.

14.3 Phosphorus-bearing wastes

Phosphorus is a waste product from the production of phosphoric acid for fertilizer production. It will also be found in urban waste-streams such as urban runoff, urban sewage and urban treated sewage.

The most likely inorganic forms of phosphorus present in wastewaters are phosphates (orthophosphate, metaphosphate and pyrophosphate) and polyphosphates. Phosphites, which are seldom found, may easily be oxidized to phosphate.

14.4 Principal industries

14.4.1 Fertilizer production

Type and size of industry

Phosphate fertilizer is produced by a series of ore treatments (washing steps) followed by production of phosphoric acid. This may then be used to produce $(\text{NH}_4)_3\text{PO}_4$, H_2SO_4 and triple superphosphate.

Type of wastes

Wastes are generated in all steps including all pollution treatment steps.

The use of wet scrubbers gives rise to a wastewater stream. Cleaning of process equipment and areas gives rise to waste flows.

Form of wastes

The wastes include PO_4^{-2} as well as SO_4^{-2} , Ca and fluoride. There may be ammonia and aluminum. The ions will be dissolved and the solution will be colored with a low pH (1-2).

Amounts

Approximately 10 m^3 of wastes are produced per ton of phosphates (expressed as H_3PO_4). The P_2O_5 concentration in actual treatment process wastes may be as high as 5000 mg/L. But in overall plant wastes, the P_2O_5 concentration is about 100 mg/L. Other compounds are: suspended solids 1000 mg/L, $\text{SO}_4 = 4000 \text{ mg/L}$, and fluoride 8000 mg/L.

Discharge patterns

Waste discharges may be intermittent depending on batch processing, water treatment and any reuse of waste streams.

14.4.2 Chemical production of H_3PO_4

Type of industry

About 12,000 tons/year of ortho phosphoric acid are produced in one large plant.

Type of waste

The process involves treatment of elemental phosphorus with hydrochloric acid. This produces phosphoric acid plus by-products. Wastes originate in purification process and plant wash down steps.

Form of wastes

The wastes are an acidic aqueous solution containing SO_4^{-2} , NO_3^{-2} , PO_4^{-2} , and F.

Total amounts

Process waste concentrations of PO_4^{-2} are in the range of 3000-6000 mg/L while plant wastes are about 3500 mg/L PO_4^{-3} . Process wastes are $850 \text{ m}^3/\text{d}$ out of a total plant wasteflow of $1000 \text{ m}^3/\text{d}$. The wastes are dissolved with some floating and settleable solids. About 3500 kg/day of PO_4^{-3} is found in the waste stream.

Discharge patterns

Discharges are continuous.

14.4.3 Metal processing

Type and size of industries

Phosphatization of metals in plating and metal processing industries is quite common. Specific metal plating industries are described above.

Type of wastes

Metals are washed in baths and ponds containing 20-50 g/litre of NaPO_4 together with 20-50 g/litre of Na_2CO_3 , 10 g/litre of NaOH and 5-20 g/litre of Na_2SiO_2 .

Concentration of phosphate in process wastes including rinsing may reach 200-500 mg/L as P_2O_5 .

Form of wastes

Wastes are alkaline, usually clear with light yellowish color and foam.

Total amounts

Approximately 8 m³ per ton of metal products are discharged from the phosphatization metal treatment.

Discharge patterns

Intermittent rinsing.

14.4.4 Other sources of phosphorus

Phosphorus may also be found in the wastes originating from water cooling processes. Phosphorus is a component of runoff both rural and urban. Indicating concentrations is very difficult because of the variability of runoff flows and variability between areas. However, concentrations may average 1-2 mg/L or less. Municipal sewage also includes some phosphorus usually in the form of phosphate.

Phosphorus concentrations in raw municipal sewage are between 6 mg/L and 18 mg/L (as P). Lime, or alum or ferric chloride treated effluents, contain less than 2 mg/L of phosphorus and with a proper filtration of such effluents concentration of phosphorus can reach below 1 mg/L.

14.5 Treatment

The classical method of phosphorus removal is chemical precipitation. For this purpose, iron and aluminum salts as well as hydrated lime have been widely used. The first two cause precipitation of the corresponding phosphates; by reacting with orthophosphates, lime causes precipitation of hydroxyapatite: $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$. Precipitation of polyphosphates is only partial while that of phosphates, when sufficient amounts of reagent are added, is almost total. In the case of domestic sewage with a total phosphorus concentration of about 10-20 ppm (about 30% ortho-phosphate, 60% polyphosphates and 10% organic phosphorus), the chemical treatment leads to residual phosphorus concentrations of 0.7-1.2 ppm.

Better results can be achieved by performing the chemical treatment downstream of the biological process, because the latter causes polyphosphate hydrolysis to orthophosphates. Therefore residual phosphorus contents below 0.5 ppm may be obtained. Chemical precipitation may be carried out by dosing the reagents in the activated sludge tank. Such a technique allows the use of ferrous sulphate, which is cheaper than ferric and aluminum salts, and which, in an aerated environment, is transformed into the ferric form. The results achieved by simultaneous precipitation are generally worse than those obtained by post-precipitation, due to the solids carry-over into the secondary sedimentation effluent. Residual phosphorus contents ranging from 0.8 to 2 ppm have normally been obtained in full scale plants.

Dosing the precipitation reagents is carried out on the basis of 1.5-2 Al (or Fe)/mole phosphorus. For lime aided precipitation the reagent is dosed to give a pH 10.5-11. In this case, consumption is strictly dependent on sewage alkalinity.

Phosphorus removal may also be achieved by the biological processes that are mainly used to remove biodegradable organic pollutants. A typical example is given by biological plants for domestic sewage.

The phosphorus removal efficiency in the conventional biological treatment is 33-41 %. Such a result has often appeared insufficient to protect semi-enclosed water bodies from the occurrence of eutrophic conditions.

The low efficiency levels of phosphorus removal during the biological process depend exclusively on the fact that the biodegradable organic matter present is low compared with the amount needed by the bacterial population to metabolize the phosphorus contained in the sewage. As a matter of fact, the calculated ratio of BOD_5 to P in domestic sewages is 25, whereas BOD and P removal by metabolic processes occurs at a BOD_5/P ratio = 90. In other words, sewage contains a 260 % excess phosphorus over the amount needed for bacterial growth.

The phosphorus removal efficiency by the biological treatment is certainly also affected by the operating load of the biological treatment plant (sludge Loading). As is known, the conditions allowing the endogenous respiration of bacteria (extended aeration activated sludge Plants) cause a decrease in biomass growth as well as the release to the sewage of nutrients which would otherwise be adsorbed by the sludge.

In the conventional biological plants operated at average sludge loadings, the phosphorus content in the biomass may be evaluated at 2.5 % (as PO_4 with respect to volatile solids). However, several experimental studies have shown the possibility for the biomass to adsorb phosphorus, under defined conditions, in higher concentrations (phosphorus luxury uptake), and achieve removal efficiencies over 90 %. The application of this process at full scale, is at present under examination in many countries.

Tertiary treatment of secondary effluents for phosphorus removal are being practice in certain countries. One of the processes is illustrated in Figure 14.1. The raw wastewaters undergo primary sedimentation, biological oxidation with activated sludge and secondary sedimentation. The re-cycled sludge is fed to a thickener in which there are anaerobic conditions which allow the release of the phosphorus from the sludge. The supernatant is treated with lime to reduce the elevated phosphorus content. The chemical sludge is separated in the primary sedimentation basin. The interest in this kind of process rather than

those chemical treatments previously described is due to the notable saving of reagent, which results.

On the subject of treatment for the removal of inorganic phosphorus, the use of algal suspensions (blue-green algae) with retention times of approximately 15-20 hours can be mentioned. Only a fraction of the phosphorus contained in the sludge is incorporated in the algal cells whilst generally a more significant fraction precipitates as calcium phosphate, if this element is present in the wastewaters. The precipitation is aided by the elevation of the pH following the photosynthesis removal of carbon dioxide.

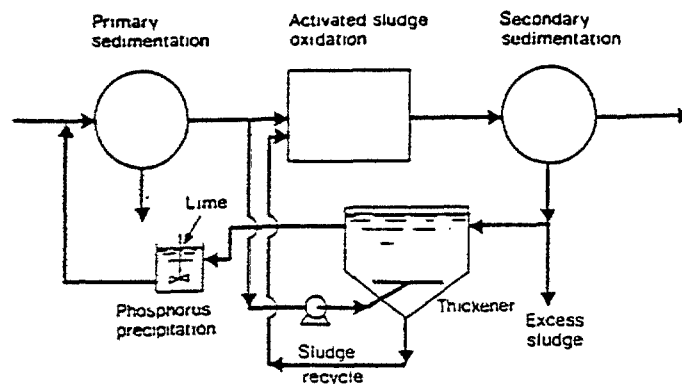


Figure 14.1 Activated sludge plant with chemical precipitation of phosphorus released by the recirculated sludge maintained in anaerobic conditions. (Patterson, 1985)

This technique is interesting for the reduced production of sludge and for the low working costs. The more evident disadvantages are the considerable area required and, in some case, the unfavorable climatic conditions.

A comment should also be made regarding the ion exchange system, based on resins which are selective towards phosphate ion. Experimental results confirm the possibility of obtaining residual concentrations of 0.1-0.2 ppm. However, the method has disadvantages of an economic nature.

15. PATHOGENIC MICROORGANISMS

15.1 Introduction

Pathogens are emitted to receiving bodies of water by municipal sewage discharge, discharge of sludges, discharge of some industrial wastes and in animal wastes. Runoff water, especially from animal husbandry and agricultural areas may also contain animal pathogens.

Due to the difficulty of isolating and identifying specific pathogens in wastewaters by routine monitoring, non-pathogenic indicator organisms are used, notably bacteria of the coliform group.

15.2 Inputs into the Mediterranean

No quantitative estimate has ever been made of inputs of pathogenic microorganisms into the Mediterranean. All municipal sewage effluents, if untreated, constitute inputs of the main intestinal pathogens. It is doubtful as to whether most municipal sewage treatment plants can eliminate viruses.

15.3 Pathogen-bearing wastes

The following are the main sources of pathogens that might affect the marine environment.

15.3.1 Municipal sewage

The municipal sewage might contain many pathogens most notably *Salmonella*, *Shigella*, *Vibrio cholerae*, *Salmonella typhimurium*, bacillary dysentery causing bacteria, amoeba cysts, poliomyelitis viruses, infectious hepatitis viruses, various enteric viruses, ECHO viruses, coxsackie viruses, and Ascaris eggs. Total coliforms and faecal coliforms and less after faecal streptococci serve as indicator organisms to all pathogens, specifically bacterial pathogens, whilst a direct count of plaque forming units (PFU) is used for virus enumeration mostly in research and special surveys.

Type and size of source

Municipal wastewater in most sewered countries amounts to between 80 and 300 litres per inhabitant per day (including contribution by public facilities). Amounts depend on the standard of living, availability of water supply and local customs. This will constitute the average sewage flow when a separate (segregated) sewage system exists but the flow may dramatically increase when combined sewage-flood water collection is practiced.

