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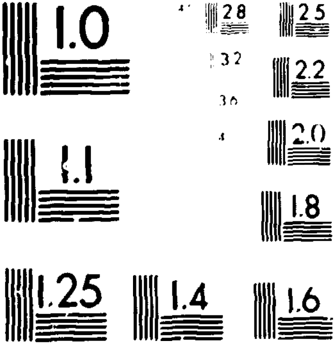
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WASTE WATER POLLUTION MANAGEMENT AND CONTROL IN THE PETROCHEMICAL AND PLASTICS PROCESSING INDUSTRY*

by

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2628

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WASTE WATER POLLUTION MANAGEMENT AND CONTROL IN THE PETROCHEMICAL AND PLASTICS PROCESSING INDUSTRY.

Sewage can be regarded as the water-borne waste products of man. When the human race was thinly scattered over the face of the earth and tended to be nomadic by nature, the disposal of waste matter did not constitute a serious problem, as large accumulations did not occur and the soil was able to break down the small concentrations into harmless end products. Difficulties arose when man started to congregate in large communities, with a consequent build-up of filth in a restricted area.

The trouble was later aggravated by the coming of the Industrial Revolution, with its attendant increase in population and growth of cities and towns.

In certain areas, industrialization brought forth further pollution by discharges of untreated trade wastes from industrial premises.

It became evident that if man was to live healthily in large communities, it was essential that he should have efficient and hygienic means of disposing of both domestic and industrial waste waters.

Since the purpose of this lecture deals with pollution originating from industrial activities, in particular from the petrochemical and plastics processing industry, we shall concentrate our attention on the industrial wastes, on their effects on the environment, on the different possible approaches to waste waters regulations and controls, and on the practical technologies currently available in order to eliminate or minimize the adverse effects of such wastes.

Let's first of all try to understand what the word "pollution" means.

All industrial wastes affect, in some way, the normal life of the water body (river, lake, shoreline or harbor areas, open sea) receiving the waste.

When the effect of the waste is such as to render the receiving water body unacceptable for its "best usage", we can say that the waste is polluting the receiving waters.

Best usage means that the water bodies should be maintained in acceptable conditions, in order to be used for all the possible purposes to which they are destined (recreation, bathing, fishing, navigation, irrigation, drinking, etc.).

Water bodies, however, can assimilate a certain quantity of waste before reaching a polluted state.

But too much of any type of polluting material causes a nuisance, and thus a polluted state exists. To call a stream polluted, therefore, generally means that the stream has been supersaturated with a specific pollutant. The following are the main categories of industrial pollutants:

Organic matter

Organic matter can exhaust the oxygen resources of water bodies and create unpleasant tastes, odors, and general septic conditions. Fish and most aquatic life are stifled by lack of oxygen, and the oxygen level, combined with other stream conditions, determines the life or death of fish.

Clean natural water is normally oxygenated and contains a large and varied number of life forms including protozoa, bacteria and aquatic plants and animals, which are interdependent, forming a complex system and keeping the waterbody in a healthy condition. The water obtains its dissolved oxygen mainly from the atmosphere by surface aeration, and this process, in case of a watercourse, is assisted by the turbulence of the stream caused by the velocity of its flow and its passage over rocks and stones; but also lake and sea water can dissolve athmospheric oxygen, mainly through the action of wind and waves.

Bacteria and aquatic organisms utilize the dissolved oxygen to break down organic matter entering the stream, and the salts and carbon dioxide formed are used by the plants, by photosynthetic means, to build up their own structures. It will be seen, therefore, that due to the presence of various organisms and dissolved oxygen, a waterbody has considerable powers of self-purification, but there is a limit to these powers. If the dissolved oxygen content is seriously reduced, some of the organisms die or are driven away, with the result that, instead of organic matter being oxidised in the normal way, anaerobic organisms begin to build up and break down the organic matter into offensive products, until ultimately a septic condition is set up in the body of water, and foul odours, due to hydrogen sulphide, etc. are emitted.

