INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

APPLIED CHEMISTRY DIVISION

COMMISSION ON WATER QUALITY*

PRESENT STATE OF DEVELOPMENT IN WASTE & WATER TREATMENT TECHNIQUES IN THE CHEMICAL INDUSTRY AND POSSIBLE FUTURE TRENDS

Prepared for publication by
K. TROBISCH
Hoechst AG, Frankfurt/Main 80, FRG

PRESENT STATE OF DEVELOPMENT IN WASTE & WATER TREATMENT
TECHNIQUES IN THE CHEMICAL INDUSTRY AND POSSIBLE FUTURE TRENDS

Dr. Karlheinz Trobisch

ENVIRONMENT DEPARTMENT, HOECHST AG, FRANKFURT/MAIN 80, FRG

Abstract: The techniques of waste water treatment have reached now-
adays a very advanced stage of development. As a result of the im-
portance that must be attributed to this area, the Commission on
Water Quality of IUPAC has decided to give a survey of processes
which are used now. Beside the conventional mechanical and biolo-
gical waste water treatment preferably flocculation, precipitation,
adsorption, evaporation, waste water combustion, wet oxidation,
ultrafiltration, reverse osmosis and extraction are discussed.

INTRODUCTION

The chemical industry is one of the branches of industry which has a rela-
tively high consumption of water. River water is mainly used by direct ex-
traction from the rivers or by bank filtration.

As a rule 80 to 90 % of the water is used for cooling purposes. In most
chemical reactions heat is evolved which has to be dissipated in order to
keep reactions under control. Cooling water remains without regard to neg-
lectable exchanger leaks in its original condition, that is to say it is
not polluted. The heat which is dissipated has only a minor or in some
cases a local   effect at chemical plants located near large rivers. The
thermal load on water-courses is above all a problem of large power sta-
tions. To reduce the cooling water quantity, and thus the water consumption,
circulation cooling is being increasingly employed. The cooling water is
used not only once, but 20 to 25 times and is cooled in each cycle by eva-
poration in cooling towers.

Part of the water entering chemical works, in most cases about 5-15 % of
the total quantity, serves as a reaction medium for chemical conversion,
as a solvent for products, as a reaction partner (e.g. in saponification)
or as a cleaning medium for chemical products, for apparatus and for off-
gas. This process water is polluted by the products it has absorbed. Type
and level of pollution are as manifold as chemical production itself. Con-
sequently the purification system for the process waste water has to be
tailor-made for each chemical plant.

Many chemical processes already operate without water, but the chemical
industry cannot do completely without process water, for water is an ex-
cellent solvent for important substances which are used in chemical reac-
tions or are formed in these reactions. Thus process water purification
will continue to play an important and expensive role.

In the following we should like to discuss by way of a survey the suita-
bility of currently known processes for the purification of chemical plant
waste water and also of treatment processes that are still in the develop-
ment stage. As mechanical and biological treatment can be presumed to be
largely known, we shall deal mainly with physical purification processes.

1. MECHANICAL PURIFICATION

This simplest form of waste water treatment is widely used in the chemical
industry for separation of the solid or liquid pollutants contained in the
waste water. Solids and liquids separated in settling tanks are either re-
turned to the production process or after dehydration are taken to a re-
fuse tip or incinerated. The process serves to clarify waste water stem-
ming from individual plants or as the primary purification step in centra-
lized waste water treatment plants of chemical works.

2. BIOLOGICAL PURIFICATION

Whilst only two decades ago biological purification of the heterogeneously
composed waste water from chemical plants was considered impossible, it
was found after initial successful experiments in the early nineteen-six-
ties that such water, too, can be purified in a biological treatment plant.

In the meantime the activated sludge process for elimination of biodegrad-
able substances had been introduced in the chemical industry as a univer-
sally applicable process. The types range from oxidation basins with large
space requirement to compact, deep aeration basins. To introduce the oxy-
gen required for the activated sludge, brushes and surface aerators are
used, or compressed air introduced into the sludge in fine bubbles through
filter cartridges, in medium and coarse bubbles by way of special distri-
butors - pipes or boxes with perforated bottom and bubble trays. By utili-
zation of the kinetic energy for distribution of the air bubbles, injec-
tors, ejectors and static mixers are also employed.

Trickling filters which have proved themselves in communal waste water
treatment technology, have now also been introduced into the chemical in-
dustry. In order to counter the risk of clogging under high loads, plastic
elements with vertically arranged orifices are used. In this design trick-
ling filters attain BOD_5-volume loads which can lie decidedly over 1 kg per
m^3d. Trickling filters, moreover, are distinguished by a lower energy re-
quirement, lower maintenance costs and generally lower operating costs as
compared to the activated sludge process.