The amounts of wastewater emitted by a municipality will be dramatically reduced when no central sewage exists i.e. when the community is served by individual septic tanks or night-soil collection.

Form of wastes

Pathogens in wastewater will be in the form of individual bacteria and virus particles or associated with other suspended and settleable matter.

Total amounts

An individual human emits between 5×10^9 to 10^{12} coliform bacteria per day and between 0.5×10^6 and 3×10^6 enteric virus units per day. Various factors have been suggested to relate pathogenic organisms to indicator organisms.

Total concentrations

Concentrations of coliforms in ordinary municipal wastewater usually range between 10^7 and 5×10^8 per 100 mL while concentration of faecal coliforms usually amount to between 10 to 60 percent of the total coliforms.

Enteric virus concentrations vary between 400 to 2000 plaque forming units (PFU) per 100 mL in ordinary municipal wastewater.

Sludges, septic tank pump-out and night soil might contain much higher concentrations of coliforms and viruses according to their solid content and the time lapse until discharge.

15.3.2 Industrial wastewater

Industrial wastes which include pathogens may originate in the following industries: dairy products, fruit processing, food canning, leather industry, feed lots, timber industry and laundries. Bacteria which may be found in the wastes from these industries include *Pseudomonas*, *Chromobacteria*, *Achromobacteria*, *Corynae bacteria*, *Enterobacteria*, *Micrococci*, *Brevibacteria*, *Caulobacteria*, yeast and viruses. In most cases industrial wastes enter the sewage system and are treated there. This may be after some treatment at the industrial site. This treatment is generally for the reduction of BOD, SS, and metal concentrations.

Apart from the industrial waste themselves industries are also producing domestic waste. The amount of which depends on the number of employees and type of facilities.

Although there is very little evidence of effective pathogenicity to humans through the marine environment with such wastes they contain a large concentration of coliform organisms.

Type and size of source

Industrial wastes may be up to 50% of the mean dry weather sewage flows. Individual industries will generate waste flows depending on their size, the season (packing plants) and water reuse considerations.

Form of wastes

The wastes may be carried in solid or liquid media. The liquid medium may be discharged to sewers or receiving wastes. The solid wastes would generally be disposed to the land. The pathogens in the form of living bacteria, viruses or spores, will therefore be found in sewage streams and at land disposal sites. Some industrial wastes from the food, beverage and brewery industries might contain non-pathogenic coliforms and klebsiella microorganisms, which can give a high coliform count on beaches and shellfishing areas which are close to points of discharge of such wastes.

Total amounts

Amounts will be similar to those in section 3.9.2.

Total concentrations

See section 15.3.1.

15.3.3 Runoff, drainage and agricultural wastes

The amount of human pathogens in streams and floodwater reaching the marine environment and which contain, among other things, runoff water, drainage water and agricultural wastes depends on the amount of sewage and other human wastes that find their way into the stream or its watershed as well as the degree of treatment of such wastes and the time elapsed. Agricultural wastes might include *Salmonella*, brucellosis organisms, anthrax organisms and other organisms of animal origin.

Nevertheless, streams and floodwaters that reach the marine environment and which are fed by watersheds with intensive agricultural activity may contain a high concentration of coliform, faecal coliform and faecal streptococci indicator organisms. These organisms will give a high coliform background concentration to the marine environment and in certain cases might surpass the allowable coliform standards at beaches and shellfishing areas close to river mouths and estuaries. In certain cases such "naturally occurring" indicator organisms may mask the presence of human point-source of sewage.

15.4 Treatment

The commonly used processes for removal of biodegradable organic matter also reduce the concentration of pathogens and thus render disinfection of final effluent more effective.

Approximately 50 % removal of coliform bacteria (which is an indicator organism for pathogens) can be accomplished by primary treatment. Conventional biological treatment can reduce coliform bacteria by between 90 to 95 percent (lime treatment can remove coliforms by to 4 orders of magnitude). Treatment by lagooning by oxidation ponds in series with a total residence time of at least 20 day may bring about a reduction of 3 order of magnitude (Table 15.1). Virus removal by conventional treatment is less efficient than bacteria removal. Primary treatment removes only 10 to 30 percent viruses, while full biological treatment can remove between 70 and 95 percent.

Disinfection of wastewater can be effective and economically feasible when performed on well-treated effluent. Although chlorination is the most common treatment method, other methods listed below can also be applied.

15.4.1 Disinfection Methods

Removal of pathogenic microorganisms is most usually accomplished by the use of (1) chemical agents, (2) physical agents, (3) mechanical means, and (4) radiation.

Chemical agents: Chemical agents that have been used as disinfectants include chlorine and its compounds, chlorine dioxide, bromine, iodine, ozone, phenol and phenolic compounds, alcohols, heavy metals and related compounds, soaps and synthetic detergents, quaternary ammonium compounds, hydrogen peroxide, and various alkalies and acids. Of these, the most common disinfectants are the oxidizing ones, and chlorine is the one most universally used. The use of ozone is increasing even though it leaves no residual.

Physical agents: Physical disinfectants that can be used are heat and light. Heat is commonly used in the food industry, but it is not a feasible means of disinfecting large quantities of wastewater because of the high cost.

Sunlight is also a good disinfectant. In particular, ultraviolet radiation can be successfully used to sterilize small quantities of water. However, it is difficult to use ultraviolet radiation in aqueous systems containing particulate matter.

Mechanical Means: Removal of bacteria can be also accomplished by mechanical means during wastewater treatment. Typical removal efficiencies for various treatment operations and processes are reported in Table 15.1.

Radiation: The major types of radiation are electromagnetic, acoustic, and particle. Because of their penetration power, gamma rays have been used to disinfect both water and wastewater.

Table 15.1

Removal or Destruction of Bacteria by Different Treatment Methods
(Metcalf and Eddy, 1979)

Process	Percent removal
Coarse screens	0-5
Fine screens	10-20
Grit chambers	10-25
Plain sedimentation	25-75
Chemical precipitation	40-80
Trickling filters	90-95
Activated sludge	90-98
Chlorination of treated wastewater	98-99

There are mainly four mechanisms that have been proposed to explain the action of disinfectants: (1) damage to the cell wall, (2) alteration of cell permeability, (3) alteration of the colloidal nature of the protoplasm, and (4) inhibition of enzyme activity (Metcalf and Eddy, 1991). Oxidizing agents, such as chlorine, can alter the chemical arrangement of enzymes and deactivate the enzymes. Heat and radiation alter the colloidal nature of the protoplasm.

15.4.2 Disinfection with Chlorine

The most common chlorine compounds used in wastewater treatment plants are chlorine gas, calcium hypochlorite and sodium hypochlorite. Calcium and sodium hypochlorite are most often used in very small treatment plant, such as package plants, where safety and simplicity are far more important than cost.

Ranges of dosages for various types of wastewaters are reported in Table 15.2. A range of dosage values is given because they will vary depending on with the characteristics of the wastewater. It is for this reason that laboratory chlorination studies should be conducted to determine optimum chlorine dosage. In the absence of specific data, the maximum values given in Table 15.2 can be used as a guide in sizing chlorination equipment.

Free chlorine and chlorine derivatives combine rapidly with the ammonia present in the effluent and give rise to the formation of chloramines which, although having a weaker bactericidal effect than hypochlorite ions and hypochlorous acid, are more stable under solar radiation. Breakpoint chlorination is almost impossible in sewage effluents unless they are fully nitrified and all reducing agents and most organic matter have been removed.

The use of gaseous chlorine requires somewhat complex plant and also careful operation with regard to safety. This is due to the characteristics of chlorine which can cause varying degrees of irritation to the skin, mucous membranes and the respiratory system, depending on the concentration and duration of the exposure. Adequate ventilation at floor level should be provided because chlorine gas is heavier than air. Emergency caustic scrubbing systems may also be required to neutralized leaking chlorine. It is for these reasons that gaseous chlorine is generally used in medium and large plants, because of its lower cost; in small plants hypochlorites, which are much easier to handle, are preferred, as is also the case when disinfection is foreseen only as a seasonal treatment or in emergencies.

Chlorination, as traditionally practiced, does not provide virus-free effluent, sometimes as essential requirement, particularly when total reuse of effluent is to be achieved. The possibility of obtaining complete removal of viruses depends on the quality of the effluent undergoing chlorination and therefore of the type of treatment process which has been employed upstream. It is, in fact, important to obtain the complete removal of suspended solids in which the viruses can become enmeshed, thus avoiding the disinfecting action. For this reason the turbidity of the waters to be chlorinated should certainly not exceed 1.0 Nephelometric Turbidity Unit (NTU) and should, preferably be less than 0.2 NTU. This necessity requires the insertion of a tertiary treatment phase upstream of the chlorination with coagulation and filtration.

Due to the poor virucidal properties of the chloramines, it is necessary that chlorination is pushed to break-point, so as to achieve a free chlorine residual. Therefore, in order to reduce the consumption of chlorine, it is important that the concentration of ammonia in the discharge is limited, by means of good nitrification during the biological phase.

As an alternative to these reducing processes, use may also be made of activated carbon, particularly because of the simultaneous action which is achieved in the removal of any undesirable chlororganics; the presence of free chlorine, although reducing it, is not capable of totally negating the adsorption capacity of the carbon for such compounds. This treatment however is considerably more expensive than the use of sulphur dioxide, and therefore cannot be justified if the only desired effect is the removal of residual chlorine.

15.4.3 Disinfection with Chlorine dioxide and ozone

As an alternative to the traditional processes of chlorination of wastewaters, other techniques of disinfection have been developed in recent years. One of them is chlorine dioxide, ClO_2 , it is stronger than chlorine and does not give rise to the formation of chloramines or chlororganics such as chloroform thus avoiding the problems already stated regarding disinfection with chlorine. Chlorine dioxide is only used in aqueous solution, being generated by chlorine-chlorite or by chlorite-hydrochloric acid process in which sodium chlorite is the chlorite source. Sodium chlorite is about ten times as expensive as chlorine, so economical considerations must be taken into account.

Table 15.2

Typical Dosages for Various Chlorination Applications in Wastewater
Collection, Treatment, and Disposal (Metcalf and Eddy, 1979)

Application	Dosage range, mg/L
Collection	
Corrosion control (H ₂ S)	2-9
Odor control	2-9
Slime growth control	1-10
Treatment	
BOD reduction	0.5-2
Digester and Imhoff tank foaming control	2-15
Digester supernatant oxidation	20-140
Filter fly control	0.1-0.5
Filter-ponding control	1-10
Grease removal	2-10
Sludge-bulking control	1-10
Disposal (disinfection)	
Untreated wastewater (prechlorination)	6-25
Primary effluent	5-20
Chemical precipitation effluent	2-6
Trickling-filter plant effluent	3-15
Activated-sludge plant effluent	2-8
Filtered effluent (after activated-sludge treatment)	1-5

Disinfection with ozone, too, until now almost exclusively used for the treatment of water for supply purposes, is receiving renewed attention in the wastewater treatment field. Despite some disadvantages due fundamentally to the selective action which does not permit the oxidation of some substances, for example ethanol, and to the poor flexibility of the treatment as regards variations of load and floe, the use of ozone appears interesting for its high germicidal effectiveness, even against resistant organisms such as viruses and cysts. This disinfection technique is, however, considerably more expensive than those in which chlorine and chlorine derivatives are used.