Let us consider, therefore, what happens if large volumes of untreated industrial waste waters containing biodegradable

organic matter in suspension, in colloidal dispersion and in true solution, are discharged into a waterbody.
The suspended solids tend to settle out, forming banks of sludge. The organic portion of the sludge tends to deprive the bottom layer of water of dissolved oxygen, and finally undergoes putrefaction, especially in warm weather, resulting in portions of the sludge being buoyed to the surface by the gas produced. In addition, the organic matter in colloidal dispersion and true solution also plays its part in reducing the dissolved oxygen content in the upper layers of the waterbody, thus possibly causing general septic conditions.
To recapitulate: when industrial wastes containing organic biodegradable matter are discharged into a waterbody, the dissolved oxygen content of the water decreases considerably in a short time, owing to the breakdown of the organic matter into harmless end products; but if the water is in a healtly state, the dissolved oxygen will then start to increase, due to the re-aeration of the water. If, however, the volume of waste is large in relation to the volume and to the capacity of re-aeration of the receiving water, and strong in character, its oxygen demand will be greater than the dissolved oxygen present in the water and that supplied by re-aeration, with the result that the receiving water will be reduced to a polluted condition and may eventually become septic. (See Figure 1).
It is normally recognized that the critical range for aquatic life to survive is 3 to 4 parts per million (ppm) of dissolved oxygen; therefore, if this limit is not infringed, the water body receiving the wastewaters is not likely to show any appreciable sign of pollution or to cause any nuisance. Often this

oxygen shortage, caused by organic matter, in itself is considered to be the most objectionable factor in a stream's pollution. Water pollution management and practices should therefore be aimed, first of all, at maintaining this minimum oxygen level in all water bodies.

Suspended solids

Suspended solids can settle to the bottom of a waterbody as a sludge, which tends to cover spawning grounds and to inhibit propagation of fish Or they can wash up on the banks where their organic portion, eventually, decomposes, undergoing putrefaction and causing odors.
Visible sludge, also, creates unsightly conditions and destroys the use of a river for recreational purposes.

Heat

An increase in water temperature, brought about by discharging wastés such as condenser waters, has various adverse effects. Warm water is lighter than cold, and stratifies; this causes most fish life to retreat to the bottom. Since there is less dissolved oxygen in warm water than in cold, aquatic life suffers, and any organic pollution discharged into these warm surface waters will have less oxygen available for natural biological degradation. Also, bacterial action increases in higher temperatures, resulting in accelerated depletion of the water's oxygen resources.

Heated stream waters are also of decreased value for industrial cooling. As a matter of fact, one industry may so increase the temperature of a stream that a neighboring industry downstream cannot use the water.

Inorganic salts

Inorganic salts, which are present in most industrial wastes as well as in nature itself, cause water to be "hard", and make a stream undesirable for industrial, municipal, and agricultural usage.

Another disadvantage is that, under proper environmental conditions, inorganic salts, especially nitrogen and phosphorus, induce the growth of microscopic plant life in surface waters. If the effluents are discharged into lakes, ponds or sluggish streams these nutrients tend to stimulate growths of phytoplankton (algal blooms), and can also stilumate weed growth. This can lead to "eutrophication" of the lake, an ageing process due to excessive discharge of nutrients. Eventually, this may go far enough to convert the lake to marshland or even dry land. (See Figure 2).

Acid and/or alkalis

Acid and/or alkalis discharged by chemical and other industrial plants make a stream unsuitable not only for recreational uses such as swimming and boating, but also for propagating of fish and other aquatic life.

Color

Color interferes with the transmission of sunlight into the stream, and therefore lessens photosyntetic action. Also, property values decrease alorg a visibly polluted water; fewer people will swim, boat, or fish in a waterbody highly colored by industrial wastes. Visible pollution often causes more trouble for industry than does invisible pollution: it is only human to complain about readily visible pollution. Therefore a highly colored industrial waste, although not necessarily toxic or dangerous for the environment, will anyway very likely focus public indignation directly on the industry discharging it.