Experience with waste water purification by anaerobic processes (fermentation) has been gained mainly in the food processing industry and has been translated with good success to the industrial scale in special cases. The waste waters having to be treated in this branch of industry are heavily polluted; the degradation efficiency of between 50 and 80 % are generally lower than in aerobic processes. Because of the different nature of the degradation processes in a reducing medium the method offers extended possibilities of eliminating classes of substances which cannot be degraded by aerobic means. Furthermore, the low energy requirement of this type of process should be emphasized.

During the last few years problems of smell and noise have attracted attention in the operation of waste water treatment facilities. As a result there has been a noticeable trend towards space-saving, compact and fully enclosed plants. By using activated sludge basins it is possible in high-rise construction to combine extensive oxygen utilization with high oxygen inputs. The quantity of residual gas is so small that the costs for deodorization or smell elimination by means of afterburning are very low.

The oxygen process that has been in use for about ten years has the same objective; in this process technically pure oxygen is introduced into closed aeration basins. The small off-gas quantities usually do not require further treatment. The fully enclosed construction has proved itself also in areas with severe winters because the facilities are protected from frost. The sludges are withdrawn from the primary mechanical treatment tanks and also from the final clarification unit, and then concentrated in circular basins. The sludge is dehydrated with the aid of filtering aids by filter presses, rotary vacuum filters, centrifuges or screen belt presses. The sludge is then either taken to a refuse tip, incinerated or in rare cases composted with solid refuse.

The inadequacy of aerobic and anaerobic degradation processes is due to the fact that biologically resistant substances cannot be eleminated. Insofar as they are undissolved or can be precipitated they are separated in primary settling tanks. However, if they are dissolved or are retained in a colloidal state in the water, physical purification processes must be employed.

3. FLOCCULATION AND PRECIPITATION

Flocculation and precipitation takes place to a limited extent in conventional biological waste water treatment plants. However, considerably greater importance is attached to them in special purification processes, above all in hydroxide and carbonate precipitation in the neutralization step, in the removal of metal ions from the waste water of electroplating plants, phosphate precipitation and in a number of special cases tailored to a specific manufacturing process. These include the elimination of fluoride as calcium fluoride, barium as barium sulfate, sulfide as iron sulfide and mercury as mercuric sulfide.

Flocculation is understood to mean the conversion of finely suspended par-
ticles or colloidal substances into a state in which separation from the
aqueous phase is possible by mechanical methods. The particles pass through
destabilization, microflocculation and macroflocculation.

Colloids are stable due to the fact that all the particles have the same
charge (in practice this is mostly negative) and are destabilized by the
addition of carriers of the opposite charge. The process is called coagu-
lation, which is followed by flocculation in which the particles agglome-
rate. Thus the general term flocculation covers two processes, namely coa-
gulation and flocculation.

In chemical precipitation the solubility of a substance is exceeded by the
addition of a precipitant and, as in flocculation, colloidal structures
pass through the phases of destabilization, microflocculation and macro-
flocculation.

The so-called adsorption coagulation process is frequently applied in in-
dustry; in this process, for example, iron ions or aluminium ions are ad-
ded to the solution; the positive charge, with concomitant partial separa-
tion by hydrolysis, brings about coagulation. The discharge of negative
particles and their adsorption in this case takes place simultaneously.
Thus the transition to hydroxide precipitation or flocculation adsorption
is gradual. The less readily precipitable ions (or colloids) are elimina-
ted together with the readily precipitable iron or aluminium hydroxides.

The theoretically possible degree of separation in chemical precipitation
is calculated from the solubility product. In practice, however, the resi-
dual solubility is very often higher than the theoretical value obtained
by calculation, because influences of foreign salts and chelating agents
have an affect, especially in mixed waste water types. The amount of pre-
cipitant used, moreover, can reduce the degree of separation, if too much
or too little has an unfavourable influence on the complex precipitation
and flocculation processes.

The compilation of solubility products (mol/l) in table1(see p.6), provides
a survey of the preciptability of different metal ions with various pre-
cipitants.