Because no chemical agent is employed, ultraviolet disinfection is considered the safest alternative disinfection system. However, the use of UV radiation for wastewater disinfection cannot be considered fully-proven.

16. THERMAL POLLUTION

The control of thermal discharges -mainly produced by cooling operations- is often associated with the possibility of heat recovery; its applications, so far predominantly at the experimental stage only, are conditioned by the low intensity of available heat and are directed especially towards agriculture and aquaculture. In the former case, applications concern the direct irrigation of crops (rice, maize, fodder) as well as the conditioning of green-houses and

sometimes of soils, in order to lengthen the growing season. On the basis of the results obtained, the use of hot water for fish culture or crustacean breeding is of particular interest, since the metabolic and growth rates of cold blooded aquatic organisms increase greatly with temperature. There is, however, still the necessity to carry out further research in order to find more ideal temperatures for particular species, especially as regards the consumption of foodstuff and conversion ratios.

Direct cooling of wastewaters may be achieved in storage basins with sprays or with other devices which increase both the exchange surface area and the relative velocity between water and atmosphere. This makes the operation more difficult, particularly because of the possibility of obstruction to the sprays. An alternative system is to operate the basins naturally in the winter months and to put sprays into operation only when heat dispersion must be greater. Compared with natural basins, if sprays are employed, the basin surface may be reduced to 5-10 %.

Another possibility uses wet cooling towers in which heat exchange between water and air is facilitated by the large contact surface, available in the inner packing. In the case of natural draft towers (Figure 16.1), air circulation is produced by the difference in density between the inside of the tower and the outside; two solutions are possible, i.e. with cross-currents or countercurrent, depending on the methods of feeding of the air and water to be cooled. Heat is mainly dispersed by evaporation of a fraction of the flow and, to a lesser extent, by heat convection from water to air. The tower performance is affected by weather conditions: evaporation in fact decreases on decreasing the temperature of air and on increasing its humidity.

Mechanical draft towers (Figure 16.2) operate according to similar principles: air is circulated by means of fans situated above the inlet of the water to be cooled. Hence towers may be more compact and lower in height, which makes their siting easier. A further advantage is greater operating flexibility, the air circulation being adjusted as a function of weather conditions. Compared with natural draft towers, the mechanical types involve lower initial investment costs but higher operating costs, especially due to the high energy-consuming fans.

If towers are used, the possibility exists of close-circuit re-use of the cooling water; in this case, the quantity of evaporated water must be restored and the salt content constantly checked.

Wet tower may give rise to environmental problems, especially due to the formation of persistent plumes, caused by condensation as moist air comes into contact with the external air. A further problem is the conveyance of water drops in the upward stream, which may be reduced, though not completely eliminated, by drop separators. The microclimate may thus be affected and persistent humidity may arise, especially in the case of forced draft towers which are lower.

In theory, such inconveniences may be avoided by using dry cooling towers. In this case, heat dispersion takes place through an exchanger consisting of finned pipes, by conduction through the metal thickness and subsequent convection, without any direct contact conveyance of droplets is eliminated; however, it being impossible to use the latent evaporation heat for cooling, as is the case with wet towers, and higher air flows and larger air temperature increases are required. This system has seldom been applied so far, due to the higher costs involved and to the tower sizing; its adaptation may presently be justified only when availability is severely limited and significant net power generation losses can be accepted.

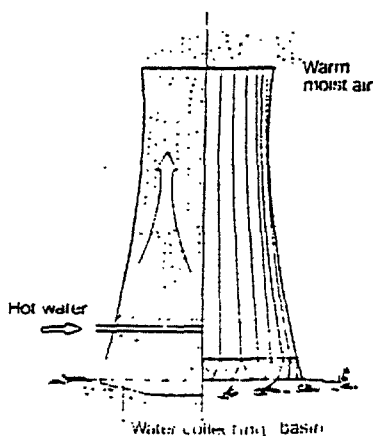


Figure 16.1 Natural draft counter-flow cooling tower.

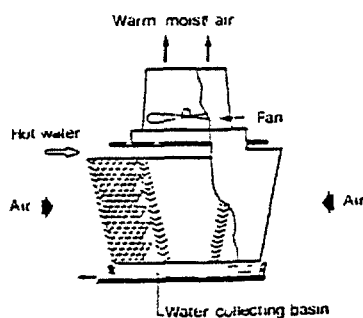


Figure 16.2 Mechanical draft cooling tower.

17. SUBSTANCES WITH A DELETERIOUS EFFECT ON THE TASTE AND SMELL OF PRODUCTS FOR HUMAN CONSUMPTION

Phenols and Aromatic Compounds

17.1 Introduction

Phenolic compounds are prevalent in the wastes of many industries. These are particularly dangerous because they are toxic to marine life, create oxygen demand and also cause taste after chlorination.

Industries giving rise to phenol wastes are coke production, organic chemical production, plastics production, pharmaceutical industry, the gas production industry and, most important, oil refineries.

Phenolic compounds and other aromatic compounds such as toluene and xylene are particularly of concern because they bring about a distinct bad taste and odor to fish, fish products and other marine products. Benzenes, toluenes and xylenes are emitted from many

organic industries such as petrochemical industries, refineries, dye industry, coal gasification etc.

17.2 Sources and inputs into the Mediterranean

No accurate information is available regarding the amounts of phenols discharged into the Mediterranean Sea through domestic or industrial discharges. An earlier survey (UNEP, 1984) estimated a total amount of 12.4×10^3 tonnes per annum, but this was reached by indirect estimation.

17.3 Principal industries

17.3.1 Oil refineries and petrochemical industries

Type and size of industry

The petrochemical industry can be subdivided into a number of production categories. They are crude distillation, cracking, reforming, visbreaking, petrochemical production, lubrication oil manufacturing and coke manufacturing. Plants may also be partly or fully integrated to include a number of these processes. Most integrated plants are large in size with capacity of at least 100,000 tons of products per year..

Type of wastes

Phenolic wastes are discharged from almost all steps of processing. After the crude oil fractionation, wastewaters contain, beside phenols, sulphides, ammonia chlorides and mercaptans. Cracking either chemical, catalytic or hydrocracking give rise to major phenolic wastewater flows. Concentrations of phenols in flows from crude distillation are 50-200 mg/L, cracking 20-100 mg/L, petrochemical 5-50 mg/L and fully-integrated 5-50 mg/L. Associated components of waste streams are BOD (up to 800 mg/L) suspended solids (<300 mg/L), oil and grease (<500 mg/L) and sulphides (<60 mg/L) to mention a few. Benzenes, toluenes and xylenes are products of petroleum and petrochemical production, especially from processes such as cracking, reforming and visbreaking. Their concentrations may vary between 20 and 100 mg/L.

Form of wastes

The wastes are a nucleus of floating and dissolved oils in fractions. The water may be usually black in appearance. It may be warm and contains both dissolved and suspended solids. There will be dissolved chemicals including heavy metals, cyanides, ammonia and phosphate.

Total amounts

Based on 1000 m³ of oil produced the phenol production is 0.04 kg from crude distillation, 4 kg from cracking, 7.7 kg from petrochemical, 8.3 kg from lube oil manufacture and 3.8 kg from integrated systems. Waste flows have been reduced greatly with the introduction of new technology. For example, 100 gal/barrel of waste was produced from crude distillation using older technology. In a new plant this has been reduced to 10 gal/barrel. Similarly for catalytic cracking 85 gal/barrel has been reduced to 10 gal/barrel.

Discharge patterns

The discharge of wastes from all processes is continuous. However, economics of operation show the high benefit of wastewater reuse.

17.3.2 Organic chemicals industries

Type and size of industry

The types of organic chemical industries may be divided into categories: they are, non-aqueous processes (e.g. vinyl chloride), processes with process contact with water as steam (e.g. methanol, acetone), aqueous liquid phase reactions (e.g. acetic acid, iso butylene) and batch or semi-continuous processes (e.g. fatty acids tannic acids).

Type of wastes

Wastes arise from steam condensate, washing down of facilities, preparation of products and regeneration of catalysts. Phenolic concentrations for the categories described under type and size of industry above are: 0-15 mg/L, 0-6000 mg/L and 0-150 mg/L, respectively. Associated waste components are BOD, suspended solids, cyanides, TOC, oil and metals.

Form of wastes

The wastes will be aqueous possibly colored and milky. There will be some floating material and the wastes may be warm.

Total amounts

Total production quantities will be dependent on the particular chemical being produced.

Discharge patterns

As the major phenolic wastes come from the aqueous phase reactions which are continuous the effluent will also be continuous.

17.3.3 Melamine and resin industry

Type and size of industry

Melamine formaldehyde and phenolformaldehyde industries are of medium and large size. Phenolic compounds are emitted from both resin production and melamine covered plywood and furniture board industries.

Production of glues and adhesives for plywood, insulation boards etc. also produce phenol and aromatic solvent wastes.

Resins such as ureaphenolaldehyde and moulding powder production are also associated with emission of phenols and other aromatic substances.

Type of wastes

Process wastes contain up to 100 mg/L phenols associated with carbolic acid, aldehydes, acetone and various ketones. Wastes are usually acidic. Total plant wastes produce 5 to 10 mg/L of phenols.

Form of wastes

Wastes are turbid, and odorous, red-black in color with suspended solids and sludge.

Total amounts

Approximately 100 m³ of wastes are produced per ton of resin of which approximately 5 m³ per ton of product are process wastes rich in phenols.

Discharge patterns

Intermittent discharge of phenol-rich process wastes.

17.3.4 Paint and dye industry

Solvents such as benzenes, toluenes, xylenes and other solvents are emitted from the paint and dye industries. Due to the diversity of such industries, no specific details are given here.

17.3.5 Pharmaceutical industry

Phenols, benzenes and other aromatic substances are emitted from the pharmaceutical industry. Due to the diversity of such industries, no specific details are given here.

17.4 Treatment

Biological treatment can be used to remove these contaminants when the concentrations are not so great as to cause toxic phenomena in bacterial flora. A high degree of biodegradability, up to 200 ppm, has been seen, in particular for phenols, whilst at higher concentrations inhibition occurs. This information however is only indicative since the kind of plant involved, and also the simultaneous presence of other organic compounds, plays a decisive part in the application of biological treatment. Whenever possible, it is advisable to treat these discharges in combination with domestic wastewaters, in conventional installations either of activated sludges or trickling filters. Should industrial discharges be consistently present, it is appropriate to make use of low loaded plants such as oxidation ditches, or lagoons, or else multi-stage plants.

Biological treatability obviously cannot be assumed for all the aromatic compounds, nor for all kinds of phenols, since the characteristics of biodegradability are connected to both the complexity of the molecular structures and to the characteristics of the substances linked to the aromatic rings.