Foam- producing matter

It is an indicator of contamination; it leads to an undesirable appearance of the receiving waterbody, and is often more objectionable than lack of oxygen itself.

Oil

Oils and greases not only make the waterbody unsightly, but also obstruct passage of light through the water, retarding the growth of vital plant food. Some other specific objections to oil in streams are that it: (1) interferes with natural re-aeration; (2) is toxic to certain species of fish and aquatic life: (3) destroys vegetation along the shoreline, with erosion as a consequence; (4) renders boiler-feed and cooling water unusable; (5) causes trouble in conventional drinking water-treatment processes by imparting tastes and odors to water, and coating sand filters with a tenacious film; (6) creates an unsightly film on the surface of the water.

Toxic chemicals

These are very numerous, and can be both inorganic compounds (e.g. lead, mercury, arsenic, selenium, chromium hexavalent, etc.), or organic compounds (e.g. phenolic compounds, insecticides as toxaphene, dieldrin, dichlorobenzene, etc., chlorinated solvents, etc.).

Toxic chemicals can be poisonous to fish and other smaller aquatic life even in extremely low concentrations.

If the receiving waterbody is used as a drinking water supply, the discharge of toxic chemicals, even in small amounts or concentrations, can easily impair this use, since drinking water standards, as regards toxic chemicals, are very strict and rigid (i.e.: chromium hexavalent, 0,05 ppm; phenolic compounds, 0,001 ppm, etc.).

Let us now consider the possible different approaches to waste water regulatory policies.

We shall recall, first of all, that the object and goal of regulations on this subject should be aimed to: promote, restore and maintain the chemical, physical and biological balance of the national bodies of water.

Balance means that water bodies should be maintained in acceptable conditions; means that they should not be impaired and that they should be preserved in order to be used for all the possible purposes to which they are destined (drinking - bathing - irrigation - fishing - industrial - navigation - etc.).

The word polluted should therefore be related to the receiving water, not to the waste water as such.

An effluent stream, may be polluting the receiving water, but only when it compromises its natural characteristics, which should instead be preserved.

We can't say that an effluent, as such, causes pollution to a waterbody when we take into consideration only the concentration of pollutants in the effluent. Other factors must be considered as well, such as:

- the volume of the waste discharged
- the flow rate of the receiving stream (or the dilution rate in the receiving water).
- the self purification capacity of the receiving waterbody
- the use to which the receiving water is destined , and the consequent water quality classification of this receiving waterbody.

Regulations should therefore be issued in order to reach this goal, which is to protect all national waters so that they can serve the best interest of the people using them.

There are two main schools of thought regarding the establishing of water pollution control policies.

One is based on "effluent standards"; the other on "surface water quality standards".

Effluent standards

The system of effluent standards requires that for all industrial effluents, the waste discharged be kept below a certain maximum concentration of polluting matter. A disadvantage to this approach is that there is normally no control over the total volume of polluting substance added to the waterbody each day. The large industry, although providing the same degree of waste treatment as the small one, may actually be responsible for a major portion of the pollution in the waterbody.

The effluent-standards system is easier to control than the surface water quality standards system, from a regulatory standpoint, and is therefore generally favoured by state control agencies.

This system, however, may not provide sufficient protection for a waterbody receiving large amounts of even treated effluents in heavily industrialized areas.

On the other hand, there can be a tendency to upgrade and generally increase the severity of the effluent standards in order that they shall provide sure protection in all possible cases.

This may lead to the general, nationwide enforcement of very strict effluent standards, which are to be applied even when they are not necessary for the retention the good natural characteristics and health of the surface waters to be protected. Fully acceptable results may be reached, in many situations, even with looser effluent limitations.

We must now recognize that it is a sound economic principle that any expenditure on treatment plants does not go beyond the point necessary to ensure that good health is maintained in the receiving water.

In this respect, strict and generalized effluent standards may appear, in some cases, an unnecessary economic burden to many industries.

Effluent standards should be based more on economics, local conditions and practicability of treatment, rather than simply on the best pollution technology available.