TABLE 1   SOLUBILITY PRODUCTS FOR HYDROXIDE-, CARBONATE-AND SULFIDE PRECIPITATION

Hydroxide precipitation

Compound	Solubility product (room temperature) $(mol/l)^n$ *)	Precip. pH +)
Fe (OH)$_3$	8.7×10^{-38}	2.8 − 4.0
Al (OH)$_3$	2.0×10^{-32}	4.3 − 5.0
Cr (OH)$_3$	6.0×10^{-29}	5.5 − 6.5
Cu (OH)$_2$	2.0×10^{-19}	5.8 − 8.0
Pb (OH)$_2$	10^{-17}	7.0 − 9.5
Zn (OH)$_2$	4.0×10^{-17}	7.6 − 8.3
Co (OH)$_2$	2.0×10^{-16}	7.0 − 9.0
Ni (OH)$_2$	5.8×10^{-15}	7.8 − 9.3
Cd (OH)$_2$	1.3×10^{-14}	9.1 −10.0
Mn (OH)$_2$	4.0×10^{-14}	7.0 − 9.0
Fe (OH)$_2$	10^{-13}	6.0 −10.0

Carbonate precipitation

Compound	Solubility product (room temperature) (mol/l) *)
CoCO$_3$	1.6×10^{-13}
PbCO$_3$	8.0×10^{-14}
CdCO$_3$	5.0×10^{-12}
ZnCO$_3$	1.6×10^{-11}
FeCO$_3$	2.5×10^{-11}
MnCO$_3$	6.3×10^{-11}
CuCO$_3$	2.5×10^{-10}
NiCO$_3$	1.3×10^{-7}

Sulfide precipitation

Compound	Solubility product (room temperature) $(mol/l)^n$ *)
HgS	4.0×10^{-53}
CuS	8.0×10^{-37}
PbS	3.2×10^{-28}
CdS	1.6×10^{-28}
β-NiS	2.0×10^{-26}
α-NiS	3.2×10^{-19}
β-CoS	2.0×10^{-25}
α-CoS	4.0×10^{-21}
ZnS(sphalerite)	1.6×10^{-24}
ZnS(wurtzite)	2.5×10^{-22}
MnS green	2.5×10^{-13}
MnS pink	2.5×10^{-10}

+) = Interval from start of precipitation to quantitative precipitation

*) n=3 for valency of metal ions = 2
    n=4 for valency of metal ions = 3

Neutralizing precipitation can be regarded as a mature process and is considered a reliable and economic method for removing metal ions. Sodium hydroxide or lime is used as the precipitant. Sodium hydroxide is more expensive, but frequently provides more readily separable precipitates. Lime is cheaper, but requires elaborate facilities for dissolution and storage, so that it is normally used only in large-scale plants. Because of its importance, the problem of possible complex formation and the inferior separation which may then be caused should be emphasized once more. Thus chelating agents such as ammonia, cyanide, ethylenediamine tetraacetic acid, etc. play a special role.

By means of carbonate precipitation metal ions can be precipitated more effectively with the aid of soda solutions than is possible in neutralizing precipitation. The good crystalline form of carbonate precipitates results in improved filtrability and reduced water content of the filter cake. If trivalent metal ions are present during precipitation, the hydroxides - owing to their lower solubility - precipitate instead of the carbonates.

Because of the elaborate equipment and the acute risk of poisoning which has to be considered when handling hydrogen sulfide (TLV 10 ppm H_2S; odour threshold value 0.1 ppm), sulfide precipitation has not attained any practical importance. However, its advantages are both the cheapness of the precipitant and the very low solubilities of the precipitated sulfides. Hydrogen sulfide can be obtained in pressurized cylinders or by evolution from iron sulfide and hydrochloric acid.

Sulfides of mercury, copper and lead are only soluble in oxidizing acids and can therefore be taken to a landfill.

When carrying out sulfide precipitation, it must be noted that excess precipitant has to be eliminated. Difficult problems also arise if the sulfide is precipitated in colloidal form.

Chemical precipitation of phosphates is employed in phosphate-containing industrial waste water, but mainly in communal waste water in areas with sluggish or stagnant water courses. Constant introduction of phosphates by way of effluents leads to gradual eutrophication of such water courses. Phosphate elimination has already been applied in the lake districts of Sweden, Switzerland, the USA and Canada. In the Federal Republic of Germany, the process is being applied in the Lake Constance area as well as in the catchment areas of the Bavarian and Schleswig-Holstein lakes and several storage dams.

Iron salts or aluminium salts and lime are suitable for precipitation. Within the operations of a waste water treatment facility, precipitation can take place with varying effect either in the primary settling basin (primary precipitation), in the aeration basin (simultaneous precipitation), or in a downstream precipitation step. In favourable cases it is possible to attain phosphate eliminations of over 90 %. Depending on the process chosen, the concentration of phosphate phosphorus in the effluent will be 1 - 2 mg/litre.