Amongst the methods of greatest interest as regards the removal of non-biodegradable aromatic pollutants is adsorption on activated carbon. The effectiveness of this process is high for polyaromatic compounds and generally for substances which have

a low solubility in water, that is to say for compounds which normally show greater characteristics of bioresistance. In this sense, adsorption is proposed as a complementary treatment to biological degradation. However, phenols show good characteristics of adsorption on activated carbon, to the extent that this technique can be applied directly to those discharges with low concentrations, where conditions would render biological treatment inefficient from the technical point of view.

As regards other treatment techniques, chemical oxidation by means of strong oxidants such as chlorine dioxide and ozone, and wet combustion may be quoted. Chemical oxidation can be used when the concentrations of pollutants to be oxidized are relatively low, such as the circumstances in which adsorption on activated carbons is conveniently applied. Wet combustion has very high specific costs and can therefore only be used for particularly concentrated discharges, or for those with very low volume.

When the concentration of phenolic compounds is high, up to 1000-2000 ppm, recovery processes based on extraction, stripping, and adsorption are often used. However, these processes need to be integrated as a subsequent stage to the treatment dealt with previously.

Extraction methods are based on the use of solvents which can then be recovered by thermal or chemical methods. For example, amongst these is benzene which, after having absorbed the phenolic compounds, can be recovered by steam stripping or -alternatively- by washing with sodium hydroxide. In this latter case, sodium phenolate is formed which in the subsequent treatment with carbon dioxide gives rise to the formation of sodium carbonate and of phenols which can then be recovered. By treating the sodium carbonate with lime, sodium hydroxide can be removed for recycling to the process. The scheme of the benzene sodium hydroxide process is shown in Figure 17.1. The residual phenol concentration in the effluent from the extraction treatment depends considerably on the nature of the phenolic compounds. However, residual concentrations of 100-300 ppm can generally be achieved.

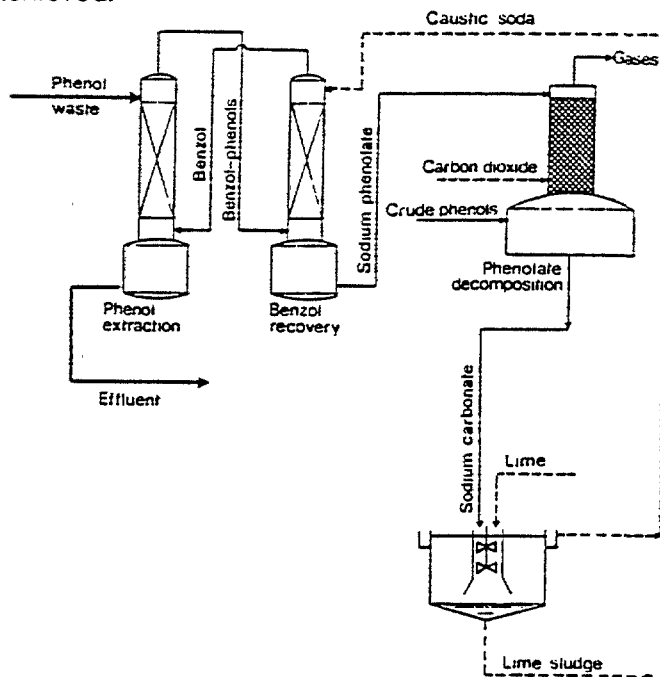


Figure 17.1 Phenol removal process using benzene, with solvent recovery by scrubbing with sodium hydroxide.

Isopropyl-acetate, tricresyl phosphate, butyl alcohol, ethyl ether, and phenosolvan are amongst other solvents which can be used for this kind of process. The last, phenosolvan, can be used in practice in accordance with the scheme shown in Figure 17.2.

The removal of phenols from wastewaters by means of steam stripping allows the recovery of phenols in the pure state, and at the same time does not cause any secondary pollution of the wastewater with the solvent, as happens during extraction processes. The phenols contained in the distillate are recovered during washing with sodium hydroxide. Hot gas (or even hot air) can be used instead of steam, as shown in the design scheme in Figure 17.3.

In Figure 17.4. a recovery plant based on adsorption on activated carbon is shown. The phenols are adsorbed onto columns of granular activated carbon which are successively regenerated with steam and benzene. The separation of recovered phenols from the solvent is carried out in distillation columns.

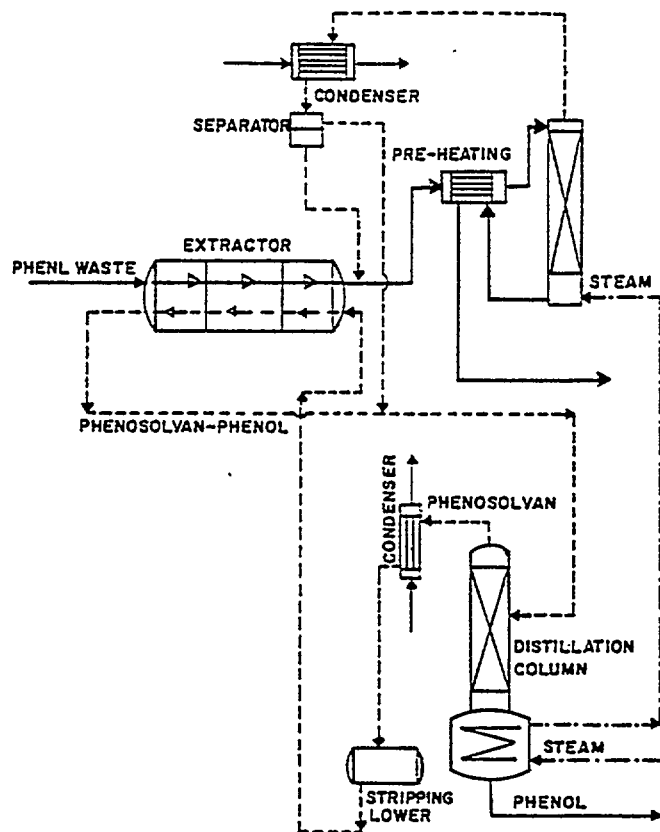


Figure 17.2 Phenol removal using phenosolvan

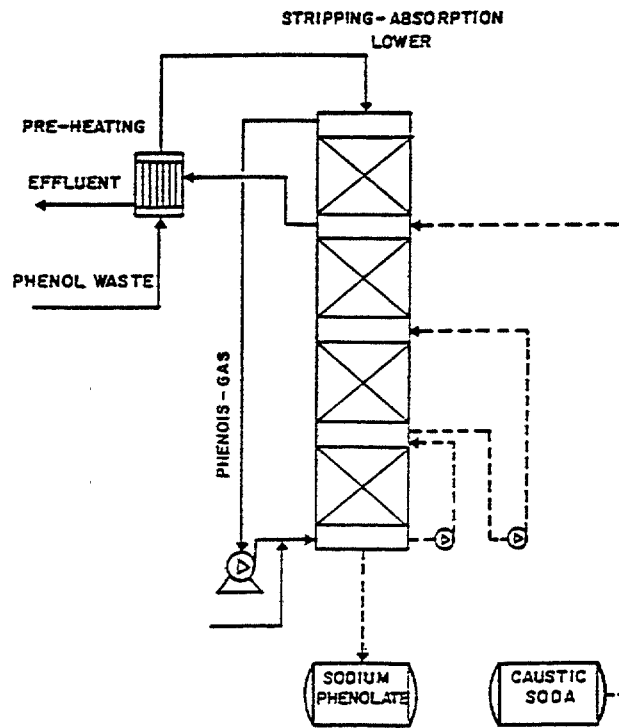


Figure 17.3 Phenol removal process using hot gas with recovery of sodium phenolate by absorption with sodium hydroxide.

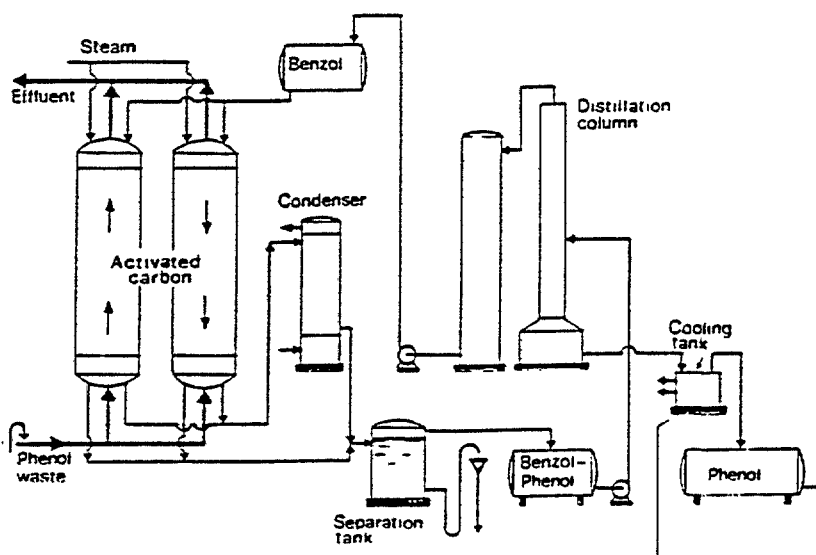


Figure 17.4. Phenol removal by adsorption on activated carbon and recovery with benzene.

18. SUBSTANCES HAVING AN ADVERSE EFFECT ON OXYGEN BALANCE

18.1 Introduction

Discharge of any biodegradable organic wastes into the marine environment will have an effect on the oxygen balance due to exertion of immediate oxygen demand and biochemical oxygen demand (BOD). The main sources of such wastes are municipal wastes and industrial wastes, particularly the food and beverage industries, breweries and distilleries, paper industries, tanneries, refinery and petrochemical industries, sugar refineries, canning industries as well as meat packing and processing and fishmeal production.

The effect of land-based point source of biodegradable organic wastes on the oxygen balance of the wide-open sea will be limited to the immediate surrounding area of the point of discharge. This is because of the enormous dilution rate in the open sea. However, the effect of oxygen depletion will be much more marked in confined areas of the sea such as estuaries, lagoons, marinas, close narrow bays and sea-enclosures. For example, raw municipal sewage with a 5-day BOD of 300 mg/L will have a negligible impact when the total dilution and dispersion in the open sea reaches a factor of 100 (usually attained within the first hour after discharge).

Sulphides, sulphites and other chemical reducing agents, whether from industrial sources or from septic municipal sewage, exert an appreciable immediate oxygen demand that might cause substantial fish kills in the vicinity of discharge, particularly in sea enclosures.

The most important factor that can affect the major oxygen balance in larger areas of the sea, still when a certain degree of enclosure exists preventing free exchange of seawater with the open sea, is eutrophication. Nitrogen constitutes the major limiting factor to algal growth in the marine environment rather than phosphorus and this chapter will discuss some of the major sources of nitrogen that might reach the sea.

