# MEASURES AGAINST WATER POLLUTION IN THE PRODUCTION OF ORGANIC CHEMICALS FROM SOURCES OTHER THAN PETROLEUM

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## ABSTRACT

The sewage of the chemical industry is generally a blend of clean (cooling water), and polluted water. The first recommendation is to separate the effluents, and to send clean water directly to the stream.

Polluted sewage comes from the general services and from the individual fabrication plants. All the pollutions, which are dangerous for safety, able to dirty or destroy the sewers, or render more difficult or more expensive the final treatment, will be treated at the source.

The sewage is treated at the general station, taking into account (i) toxins (ii) BOD (iii) COD and (iv) suspended material, and from the stream to which purified sewage is sent.

In all cases a flocculation-settling will be necessary, the treatment being eventually completed by a biological step.

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Some tens of years ago, when a manufacturer intended to build an organic chemical plant, he chose, as far as possible, a place with a generous source of water, preferably a subterranean sheet or close to a sufficiently large flow stream able to receive its effluents.

The circumstances have changed, the industries have expanded, the water sheets are no more sufficient, and the pollutions exceed the amount which can be accepted by the rivers. In those conditions, the plant such as I roughly described it, belongs to the past, and the manufacturer is, at present, faced with two problems: water supply and sewage.

## I. WATER SUPPLY

This problem is not strictly a part of the subject we discuss here, but we must however say some words about it. More and more, the water supply is obtained from the rivers and that water can seldom be directly used. Consequently, in the most general case, different treatments are applied to the raw water. They are: flocculation, settling, filtration, and conditioning.

The operations of flocculation and settling are especially interesting: they bring the first of the residues we shall have to separate. We shall see ultimately that the separated floc can be useful in the sewage treatment.

## II. SEWAGE

This can be divided into two classes: non-polluted waters and polluted waters.

### Non-polluted waters

They are used generally to cool apparatus, condensers, hot wells, compressors, and so on. The cooling systems can be simple 'once through' systems and, in that case, water carries out heat only, and the conditioning products which are eventually added. Generally, they are small amounts of polyphosphates (a few ppm) and traces of chlorine, which practically do not modify its quality. When cooling water is used in open recirculation systems, the blowdown can be sent to the clean water sewer, if the treatment of the system (against scaling, corrosion, algae) is not made with toxic products. According to our personal experience, in an organic chemical plant, the proportion of clean water is about 50–80 per cent of the total water consumption.

### Polluted waters

The general factors which generally take place in polluted waters, and especially in organic chemical plants are: toxic products, suspended matter, BOD and COD.

Let us now look at some sources of pollution in our plants, and the nature of the pollutants they send to the sewer.

(*a*) *General services*

Even though the effluent from these is not particular to organic chemical plants, it must be taken into account in the final treatment. The services are generally:

1. Sanitary i.e. showers, toilets, etc. which consist mainly of suspended matter and BOD.
2. The canteen, both BOD and suspended material.

If we say that one average person represents 60 g BOD and 90 g of suspended material each day, we can estimate that a half to one third of this pollution is made in the works. That is to say we can estimate 20–30 g BOD and 30–45 g suspended material per person per day.

3. Maintenance workshops: The pollution generally consists of suspended material, oils, grease and occasionally metal treatment products.
4. Garages: generally drainage oil, detergents and greases.
5. Boilerhouse: The pollution here is usually oils, suspended material *i.e.* cinders, soot and blowdown products (blowdown products contain phosphates in solution or suspension).

(*b*) *Manufacturing processes*

Firstly we must divide the pollution brought by the manufacturing processes into two groups: (i) toxins and (ii) classical pollution, BOD, COD, suspended materials.

(*i*) *Toxins.* These include raw materials, intermediates, finished products and by-products.

They may be inorganic, *e.g.* sulphides (from organic sulphurations), cyanides (preparation of acrylonitrile and nitrilotriacetic acid). Sulphides and cyanides are especially hazardous when, in the sewers, they meet regular or accidental additions of strong acids: the evolved acids are particularly dangerous. Amongst the organic toxins the most well known are the phenols and their derivatives.

I mention also the pesticides whose influence is mainly on the natural source destroying river vegetation and fish whenever the amount put into the river reaches a certain level.

(ii) *Classical pollution.* As for all effluents, the classical criterion BOD, COD, and suspended matter are still valid. On the other hand, what is specific to our industry is the fact that, for a given COD, BOD can vary considerably. To put it another way, the rejected effluent could be totally fermentable, or partly, or even not at all. This is an important point which we shall discuss again when dealing with the treatments.

In our industry the manufacturing processes can be divided into two groups: anhydrous and aqueous.

Those in an anhydrous medium include, for example, chlorations (chlorinated solvents, aliphatics or aromatics, chlorophenols, D.D.T., lindane, chloracetic acids, vinyl derivatives), nitrations (nitrophenols, explosives), condensations (alkylbenzene, bisphenol, alkylphenol, etc.) and non-azeotropic esterifications. Theoretically their manufacture does not give any residual water. However small quantities accidentally escape giving pollution which can be found either in the upper layer if the products are less dense than water or in the lower layer if they are more dense than water, or alternatively in solution if they are water soluble, in which case they have both BOD and COD.