To conclude, we recall that strict, nationwide effluent standards may not be necessary in all situations to ensure a safe and healthy environment in the surface waters, and that a system which allows elasticity to effluent standards, according to local conditions, is certainly to be preferred to a rigid one.

Surface water quality standards

The surface water quality standards system is based on establishing classifications or standards of quality for a waterbody, and regulating any discharge into it to the extent necessary to maintain the established classification or quality. The primary motive of surface water quality standards is to protect and preserve each waterbody for its best usage.

It is in fact established, case by case, by the pollution control authority, the extent of treatment each industry must secure, and the maximum pollution load that can be safely discharged, to meet the quality standards in the reciving water. The main advantage of the surface water quality standards system is the prevention of excessive pollution, regardless of the type of industry, or other factors such as the location of industries and municipalities. This system limits the loading to that which the stream can safely assimilate, and hence may impose a hardship on an industrial plant located at a critical spot along the stream.

On the other hand, pollution abatement should be considered in decisions concerning the location of a plant, and effluent standards may be relaxed , according to favorable local conditions.

As an alternative to the previous approaches, to be considered are also the two following based, respectively, on money charges alone, and on a combination of effluent standards-surface water quality standards-money charges.

Money charges

In principle, neither tolerance limits nor total pollution load are fixed. But money charges are applied to the waste waters, proportional to the amount of pollution discharged.

This kind of taxation, practically, induces a great limitation to the discharge of pollutants.

Combination of: Effluent standards- Surface water quality standards- Money charges.

Surface water quality standards are first set.

As a next step, two lists of effluent standards are established by the responsible authority, case by case;

the stricter list (guideline) is based on the best pollution control technology available, the second one (maximum acceptable concentration -m.a.c.) is to be considered the maximum acceptable pollutant concentration that do not impair the established quality standards of the receiving waters.

Wastes that do not respect the guidelines limits, but only the m.a.c. should pay a money charge, according to the following formula.(A. Margola):

$$C = \sum_{1}^{n} {}_{i} \quad r\, c\, y_n \frac{(a_{ix} - a_{il})}{a_{il}} Q_i \qquad \text{(see Figure 3)}$$

where:

C = total money charge/year

r = reduction factor (e.g.: 0.10 for the first year

0.10	for	the	first	year
0.30	"	"	second	"
0.65	"	"	third	"
1.00	"	"	fourth	"

c = money charge/m^3

y_n = factor related to the class of the pollutant

(e.g. y_n = 2 for heavy metals, toxic pollutants, etc.

y_n = 1 for BOD5, COD, S^-, CN^-, etc.

y_n = 0.5 for Cl^-, $SO_4^=$, etc.)

a_{il} = guideline tolerance limit for the "i" pollutant

a_{ix} = average concentration of the "i" pollutant in the effluent.

Q_i = volume of the waste (m^3/year) containing the "i" pollutant.

Let us now take into consideration, practically, the steps that should be followed, to face the pollution problems related to the industrial sector of our interest.
It is not the purpose of this lecture to provide details of each and every possible waste from the petrochemical and plastic processing industry, or to explain generally applicable techniques or treatment technologies. As a matter of fact, such techniques, valid in any case, do not exist.
In fact, we should keep in mind the broad extension of processing and complexity of petrochemical activities, to understand that different petrochemical productions, or plastic processings, will have a different and specific impact on the character and quantity of contaminants entering the final sewage system.
It has been stated many times that no two industrial effluents are exactly alike, which is one of the factors making the science of waste water purification so interesting.
Therefore selection of the basic process design and sizing of plants need to be studied and designed case by case, to meet the specific characteristics of the effluent to be treated.
Characterization studies should therefore be carried out in any case, through site inspections and analyses of the waste water, whenever possible and samples are available, or, as a minimum, through the collection of the best theoretical literature data on the subject, prior to selecting the pollution control techniques and to establishing the final process design of the treatment plant.