18.2 Inputs into the Mediterranean

A survey conducted in 1976/77 (UNEP, 1984) estimated that a total of 800×10^3 tonnes per annum of nitrogen was reaching the Mediterranean Sea from anthropogenic sources, 200×10^3 tonnes from coastal discharges and the rest through rivers. These figures, however, were reached by indirect estimation.

18.3 Principal sources and wastes

18.3.1 Biodegradable organic matter

Raw municipal wastes might exert between 200 to 1000 mg/L BOD, depending on water consumption and the contribution of industrial wastes to the municipal sewerage system. Such wastes might exert an immediate oxygen demand of up to 30 mg per litre per hour, particularly when the sewage is septic and contains sulphides and other reducing agents.

Industrial organic wastes such as those coming from distilleries, meat packing, paper making, tanneries and petrochemical industry might have BOD values measured in thousand and tens of thousands mg/L.

It should be noted that as far as ordinary municipal sewage is concerned, especially following primary treatment bringing BOD levels to between 150 and 300 mg/L, a well engineered deep enough marine outfall with a proper diffuser will usually not significantly affect the oxygen balance in the open sea when the normal current situation exists.

When discharging into estuaries, lagoons or other sea-enclosures, secondary treatment of wastes can bring about BOD values of less than 50 mg/L and immediate oxygen demand of less than 2 mg/L per hour.

18.3.2 Reducing chemicals

Septic sewage might contain a multitude of reducing agents as indicated by oxidation-reduction potential (ORP) of much below -200 millivolt. Sulphides, mercaptans and reduced metals constitute a major part of these reducing agents. Strong septic municipal sewage may exert an immediate oxygen demand of up to 50 mg/L per hour and more which might cause a severe depletion of oxygen in the immediate vicinity of the point of discharge unless the immediate dilution is large enough.

A multitude of industries discharge reducing agents with their wastes, such as sulphides, sulphites, reduced metals, etc.

Usually good aeration system and occasionally chemical oxidation (or mixing the wastes with oxidizing wastes) can eliminate the problem. In a few occasions excess thiosulphate used for dechlorination causes oxygen depletion in the immediate point of discharge. In the design of large municipal sewerage collection systems and outfalls it is advisable to prevent severe septicity by various methods such as aeration, cascaded flow and other methods which also are essential to prevent sulphide-borne corrosion.

18.4 Nitrogen source

Nitrogen is a major limiting factor in the marine environment and a few sources of nitrogen will be briefly discussed herein.

18.4.1 Municipal wastewater

Municipal raw wastewater contain between 40 to 120 mg/L of nitrogen usually in the form of organic nitrogen and ammonia. Ordinary primary and secondary treatments do not remove nitrogen, although good secondary treatment can oxidize the nitrogen into nitrates.

Applying ammonia stripping or nitrification-denitrification techniques can produce effluents with less than 10 mg/L of nitrogen.

18.4.2 Runoff, drainage water and agricultural wastes

Depending on the intensity of agricultural utilization of the watershed, streams and rivers might contain appreciable amounts of nitrogenous compounds that might cause severe eutrophication in enclosed and semi-enclosed marine bodies of water in the areas surrounding the river mouths. Good agricultural waste management can reduce this problem.

18.4.3 Nitrogenous compounds from industrial wastes

Nitrogen compounds are ubiquitous in nature and industrial processes. They may be of the following forms: nitrate, nitrite, ammonia and organic nitrogen. Most commonly they will be found in the effluents from nitrogenous fertilizer plants, urban wastewater, water treatment plants, nitric acid plants, tannery wastes and textile wastes.

The nitrogen compounds, being so common in nature, may be easily utilized in the environment. The results of these may be the degradation of the environment through the process eutrophication by affecting the oxygen balance of the receiving body of water.

Ammonia will be toxic if discharged at concentrations higher than 10 mg/L. The fertilizer effects of nitrogen compounds can cause problems in both inland waters and the sea.

18.5 Principal industries

18.5.1 Fertilizer industry

Type of industry

The production of fertilizer may involve the production of the following chemicals: ammonia, urea, ammonium nitrate, nitric acid and ammonium sulphate.

Type of wastes

The wastes are aqueous solutions produced from potassium nitrate processes. The potassium nitrate is produced from potassium chloride and nitric acid. These are nitrate wastes. Ammonia wastes arise from the production of ammonia and ammonium salts.

Form of wastes

The wastes are usually soluble ions in aqueous solutions. There may be smells arising from ammonia wastes.

Total amounts

The potassium nitrate plant produces 10 m³ of wastes per ton fertilizer with 1.5 m³ per ton from the potassium nitrate process. The process wastes are 4000 mg/L NO₃⁻ while the plant wastes are 20,000-40,000 mg/L. From the ammonia fertilizer plant, about 5000 m³/day of waste are produced. The ammonia process wastes are about 400 mg/L NH₄⁺.

Discharge patterns

Discharges of nitrate wastes are continuous while the ammonia wastes are intermittent.

18.5.2 Tannery wastes

Type and size of industry

See Section 8.4.4.1, Type and size of industry.

Type of wastes

See Section 8.4.4.1, Type of wastes.

Form of wastes

The wastes contain various forms of ammoniacal nitrogen including $(\text{NH}_4)_2\text{SO}_4$, NH_4OH etc. They will be associated with oils, fat, hair etc. The ammonia is soluble, without color.

Amounts

The nitrogen will be about 400 mg/L as N in about 1000 m³/day of waste. This is about 400 kg/day of NH_3 as N.

Discharge patterns

The discharge are intermittent.

18.5.3 Oil refinery

Type and size of industry

Integrated plants producing heavy oils as well as petroleum products and LPG. The annual production can vary between 100,000 and 10 million tons per year.

Type of wastes

The wastes originate in the thermal fractionation of the oil as well as in cooling water and drainage water (washing down).

Form of wastes

The nitrogen is in the form of ammonia (dissolved) and is associated with many other pollutants such as oils, scum, phenols, chlorides and sulphates. The waste also smells, is opaque (turbid) and warm.

Amounts

Total plant waste flows are about 10-20 m³ per ton of oil processed. Ammonia concentrations are about 300 mg/L.

Discharge patterns

Discharges are intermittent depending on plant operation and water recycle requirements.

18.5.4 Textiles

Type and size of industry

The textiles industry may be divided into two subsections, raw fibre treatment, and processed fibre finishing. The former may involve wool scouring, wool finishing and dry processing while the latter involves woven fabric production and finishing, as well as dyeing

and carpet production. Plant size may vary between shop size and large industrial complexes.

Type of wastes

The wastes originate in all the process steps particularly in the raw fibre processing. Urea is used in some processing which gives rise to organic ammonia.

Form of wastes

The wastes are dirty, containing floating oil, scum, and chlorides. They may be turbid and smell. They may be colored with dissolved pollutants. Generally the wastes are characterized by BOD, suspended solids and grease.

Total amounts

The BOD from raw fibre processing may reach 8000 mg/L while in other processes the range is up to 2000 mg/L. The suspended solids may be up to 10,000 mg/L for the former and up to 800 mg/L for the other processes. Organic nitrogen is of the order of 15-20 mg/L. Overall flows of 20,000 m³/day are found nationwide. Hence approximately 200-500 kg/day of nitrogen are produced.

Discharge patterns

Discharges will be batch for small operations but for large industrial complexes they may well be continuous.

18.5.5 Electronic printed circuit industry

Type and size of industry

Type and size of industry is specified in the metal plating sections above (copper).

Type of wastes

Metal plating circuits especially when copper is used involved the use of NH₄OH, (NH₄)₂SO₄ and Cu(NH₄)₄(SO₄)₃. Plating baths wastes may contain 160-200 g/L ammonia while total plant wastes 200-400 mg/L.

Form of wastes

Slightly turbid bluish alkaline wastes with ammonia odor.

Total amounts

Total plant wastes are 15 m³ per square meter of printed circuits while ammonia containing bath and rinsing wastes are 1-2 m³ per m² of circuits.

Discharge patterns

Batches of concentrated bath wastes and semi-continuous rinse water.

18.6 Treatment

The risk of deoxygenation of the receiving water is generally connected with the discharge of biodegradable organic matter and with the consequent action of bacterial self-purification. Inorganic pollutants in the reduced form which, in a natural environment, can undergo reoxidation (e.g. sulphides, sulphites, reduced metals) are of minor importance. Purification of biodegradable organic effluents is almost always achieved by biological treatment (mostly aerobic and sometimes anaerobic). Only under exceptional circumstances is the biodegradable organic matter removed by physicochemical (flocculation and adsorption) or simply chemical (oxidation) processes. Deoxygenation can be also indirectly produced by the enrichment of the aquatic life due to nutrient discharge. Phosphorus removal has already been discussed in Paragraph 14.5. The main nitrogen control techniques are described in this section.

18.6.1 Activated Sludge Process

The activated sludge process presently constitutes the most widely used form of aerobic biological treatment; it is based on the aeration of effluent in contact with an established bacterial population which, due to bioflocculation phenomena, tends to form flocs which are readily separable by sedimentation. The biodegradable organic matter in the effluent constitutes the substratum that bacteria use as an energy and material source for the production of new cells. It is thus separated from the effluent and biochemically transformed partly into living organic matter, or at any rate adsorbed onto the flock, and partly into stable final products.

Activated sludge processes are governed by the ratio between the biodegradable organic substrate introduced in the influent and the bacterial mass present in the system (food-to-microorganism ratio) and also by the mean cell residence time which relates the quantity of solids lost in the effluent and excess solids withdrawn in the waste sludge. Such parameters condition the system efficiency, the process oxygen demand and the production of new cellular mass that, under steady-state conditions, must be removed, since it constitutes surplus sludge. Figure 18.1 shows the effect of organic loading on substrate removal efficiency.

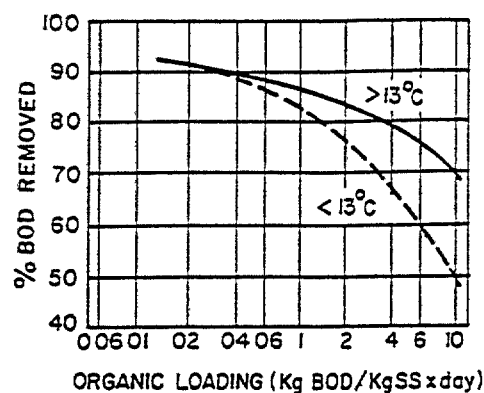


Figure 18.1 BOD removal efficiency versus organic loading for activated sludge treatment of municipal wastewater.

Usually conventional activated sludge process is designed with a mean cell residence time between 3 to 15 days, which with typical domestic sewage gives a reactor space time (reactor volume/discharge to the reactor) between 4 and 8 hours if the mixed liquor suspended solids concentration is around 2000 mg/L. The recycle is generally between 10 and 30 % of the influent flow and sludge wastage is from either the settler underflow or the aeration basin. At high recycle ratios, although still in the range which allows a satisfactorily efficient removal of organic pollutant, surplus sludge exhibits a marked putrescibility. Subsequent stabilization processes are therefore required, which are almost always carried out by biological means. Instead, by decreasing the surplus sludge, production may also be decreased and sufficient stabilization may then be guaranteed within the process itself.