Reductive precipitation of nobler metals is worth mentioning. In most cases iron is used for reduction, as it is inexpensive and does not pose any problems in the subsequent waste water purification steps.

For precipitations adapted to specific production processes, for example, precipitation of barium sulfate, iron sulfide, calcium floride and mercury sulfide, the importance or the difficulties mentioned above varies.

Thus calcium fluoride, for example, despite its very low solubility (15.6 mg/1 or fluoride 7.6 mg/1), because of the competitive nucleus-forming processes, destabilizing processes and flocculation processes, can only be precipitated and separated to such an extent that fluoride concentrations between 40 and 70 mg/litre are considered obtainable in practice in the effluent of a precipitation unit.

In the field of flocculation the auxiliaries formerly used, namely starch and alginates, are only of less importance. Synthetic polyelectrolytes with greater efficacy are employed nowadays. The filtering aids based on acrylamide/acrylic salts are generally anionic and those based on ethylenimine, methacrylic acid or acrylic esters generally cationic. Nonionogenic ethylene oxide polymers with a neutral reaction are also used. The filtering aid quantities generally applied are 0.1 to 2 g/m^3 turbid water or 100 to 200 g/m^3 fresh sludge. Experience has shown that this corresponds to 2 - 20 g filtering aid per kg sludge dry substance.

In practice the following points are important for carrying out flocculation and precipitation in practice; in the first step the precipitant, as far as possible in the ionic form has to be quickly homogenously distributed in the solution. Filtering aids which do not become effective until the subsequent step, can be added at the same time. In the subsequent flocculation chamber macro-flakes form with slight agitation. The mixture flows into settling basins where sedimentation takes place in 1 to 4 hrs. The sludge removed with the aid of sludge scrapers and pumps are of varying concentrations, e.g. 2-5 % dry substance in neutralizing precipitation. In subsequent dehydration on filter presses, screen belt filters or vacuum rotary filters solid contents of 20 - 40 % are obtained. Enviromentally compatible elimination of filtrates and filter cakes must be ensured.

4. ADSORPTION

In many production processes adsorption is employed for the treatment of
aqueous and nonaqueous solutions. Adsorptive purification with the aid of
activated charcoal has found wide application in the preparation of drin-
king water where substances which have to be removed are in very low con-
centrations. Long service lives of the adsorption columns result in low
costs per unit of water treated. Because of the high pollutant concentra-
tions in waste water, treatment with activated charcoal is expensive, so
that competitive processes are usually cheaper to operate. On the whole
the adsorption process has not been attended with the success that had
been hoped for, owing to the many different types of waste water, con-
stituents, their varying adsorbability and the displacement adsorption
which occurs occasionally. Its application has been limited to special
cases. In contrast, adsorption in its wider sense, particularly in combi-
nation with flocculation, is playing an increasing role in waste water
technology.

Adsorption is understood to mean reversible binding of foreign molecules
by means of valency forces and residual valency forces (van der Waal's,
dipolar or partly also ionic forces).

Activated charcoal is currently taken for the elimination of hydrophobic
organic compounds, whilst aluminium oxide is used mainly for hydrophilic
organic pollutants. In the case of filtering aids such as iron salts,
aluminium salts and sodium silicates, when employing the so-called collec-
tor precipitation process, the transition from pure adsorption on the
flake to chemical precipitation in the form of mixed crystal formation is
continuous.

Compared to activated charcoal, distinctly lower adsorption capacities
roughly 1/10 are measured for aluminium oxide, as adsorption of hydrophi-
lic compounds is concerned which are readily soluble in water because of
this very property, and exhibit a lower tendency to adsorption.

Adsorption can generally be described with the aid of the well-known ad-
sorption isotherms of Freundlich or Langmuir, although it has been found
in practice that the assumed reversibility of adsorption is not always
fully operative. The adsorption capacities of the adsorbent can be esti-
mated by first approximation from the adsorption isotherms.

Adsorbents can be applied by the stirring-in or percolation process. Since
in the former case the adsorbent is mixed in powder form with the waste
water and has to be separated at low residual concentrations, the specific
adsorption capacity that comes about at equilibrium is low. The simple
apparatus required for this process is considered an advantage.

In the percolation process the water, whose suspended constituents have
been separated by filtration, is passed through an adsorber column; equi-
librium is then reached at maximum concentrations. The adsorption capa-
city achieved is thus óptimal. As a rule several adsorber columns are
connected in series. When the first is loaded to capacity, it is emptied
and newly charged. Whilst the next columns move up, the fresh one is pla-
ced in the last position. Size and number of adsorption columns depend
on the required residence time, which must be provided for an acceptable
efficiency. For large facilities, so-called moving bed adsorbers are sui-
table, in which the activated charcoal granules are added from above
and the waste water is introduced in counterflow from underneath.