Nevertheless, the system analyses to be performed, and the process to be selected, basically fall more or less into the following general pattern:

- process changes, or equipment modifications, in order to obtain a waste strength reduction;
- segregation of wastes, to reduce the strength of the main volume to be treated, while the small-volume strong waste can be handled with methods specific to the problem it presents:
- equalization and proportioning of wastes, if plants produce various waste-waters different in strength, at different times;
- removal of non emulsified oils and of settleable matter;
- removal of suspended solids and colloids;
- removal of organic oxydiable dissolved matter;
- removal of nutrients.

To be considered also, generally for specific small-volume strong wastes, are the following stages:

- removal of emulsified oils;
- removal of specific organic matter immune to aerobic biological treatment;
- neutralization of spent caustic or acid liquors.

It should be remembered, however, that the methods of carrying out the various stages of treatment may differ from plant to plant, as may also the sequence, and that, finally, some stages may be omitted altogether (see Figure 4).

We shall now review some of the principal conventional and new techniques for the accomplishing of the above listed stages.

Removal of non emulsified oils

The basic unit for recovering oil is the gravity-type oil-water separator, which is in general use throughout the petroleum industry (See Figure 5). Operation of the separator depends on the difference in specific gravity of the oil and water. Flow rate, oil gravity, and water temperature are the main factors affecting the design of such plants.

It should be noted that gravity separators will not prevent the escape of emulsified oil.

Oil-water separators should be maintained as free of accumulated oil and sediment as possible; for this purpose, separators are often equipped with flight-scraper devices or other mechanical means for skimming and removing oil and sediment under service conditions.

Removal of suspended solids and colloids

The most common and practical method of removing these solids is by chemical coagulation (see Figure 6).

Chemical coagulation is a process of destabilizing colloids, aggregating them, and binding them together for ease of sedimentation. It involves the formation of chemical flocs that absorb, entrap, or otherwise bring together suspended matter; more particularly, suspended matter that is so finely divided as to be colloidal. The chemicals most commonly used are alum, $Al_2(SO_4)_3 \cdot 18H_2O$, and copperas, $FeSO_4 \cdot 7H_2O$.

Removal of organic oxydiable dissolved matter

The activated-sludge process has proved quite effective in the treatment of organic wastes. (see Figure 7).

In this process, special bacteriologically active sludges are developed, which are able to absorb organic matter from the wastes and convert it by oxidation-enzyme systems to simple end products, such as CO_2, H_2O, NO_3 and SO_4.

The living masses of organisms are highly active centers of biological life; hence the term "activated sludge".

Removal of nutrients (phosphates, nitrates)

One emerging technology which is receiving increased attention on this subject, as both a cost-effective and energy-efficient alternative, is aquaculture.

Aquaculture pertains to the use of plants such as water hyacinths, duck-weed or algae in a relatively natural environment for the purpose of achieving treatment objectives. The major difference between aquaculture and conventional treatment systems is that conventional systems typically use a highly managed and controlled environment consuming chemicals and energy, for the rapid treatment of the wastewater. In contrast, aquaculture systems use a comparatively natural environment in which treatment occurs at a slower rate, through a combination of physical, chemical and biological means. It is largely due to the more natural environment that aquaculture treatment systems can reduce the cost of necessary plant and equipment as well as operating costs, to meet wastewater treatment objectives. (see Figures 8, 9).

In aquatic plant systems, periodic harvesting is required to maintain high system performance. The plants harvested have potential economic value for such uses as composting, and animal feed supplements.

Removal of emulsified oils

Ultrafiltration is the most suitable depurative system for water polluted by oil-emulsions. (see Figure 10).

It consists of a pressure-driven membrane process for separating and fractionating components of liquids. The separation is performed by a porous membrane which permits passage of water and other low molecular substances. Larger molecules and micro-emulsion droplets, as well as any suspended solids, are held back. Ultrafiltration can selectively concentrate solutions and brake oil emulsions.

Ultrafiltration works at a low pressure, without heating or chemical additives.

Separation problems, which previously required more expensive and complicated methods, can now be solved using ultrafiltration.

In figure 11 we have represented a combination of different stages of purification which may be suitable for the treatment of a large variety of wastes in the petrochemical and plastic processing industry.

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