Process Modifications: Extended Aeration Activated Sludge

This above mentioned technique, known as extended aeration, is a practice applied only to small plants: it is evident that with low loadings and consequent long detention times, large volumes are required for the aeration tanks. A small quantity of sludge periodically wasted to maintain the mean cell residence time between 20 and 30 days, and thereby excess solids discharges in the effluent is prevented. On the other hand, the process is very simple as regards plant and operational requirements and therefore is preferable whenever complex management would present problems.

The waste sludge from the process is usually well oxidized and can be disposed of directly without further biochemical treatment. Most extended aeration activated sludge systems employ completely mixed reactors but the recycle ratios are higher (0.75-1.5) because of the higher MLSS concentrations. Many package plants employ this concept and thus it finds considerable use as the wastewater treatment in small communities.

Due to high sludge age values which are maintained in the system, an extended aeration process is also capable of accomplishing complete nitrification (except perhaps when working under very severe weather conditions), thus allowing the nitrogenous oxygen demand to be satisfied without necessarily having to provide a 2-stage oxidation treatment. This latter is shown in Figure 18.2. The first stage is made up of a high rate activated sludge process, during which little nitrification occurs, due to the short solids retention time, but where a large part of the normal BOD is removed. The wastewater then enters the nitrification unit operated with a high sludge age value, compatible with the correct development of the nitrifying bacteria.

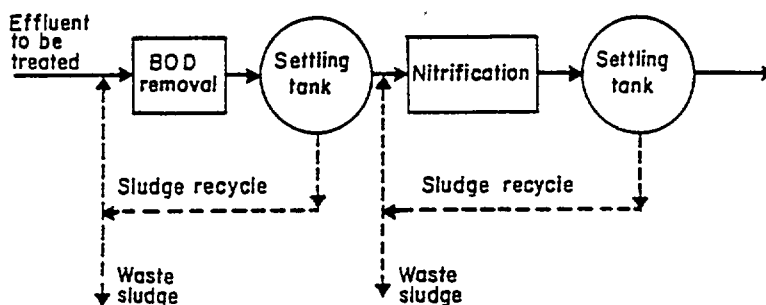


Figure 18.2 Activated sludge treatment plant, with separate nitrification stage.

Tapered Aeration

Another process modification for activated sludge process is tapered aeration. It is evident that the flow pattern of the tapered aeration modification is identical to the conventional process. The actual difference between the two processes is found in the diffuser arrangement. In tapered aeration the diffusers are spaced so that more air is supplied at the head of the tank, where the oxygen demand is greatest, and is then decreased along the tank length as the demand decreases. Such an arrangement is more economical than supplying a constant amount of air along the entire tank (Benfield and Randall, 1980).

Step-Aeration Activated Sludge Process

Figure 18.3 illustrates the flow pattern for a typical step-aeration process. In this modification, return sludge is mixed with a portion of the wastewater and enters the head of the aeration tank. Wastewater is also fed into the tank at different points along its length. Advantages of this process modification are (1) better equalization of waste load, (2) lower peak oxygen demand, (3) better distribution of oxygen demand over tank length, and (4) smaller overall aeration tank volume. This process also provides an additional degree of operational control when one or more stages are used to add or remove sludge with variations in the wastewater (Benfield and Randall, 1980).

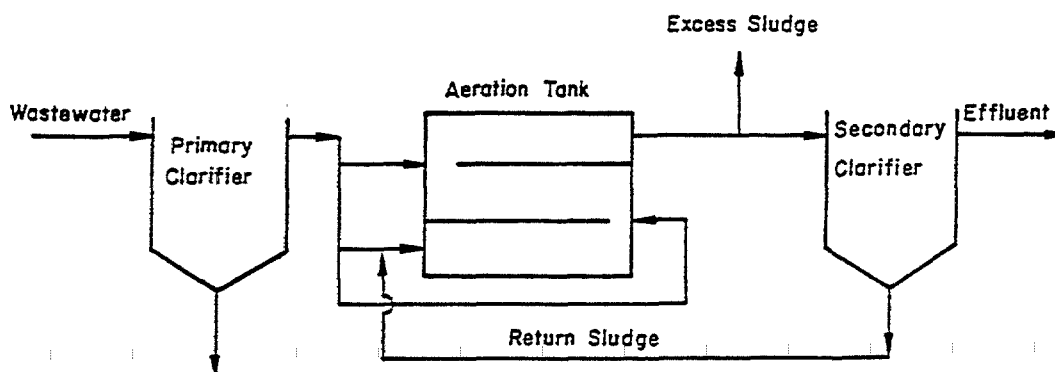


Figure 18.3 Step aeration activated sludge process

Contact Stabilization Activated Sludge Process

The contact-stabilization process was developed to take the advantage of the absorptive properties of activated sludge. The flowsheet is shown in Figure 18.4. In some cases, primary settling is eliminated. It has postulated that BOD removal occurs in two stages in the activated sludge process. The first is the absorptive phase, which requires 20 to 40 minutes. During this phase most of the colloidal, finely suspended, and dissolved organics are absorbed in the activated sludge. The second phase, oxidation, then occurs, and the absorbed organics are assimilated metabolically. In this process modification, the two phases are separated and occur in different tanks. The biomass is then separated from the wastewater in a secondary clarifier and the biological sludge channelled to the second aeration tank, where the organic material adsorbed to the biomass surface is metabolized or "stabilized".

The very brief retention time of the main wastewater stream in the contact tank offers considerable saving in the total tank volume, because the further detention of the settled sludge for stabilization occupies much less volume than would be the case if the entire waste stream was contained in this tank.

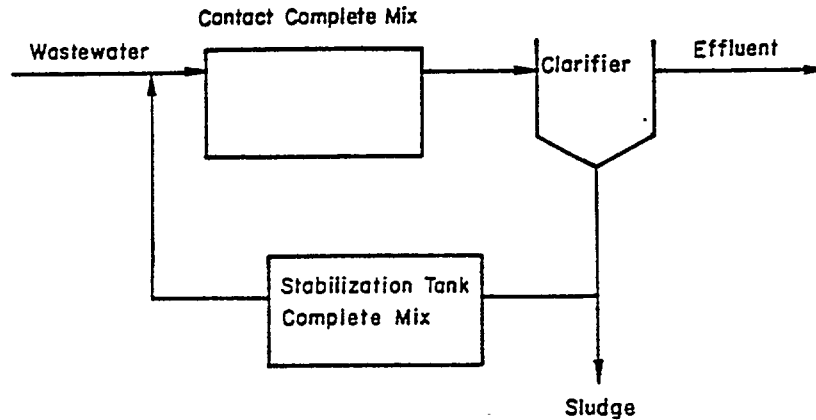


Figure 18.4 Contact stabilization activated sludge process

Activated sludge processes are carried out in basins where aerobic conditions are constantly maintained by artificial aeration provided either by surface mechanical aerators or by the direct diffusion of air into the liquid mass. Despite the fact that the removal of BOD generally follows a first order kinetic reaction, completely mixed reactors are generally to be preferred to those of the plug flow type. Apart from greater plant simplicity, completely mixed systems are, in fact, able to ensure a major dilution of the incoming wastewater into the entire basin volume; this allows less variation in organic loading and reduced shock effects, whether organic or toxic in nature. These advantages are particularly important as regards industrial or combined wastewater treatment, where variations in influent conditions can often occur.

As regards wastes with a high BOD concentration, the activated sludge process can be implemented more conveniently in 2 or more successive stages, each having a sedimentation phase; in this way concentrations of substrate and bacterial population are different from stage to stage, and thus removal rate - which for first order kinetics is in proportion to the concentrations themselves - is on average higher than for a single-stage reactor.

Recently there has been a renewed interest in the use of pure oxygen, rather than air, in activated sludge systems and a relatively high number of plants of this kind have been built in recent years. A schematic diagram of the most commonly used pure oxygen activated sludge process is shown in Figure 18.5. It comprises a series of completely mixed reactors, covered so as to allow recirculation of the oxygen. Due to the higher partial pressure of oxygen above the liquid, there is the advantage of an increase in the oxygen concentration gradient between the gas and the liquid phase.

It is then possible to maintain higher cell concentrations (generally above 5000 mg/L) and consequently a better substrate removal rate and thus shorter hydraulic residence times, with reduced aeration capacity, can be achieved. Considerable improvements are also reported as regards sludge settleability and lower surplus sludge production.

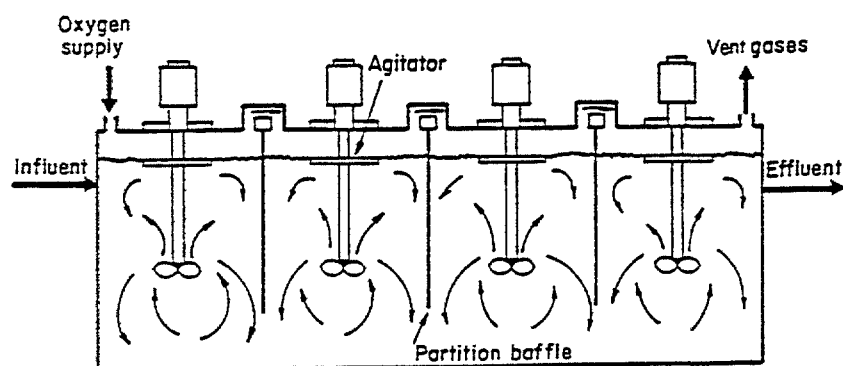


Figure 18.5 Schematic diagram of pure oxygen activated sludge reactor

Pure oxygen activated sludge reactors commonly are covered tanks, usually of concrete, that are built with common-wall construction. Although submerged turbines were first used as the oxygen transfer devices, subsequent designs have used mechanical surface aerators as well. Because high oxygen transfer rates are possible, pure oxygen activated sludge systems use mixed liquor suspended solids concentrations in the range of 400-8000 mg/L, with mean cell residence times in the range of 3-15 days. This results in reactor space times on the order of 2 hours for many wastes. The sludges compact well. However; so that even with the high mixed liquor suspended solids concentration recycle flows are still between 25 and 50 % of the influent flow.

18.6.2 Lagooning

This form of biological treatment also employs bacterial suspensions; however it is far more extensive than the activated sludge process. In its simplest form, it does not require an artificial oxygen supply, obtaining it by atmospheric molecular diffusion and more especially by the photosynthetic action of the algae, which develop in the lagoon upper layers. In very shallow aerobic ponds, the presence of oxygen is guaranteed at all levels; in facultative ponds, which are most frequently used, it is limited to the upper layers; on the bottom and in particular in the settled matter level, transformations occur under anaerobic conditions. In this treatment, no cell recirculation is practiced; therefore it is impossible to artificially control the bacterial concentration at the same levels established by the kinetics of biological reactions. Therefore, in comparison with intensive processes, the volumetric loads that may be applied to lagooning are considerably lower; consequently large surface areas are needed. This is the main drawback of the system, which does however offer two advantages: a great simplicity and complete energy saving, made possible because no aeration is needed.