Examples of processes in an aqueous medium, or including washing operations with water, are azeotropic esterifications, saponifications, preparation of phenols, propylene oxide, glycerine, glycols, oxidations of hydrocarbons to give acids, oxidations with hydrogen peroxide, sulphonations, nitrations, Friedel-Crafts condensations at the washing stage, reductions (nitrated products to give amines) preparation of amines from alcohols, alkanolamines, preparation of para-formaldehyde, of hexamethylene tetramine and melamine etc.

The production of the alcohol type gives fermentable effluents. On the other hand the others give rise to effluents which are either slightly or not at all fermentable.

**Overall composition of an effluent**

Thus in absence of treatment, at the outlet of the works, we find a mixture of clean and polluted water which can contain:

1. Toxins
2. Oils and solvents in the upper layers
3. Heavy solvents and greases in the bottom layers
4. Suspended materials
5. Dissolved organic products, fermentable
6. Dissolved organic products, non fermentable
7. Dissolved inorganic salts.

We shall now consider by what means these diverse products can be eliminated leading to, at the outlet of the effluent treatment plant, a clear effluent free from toxic materials and with a moderated COD.

## III. TREATMENT OF RESIDUAL WATER

In an organic chemical works, I think that the following principles must be applied:

1. Separation of the clean water from the polluted.
2. Treatment at the source of the pollution, if it is necessary to make possible or to simplify the final treatment.
3. Treatment of the whole of the polluted effluent.
4. Mixing the clean and the treated water before putting back into the natural source.

### Separation of clean and polluted water

At the level of the individual plant this involves the collection of clean water from the cooling systems on one hand, and on the other polluted water and water from washing the apparatus, treated or untreated against specific pollution. Two separate sewers carry the clean and polluted water to the general sewer network.

At the works level a double network of sewers is involved: the clean one which flows freely after the general sewage purification plant, and the polluted one which collects the total polluted water plus eventually the rain water from the yards which may have been polluted. However it is good to have some means of rainwater storage so as to ensure a constant flow rate to the treatment plant.

When constructing a works, it is necessary from the beginning, to envisage this double network in the individual plants and roads. The extra expenses are generally acceptable. On the other hand, for an old plant, the creation of a separate network poses technical and financial problems. From a technical point of view, the separation of sewage in the individual plants and the opening of trenches in the roads are often difficult. For that reason the branches for the collection of polluted water can frequently be made to run overhead, using existing installations such as those used for carrying steam and product lines. This is a safe and economic solution if the quantity of water transported is not too high.

### Treatment at source of specific pollutions

In order to (i) protect the sewers and the maintenance workers, (ii) eliminate more easily and more effectively certain types of pollution, and (iii) to make the final treatment easier, it is desirable to eliminate at the individual plant level certain types of pollution. But it must be pointed out that the multiplication of small purification stations is not an economical way.

Referring back to the preceding order we shall now see what can be done in each case.

(a) *Treatment of industrial water*

The sludge obtained is essentially inorganic. It is composed of particles of clay, slate and so on coated with aluminium or iron hydrates. It shows a power of adsorption which is not negligible. Thus it is generally profitable to run it into the polluted sewer network.

(b) *General services*

(i) *Sanitary—canteen.* Unless the sanitary water is to be used as a nutrient in a biological treatment plant, it is recommended that it is passed through septic tanks before it is discharged into the sewer. Thus we eliminate BOD at no extra cost.

(ii) *Maintenance workshops, garages and boilerhouse.* The polluted effluent from these can be discharged directly into the polluted sewer without any inconvenience. It is imperative to collect in a settling tank the greater part of the oils and greases to avoid dirtying the sewers unnecessarily or to impair the final purification.

(iii) *Open recirculation cooling water subjected to special treatments.* The blowdow from these cycles may contain:

1. Suspended material of no particular importance.
2. Toxic materials used to prevent the growth of algae, fungii, etc. some of them in proportion much lower than 10 ppm are significantly toxic towards fish and bacteria of the biological treatment plants. A specific treatment is very difficult to define, due to the volume and the dilution but it is necessary in many cases. Passing over active carbon gives good results.
3. Conditioning products the discharge of which is forbidden. This is the case with chromates. Their transformation to Cr 3 realised without difficulty in the metal treatment industries by using reducing agents is, owing to the extreme dilution, difficult to apply and to control. For this reason their use has been banned in certain countries.

(c) *Manufacturing processes*

(i) *Toxins.* For inorganic toxins, there are well known processes used by the industries concerned in making these products in large quantities. For the cyanides, according to the conditions, we can choose between various oxidation processes, chlorine or persulphuric acid for example. As regards the organic toxics, it is the elimination of phenols and their derivatives which has been the most studied and which is the most fully covered in the literature.