Aerated lagoons, in which aerobic conditions are maintained by surface aerators, are in more frequent use due principally to the fact that they require much less space; wastewater is treated on a flow-through basis, generally without any recirculation of cellular matter. When aerobic conditions are homogeneous throughout the whole system, which then operates as a completely mixed reactor, it is impossible to achieve any solids sedimentation. The essential function of this type of lagoon is waste conversion; in general the influent may contain more than one-third of the value of the incoming BOD in the form of cell tissue and

it is therefore necessary to include a final phase of sedimentation in order to limit the suspended solids contained in the effluent.

Frequent use is also made of aerated lagoons which are maintained in a state of incomplete mixing so as to allow a large portion of both the incoming solids and the biological solids produced from waste conversion to settle onto the bottom; there, they undergo anaerobic decomposition, being deprived of oxygen in this zone. This form of aerated lagoon allows a considerable saving of energy (Figure 18.6).

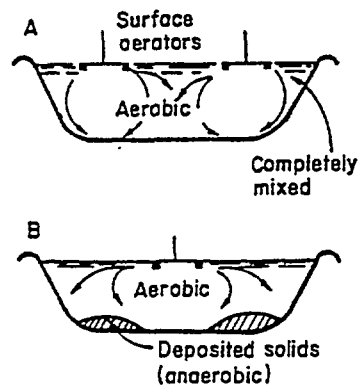


Figure 18.6 Two types of aerated lagoons: completely mixed (above) and with anaerobic decomposition of deposited solids (below)

18.6.3 Trickling Filter

This form of biological treatment consists of a bed of highly permeable media to which microorganisms are attached, and through which wastewater is percolated or trickled—hence the name. In its traditional form, with stones or similar material as filter media, it is less and less used in comparison with the activated sludge process due to considerably higher space requirements. Larger problems also exist over the possible presence of odors and insects and there are some disadvantages also concerning operational elasticity. The recent introduction of plastic media with higher surface areas per unit volume and higher voidage ratios, which allows high resistance to clogging, has aroused renewed interest in this kind of treatment, especially in the case of strong industrial wastes in which the trickling filter can act as a primary high load biological phase, with relatively low efficiency, upstream from the main activated sludge process; the graphs in Figure 18.7 in fact give an example of those results obtainable for some industrial wastewaters.

Trickling filters may be either low-loaded or high-rated depending upon the hydraulic load and on the organic load applied. High-rate filters, in comparison with the low-rate ones, operate with much higher loading and the fairly considerable liquid stream will remove all relieving films, by continuously conveying them outside the trickling filter. Consequently, the amount of material that is found as a sludge in the final sedimentation tank is higher than that of low-loaded filters which in turn results in the larger sized digester. The higher load brought on the high-rate filter (even more than 10 times as that of a low-rate one) allows one to remove a higher amount of BOD per filter unit volume. However, the effluent still exhibits a

high organic matter content. In order to increase the efficiency of BOD removal, an effluent recirculation is carried out, by causing the sewage to pass through the filter several times.

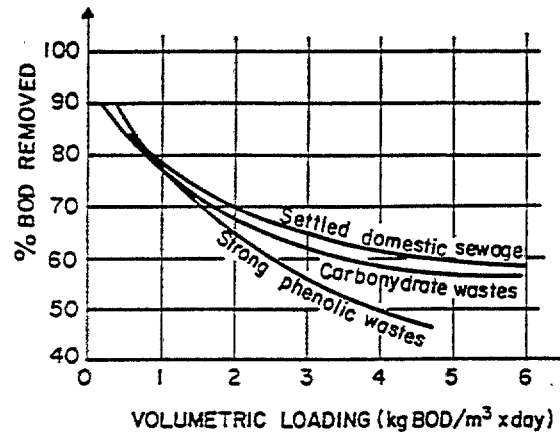


Figure 18.7 Performance of Plastic Media Trickling Filters, in Treating Different Types of Wastes

In the domestic field, again referring to plants of moderate dimensions, other techniques using biological films attached to supports have recently been developed with the introduction of rotating discs that, although having positive aspects mentioned above as regards trickling filters, also have limited space and head losses which are comparable with those of activated sludge systems.

18.6.4 Anaerobic Process

Unlike aerobic operations, which contain diverse microbial communities and complex food chains, anaerobic operations contain communities which are essentially totally bacterial. In spite of this apparent simplicity, interactions among the bacterial species have a severe effect upon system performance. Early attempts to design and control anaerobic operations were hampered by our ignorance of these interactions, which caused the operations to acquire a reputation for being unreliable and difficult to control. As a better understanding of the ecosystem was obtained it was recognized that the poor reputation was unwarranted, leading to a resurgence of interest in anaerobic operations.

The convenience of applying an anaerobic treatment for the partial removal of organic pollutants is connected with possible energy savings, since it avoids the adaptation of aeration devices; energy-saving may be very significant in the case of effluents with strong organic pollution (a BOD of at least several grams per litre). To obtain a high rate of removal the process can be carried out following a technique (anaerobic contact process) which is substantially similar to the activated sludge process. It includes a totally mixed anaerobic reactor, followed by a phase of separation and recovery of the suspended anaerobic colonies which are recycled to maintain the necessary bacterial concentration. To obtain higher removal rates, the effluent is heated to the range of mesophilic digestion using methane produced by the anaerobic transformations. The treatment does not achieve the common effluent discharge standards and therefore the process can only be included as a primary phase before a successive aerobic phase.

However, in a recent study, Rintala (1991) indicated that high-rate anaerobic treatment can be applied to different types of industrial wastewaters under varying conditions. The results obtained from a laboratory-scale upflow anaerobic sludge blanket reactor have shown that high-rate anaerobic treatment can be applied to different types of industrial wastewaters under varying conditions.

18.6.5 Chemical-Physical Treatment

The use of chemical-physical treatment (Figure 18.8) for the removal of organic pollutants from wastewaters, by means of flocculation followed by adsorption on activated carbon, is generally only applicable under particular conditions in connection with those pollutants which are only poorly biodegradable, or with regard to intermittent effluents which do not allow proper functioning of biological processes. Even in the case of municipal wastewater, they could nonetheless add considerable advantage when compared with simple biological techniques, particularly due to the regularity with which they can be operated (which is insensitive to the ever-possible presence of toxic agents), the greater flexibility and, in many cases, the greater treatment efficiency, particularly for the removal of a long list of organic compounds which are not biodegradable and which therefore can be found, unaltered, in biologically treated effluents (ABS, pesticides, phenols, pyridine, acridine, various hydrocarbons, etc.).

The chemical-physical processes, if complete with adsorption phases, do not compete economically with the biological ones, for which reason their practical application in municipal plants is limited to the first stage of flocculation, which only allows the removal of the suspended component, with a limited influence as regards dissolved solids. However, for some industrial discharges, activated carbon is widely used for the removal of those organic components which cannot be eliminated by other means.

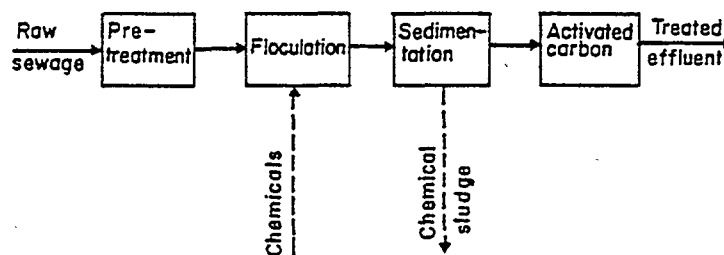
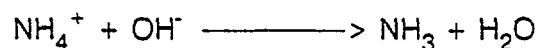


Figure 18.8 Physico-chemical treatment plant for municipal wastewater

18.6.6 Nitrogen Removal

When present as ammonia, nitrogen can be removed by chemical/physical methods. Stripping can be achieved using steam when the ammonia is present in considerable concentrations, in the region of some g/L, in view of its recovery as ammonium sulphate. More frequently stripping with air is adopted, which however requires alkaline conditions in order to transform the ammoniacal ions into free ammonia, as in the reaction:



The equilibrium is completely towards the right for pH values over 11; it is necessary to operate under these conditions to obtain high level removals with residual ammonia concentrations of the order of 5-10 mg/L. The limitations in the application of this process are essentially derived from the serious problems of scaling met with lime is used as an alkalizing agent, and from the transfer of the pollution into the gas phase. This could however be avoided by means of acid absorption and eventual recovery, but this is little used nowadays for economical reasons.

A possible alternative is the use of chlorination processes taken up to breakpoint or limited to the formation of chloramine which can possibly later be removed by means of activated carbon. The field of application of this method is limited to wastes having low concentrations of ammonia, because of the high operations costs involved with the consumption of large amounts of chlorine which almost always necessitates further dechlorination treatment, with a reducing agent. A final limitation in applying this process is the presence of organic substances or compounds which constitute an additional chlorine-demand.

The recovery of the ammonia present in industrial wastes can be achieved by ion exchange. A recovery process is available in which the ammonia from the regeneration eluate is treated with sulphuric acid followed by evaporation and crystallization of ammonium sulphate.

The predominant tendency nowadays is the removal of ammonia, as with other forms of nitrogen, is the use of biological processes with the formation of gaseous nitrogen as the final product. As regards domestic wastewater or, at any rate, discharges in which there is an internal source of carbon, the process scheme is as shown in Figure 18.9. The biological oxidation stage is carried out according to extended aeration techniques, so as to obtain nitrification of organic nitrogen and ammonia. The effluent so oxidized is partly recycled to primary anoxic biological phase in which the action of facultative denitrifying bacteria contained in the recycled biomass determine the reduction of nitrates to molecular nitrogen. The removal efficiency is related to the rate of recycle (mixed liquor plus sludge return). The second anoxic stage can be included for the complete biological removal of the nitrogen to residuals below 1 ppm. The source of carbon in this phase is almost completely made up of endogenous carbon. In plant only having predenitrification stage nitrogen removals of 80-90% can be achieved with an overall recycle rate of 500-600 %.

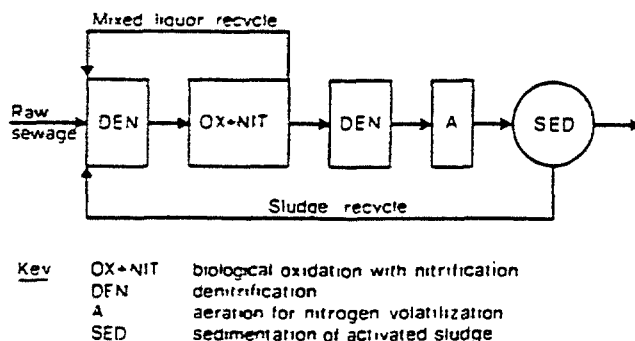


Figure 18.9 Process scheme for the removal of ammonia using biological process with the formation of gaseous nitrogen

In all those cases in which it is necessary to achieve high removal efficiencies it is essential to verify that the availability of BOD in the effluent is sufficient to meet the demand. In the case of domestic sewage a ratio of available BOD_5/N of 3,5-4 is necessary; thus it follows that in order to produce high denitrification efficiencies it is essential to avoid primary sedimentation. The final stage, shown in Figure 18.9 consists solely in the stripping of the nitrogen formed, by means of mechanical agitation or air diffusion.

In the denitrification of those industrial wastes lacking in BOD, the process can only be maintained by supplying supplementary organic carbon. Use is often made of methanol to this end.

For industrial wastes polluted by nitrates, biological denitrification processes with anaerobic submerged beds may be utilized. This process allows high concentrations of bacteria to be maintained, and thus high volumetric loadings, without the necessity of recirculating the biomass which is attached to the media. However there are limitations which relate to the risk of clogging, due partly to possible suspended matter in the wastewater, but particularly because of the bacterial growth in the bed.

Finally, among the other possible removal processes, ion exchange on selective resins may be cited. For economical reasons interest in this method is limited to discharges with relatively low concentrations of pollutants.

19. TREATMENT AND DISPOSAL OF WASTEWATER SLUDGES

19.1 Introduction

Almost all the forms of treatment described produce sludges for which adequate treatment and disposal must be provided in order to remove any risks of contamination of the environment.

It is useful to make a general distinction between organic sludges and sludges which are prevalently made up of inorganic compounds, the so-called chemical sludges.

19.2 Organic Sludges

Essentially these come from biological treatment plants and from primary sedimentation of organically polluted wastewater.

The principal problem as regards these sludges is stabilization, in order to prevent phenomena of unchecked biodegradation in the ultimate disposal phases. Except in exceptional cases, plants generally provide stabilization by means of biological digestion.

The operations and processes used in solids handling in biological wastewater treatment plants may be classified as thickening, stabilization, conditioning, dewatering, incineration, and disposal. Primary sludges and secondary sludges, such as excess activated sludge and trickling filter humus, are frequently mixed by adding the secondary sludge to the incoming raw wastewater and resettling it in the primary clarifiers. This thickens, to a certain degree, the primary sludge and, in the case of excess activated sludge, the secondary sludge (Reynolds, 1982). Typical solids handling systems for primary and secondary sludge mixtures mixed in this manner are (1) anaerobic digestion, sand-bed dewatering, and landfill disposal of the solids; (2) anaerobic digestion, chemical conditioning,

vacuum filtration or centrifugation, and landfill disposal of the solids; (3) gravity thickening, chemical conditioning, vacuum filtration, flash drying, and land disposal of the solids as a fertilizer (Reynolds, 1982). Figure 19.1 shows the components of the most widely used treatment processes.

19.2.1 Thickening

Thickening consists of increasing the solids content of a sludge which, as a result, reduces the volume of sludge to be processed by subsequent units. Gravity thickening which is the most common type of thickening method and can be used when the specific gravity of the solids is greater than one. The other type, flotation thickeners which are able to handle higher solids loadings are utilized when the specific gravity of activated sludge is near unity.

19.2.2 Conditioning

Conditioning consists of treating a sludge prior to dewatering and sometimes thickening to enhance its dewatering characteristics. Conditioning may be achieved either by the use of certain chemicals or by the heat treatment. In chemical treatment, both organic and inorganic coagulants have been used for conditioning. Heat treatment has, in particular, been used to condition waste activated sludges (Reynolds, 1982). Heat treatment involves heating the sludge under pressure to break down the cells. The thermally treated sludge is sterilized, deodorized, and it can be filtered without chemicals.

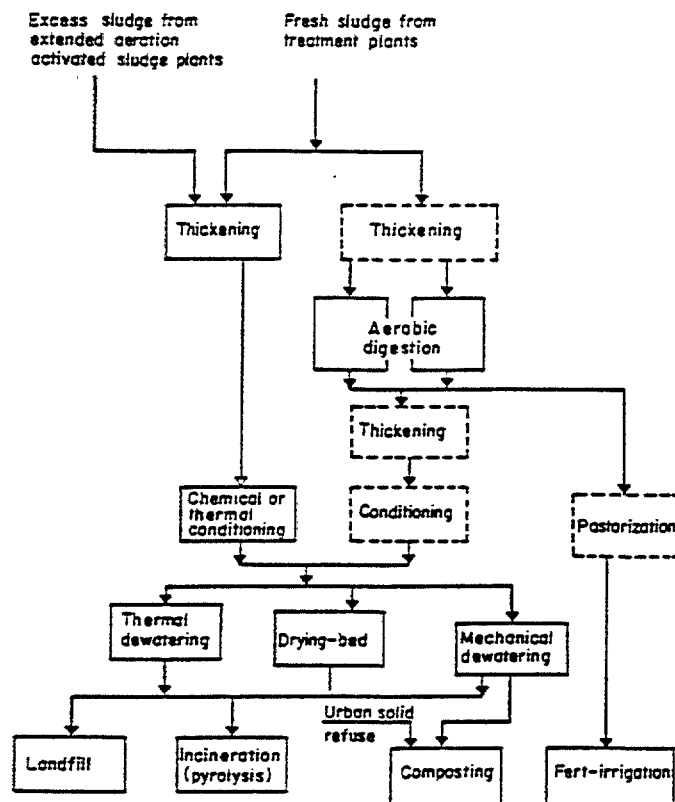


Figure 19.1 Components of the most widely used processes for the treatment and disposal of wastewater sludges.

19.2.3 Dewatering

Dewatering consists of removing water from sludges to a level where they can be handled as damp solids rather than as liquids. As a semi-liquid, the sludge has a more suitable form for landfill, spreading, incineration, heat drying, or transportation. The most common methods applied for dewatering are those using band and pressure strainers, centrifugation and vacuum filtration. The solids content of the wet cake from these processes generally ranges from 15 to 40 % depending upon the nature of the sludge and the operating conditions. Another method of dewatering which is employed for small wastewater treatment plants is air drying on open or covered beds of sand. The dried sludge reaches a solids content of 20 to 50 % after a period of 1 week to 2 months.

19.2.4 Stabilization

Stabilization consists of treating the sludge so that future decomposition by biological action does not occur. It results in a sludge that will not undergo bacterial decomposition, has good dewatering characteristics, and has very little odor. Anaerobic and aerobic digestion stabilize sludge biologically by partially degrading it into liquid, dissolved solids and gases. In addition, digestion reduces the volume of sludge solids and the number of pathogens. One advantage that aerobic digestion has over anaerobic digestion is that less technical skill is required in operation since the process avoids many of the operational problems of anaerobic digestion. The advantage of anaerobic digestion is the production of methane gas which is a useable by-product.

Anaerobic sludge digestion is used in medium-high capacity plants; that is to say for more than 40000-60000 inhabitants served, in the case of treatment of domestic wastewater. For small capacity plants, aerobic sludge digestion is generally adopted due to the greater simplicity of operation, even if unit operating costs are considerably greater. However, various cases are known in which aerobic stabilization of sludges is carried out in plants with a capacity of more than 50000 equivalent inhabitants. As is known, stabilization can be carried out in an oxidation basin in which the sludge loading is maintained very low so to produce an extended aeration system (see 18.6.1).

Interest in the use of anaerobic digestion for large capacity plants is being centered on the possibility of recovering the digestion gas and making use of its heating power for the production of steam and electricity. The steam is generally used for heating the sludge digestion plant and the buildings in which plant operation personnel are housed. The digested sludge then undergoes dewatering, either mechanical or on drying beds, before disposal by controlled tipping or by incineration.

19.2.5 Incineration

Incineration processes burn the organic matter in sludge and produce an inert ash. Since the combustible portion of most sludges is below 75 %, a substantial amount of ash remains for disposal.

It is useful to observe that in those cases in which incineration is envisaged, digestion of the sludges can be avoided, thus achieving considerable savings on both investment cost and running costs of the incinerator, since the heating power of the digested sludge is up to 50 % less than that of fresh sludge (3500-400 Kcal/kg SS for fresh sludge; 1800-2500 Kcal/kg SS for well digested sludge). Elimination of the digestion stage, however, presents disadvantages of a different nature: a) a larger dimensioning of the dewatering risk and

incineration units, the undigested sludge containing a larger amount of solids; b) the greater risk of objectionable odors if the plant is not well run; c) the need of a reserve incinerator in case of breakdown.

Amongst the systems for sludge disposal, mention must be made of discharge to sea by means of underwater pipelines. However, the use of this form of disposal must be subject to an examination of the receiving capacity of the sea area concerned and the relative sea bed, in order to avoid serious consequences of both ecological and economical nature. Amongst the major difficulties as regards discharging into the sea is the frequent presence in the sludge of persistent compounds such as, for example, chlorinated hydrocarbons and more particularly heavy metals. The difficulty of exercising an efficient control over the pollution which can be caused by this form of discharge is understandable.

The risk to human health and animal life is determined by the persistent toxic compounds, which must be carefully evaluated in relation to the use of this sludge in agriculture.

19.3 Inorganic Sludge

Controlled tipping is the method most usually adopted for the disposal of inorganic sludges.

In practicing this form of disposal, care must be taken in the choice of the area, in order, to ensure that no leachate reaches either the surface waters or the sub-soil waters, polluting them. These basic considerations are also applicable to the discharge of organic sludges. However, for inorganic sludges derived from the treatment processes under consideration, the problem is usually considerably more complex due to the greater risks of contamination of the environment. In particular, the toxic characteristics of the sludges containing heavy metals, oil residues, chlorinated hydrocarbons and pesticides can be cited as examples.

In order to avoid the leakage of leachate, both the bottom of the tipping site and the side walls should be essentially water-proof. When the protection constitutes natural clay layers it is necessary that the bulk permeability is such as to produce very long times for the leachate to reach the aquifer. Some organizations suggest a time of 250 years. When this geological condition is not present, it is essential to provide other means of waterproofing such as covering with plastic or cement or with bituminous materials. The water-proofing of the top of the tipping site, to totally contain the sludge, greatly helps to limit this risk factor, in that it prevents the entry of rain water. In any case it is advisable to provide the tipping sites with both bottom and lateral drainage for surface water. On the other assumption that the tipping sites is totally waterproofed, drainage of the bottom has the sole function of showing up accidental infiltration. However, during the operation of the tipping site, the drainage also collects rain water which washes away those sludges which are not protected on top. In this case the tipping site must be equipped with systems for the collection and treatment of drainage waters.

Amongst other alternatives to the system of direct discharge on tipping sites, mention can be made to the system of polymerization or chemical fixing, which is based on the addition of chemical compounds to sludge, capable of producing polymerization, and thus the consolidation, of the sludge mass. This method, albeit interesting, does not however completely eliminate the problem of leachate and has a limited range of application to sludges of well-defined characteristics. The method is economically burdensome, as is also

the high temperature roasting method used for the transformation of the heavy metal hydroxides into associated oxides of extremely low solubility. In future it is to be hoped that processes to recover metals and other valuable compounds can be further developed. In fact, there are rare applications of recalcination systems for sludge rich in calcium carbonate, for recovery of quick lime, and of acid recovery of aluminum sulphate from sludges rich in aluminum hydroxide.

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