According to the quantity of phenols to be eliminated and their proportion in water we have to choose among the following processes:

1. Complete oxidation by chemical reactants for small quantities dissolved in relatively small volumes and in the absence of any great amount of COD. For this we can use: sodium permanganate in acid medium, chlorine dioxide or chlorine, taking care to use it under such conditions as to prevent the formation of chlorophenols which give at very low rates an especially bad taste to drinking water. In order to eliminate the last traces of phenols, good results are obtained by passing over active carbon.
2. Adsorption on active carbon in general is useful for small quantities of phenols diluted in large volumes of water.
3. Extraction, for large volumes and relatively high concentrations. Various solvents can be used, for example, isopropyl acetate or acetophenone. This form of treatment however efficient still leaves appreciable quantities of phenols

which must be removed by one of the preceding methods.
4. Biological treatment, for proportions of phenols less than 300 ppm and certain of the lesser substituted phenols. This process in some cases is preferred to chemical or physico-chemical methods.

We must finally mention products with a high toxicity. In these cases we must try above all, to avoid using water in the course of the manufacture. If this precaution is taken then the volume to be treated is often small and we can use an expensive technique such as lost active carbon. This is the case of pesticides.

It is not possible to say beforehand for toxins whether it would be better to treat them before putting into the sewers.

(ii) *Elimination of oils, greases and solvents.* The process used for this purpose is the same in all industries. Yet, we must not forget the danger constituted for the operatives by the presence of flammable or toxic solvents.

(iii) *Elimination of suspended matter.* This operation must be done with the greatest care. When it is conveniently done, it allows to eliminate at the same time an important part of the BOD and COD, by adsorption on the flocs (often 30–70 per cent). To obtain such results, the pH must be regular or, if not, regulated at the inlet of the station, and the addition of flocculating agent (iron or aluminium salt) and additive (polyelectrolyte) must be proportional to the pollution entering in the station. This operation is generally done at the final station.

(iv) *Elimination of fermentable organic matter.* Unquestionably, it is the most difficult problem in our industry. It is generally admitted that, for a BOD/COD ratio over 0.6, fermentation is possible without any difficulty. Between 0.3 and 0.6, it remains possible, but it is often necessary to use specially adapted bacteria. Under 0.3, such a process is practically impossible to use.

Generally, in our industry, the ratio is comprised between 0.2 and 0.5. In that case, we must, nearly in all cases, add nutrients to obtain the classical ratio BOD/N/P of 100/5/1. Sometimes, we must add, from time to time, fresh bacteria. The accidental introduction of toxins stops the biological process for long periods, especially when trickling filters are used. Sometimes, for that reason, it is preferred, when the greatest part of the fermentable pollution comes from one individual plant, to proceed to the biological treatment before discharge into the general polluted sewer.

(v) *Elimination of non fermentable organic matter.* Properly said, it is not possible to eliminate that type of pollution, except, perhaps, by the costly means of active carbon. This problem must be carefully studied before the construction of the plant, in order to see, which recyclings or which operations (concentration, combustion, and so on) would allow reduction of this amount of non fermentable products.

**The final station**

Just how complicated the final station will be depends upon:
1. The nature of the polluted effluent entering into the station.
2. The proportion of the polluted effluent to the total effluent.
3. The proportion of total effluent to the flow of water, in the river.
4. The specifications imposed on the discharged water.

In every case, after the classical operation of the elimination of sand, oils, greases and so on, it will include a careful flocculation-clarification.

At the outlet, the effluent will be free from suspended materials, a part of BOD and COD, function of the nature of the organic pollutant, and of the flocculants used in that operation. According to its characteristics, it will be sent for mixing with clean waters or for complementary treatments. These include: safety treatment for the elimination of traces of toxins (active carbon for instance), elimination of BOD in a biological step, cooling and aeration. These treatments, often necessary, are generally costly.

I have not mentioned the problem of sludges, their drying, and their destruction. It does also exist in our industry, and all the solutions are expensive. Particularly, their calorific value is weak, and their destruction must be combined with those of other by-products or residues with which our plants are often encumbered.

**Mixing of non-treated and treated sewage**

In all cases, this operation is profitable. It allows to decrease the COD by dilution, and to remain below the limits fixed by law for the suspended matters and BOD which accidentally could escape from the treatment.

## IV. CONCLUSIONS

In conclusion, I believe that the purification of waste water from the organic chemical industry is a difficult business. We must observe two main principles: (i) the separation of clean and polluted water, and (ii) the treatment at the individual plant level of the specific pollution which can disturb the final purification, in order to be able to exploit in convenient conditions the final purification which in all cases should consist of a carefully controlled flocculation-clarification operation and, if necessary, biological treatment.

The application of those principles is relatively easy in the case of a new plant, in which all individual plants can be planned on the new basis. But it is difficult in an old factory technically, for the reasons formerly given, and also economically as the surrender of the old processes, and the destruction of the individual plants are foreseen in the near future. In all cases the purification of waste water is expensive and often raises the production cost substantially. Henceforth, in all industrial countries, the chemical plants must be planned on these new bases, but a long enough period must be allowed for the old plants. Be that as it may, and whatever the difficulties encountered, the treatment of our sewage and the destruction of our wastes is a social duty. In these last years much has been done but much still remains to be done. By the instigation of governments with the cooperation of industry, we are certain that, in the following years, the amount of pollution emitted by our plants will diminish considerably.