In the case of mixed waste water which contains several different dissol-
ved organic substances, displacement reactions and chromatography effects
take place on account of various adsorption properties on the adsorbent.
Thus the adsorption capacity and purification efficiency of the process
vary within very wide limits. Estimating the adsorption capacity via
adsorption isotherms and kinetics from laboratory tests is virtually no
longer possible. Industrial scale trials are indispensable.

Thermic porcesses are available for the regeneration of activated charcoal
granules: first the loaded activated charcoal is freed from water adhering
to the surface. The residual water content is in the order of magnitude of
up to 50 %, and through the costs of evaporation has a considerable in-
fluence on economical operation. Regeneration takes place at about 850° C
in rotary, multiple hearth or fluidized bed furnaces, the air of combustion
and steam being introduced in the appropriate quantities. Losses occuring
during combustion and losses due to abrasion are between 3 and 10 % in
continuous operation, provided that the process is appropriately control-
led. The results are influenced by the regeneration conditions and among
others the activated charcoal quality, the conveying system and the waste
water composition. Thus it is understandable that losses due to abrasion
up to 15 and 20 % have been mentioned and even such values are to be ex-
pected in practice. The total regeneration costs can amount to 25 to 50 %
of the price of fresh activated charcoal, depending on the type of char-
coal and type of waste water. Regeneration furnaces operate economically
as from an activated charcoal consumption of several tonnes per day.

Regeneration of granulated aluminium oxide, which has so far only been ex-
perimented on a pilot plant scale, is carried out at approximately 650°C.

During a regeneration cycle it is possible for the adsorbent to lose part
of its adsorption capacity. The residual reactivity will depend on the
regeneration conditions, the quality of the adsorbent, the salt content
of the waste water and the type of waste water constituents and has to be
established experimentally.

A few problems arising from the adsorption technology for the subsequent
treatment steps should be mentioned briefly; during the stirring-in pro-
cess very fine particles of the activated charcoal powder remain in sus-
pension in the sedimentation basins and cause the effluent to be grey or
black. If this happens, it is advisable to use filtering aids . Sludges
from this process or from flotation adsorption have to be dehydrated. They
are subjected to thermic combustion or if possible taken to a landfill. In
thermic regeneration processes the off-gas has to be cleaned if the adsorbed
compounds contain sulfur, nitrogen or halogens in larger amounts. Special
attention has to be directed to problems of corrosion protection in the
part of the plant where the waste gas is treated.

5. EVAPORATION OF WASTE WATER

In principle, evaporation is a concentration step within a waste water dis-
posal process, whose final steps, unless re-use is being considered, con-
sist in combustion of the residue of evaporation or taking it to a land-
fill, and biological waste water treatment of the condensates where re-
quired. The main purpose of evaporation is separation of the nonvolatile
constituents of the mixture, in contrast to destillation, in which separa-
tion of the volatiles takes precedence.

For evaporation a considerable amount of heat has to be introduced into
the water. To convert water at $100^{\circ}C$ into the gas phase 2,300 kJ/kg (550
kcal/kg) is required and for heating water at $30^{\circ}C$ to $100^{\circ}C$ - assuming the
efficiency of the evaporator to be 90 % - approximately 630 kJ/kg (150
kcal/kg) this consequently amounts to a total of some 2,900 kJ/kg (700
kcal/kg).

If such a simple procedure is adopted, the operating costs of evaporation
would not be economically justifiable in nearly all cases. That is why
multi-stage evaporators are employed; in these plants the vapours of one
evaporator are used for heating a second evaporator and the vapours of the
second for heating a third, and so on. The theoretical steam consumptions
of a plant consisting of one, two, three or more stages are as follows:
$1:\frac{1}{2}:\frac{1}{3}$, etc. The vapours of the last stage can be utilized for heating the
waste water entering the plant. In order to be able to employ this mode
of operation, differences in the boiling points between the stages are re-
quired, which are obtained by reducing the pressure from stage to stage.
Minimization of the energy costs of an evaporation plant by increasing the
number of stages is countered by higher capital expenditure. Consequently
plants with 4 to 6 stages are rare.

Plants operating particularly economically are complicated and make special demands on the waste water to be treated. Thus fluctuations in the composition of waste water, such as occur frequently, are problematical. Even small quantities of additional constituents, for example, surfactants (foaming) or water hardness constituents (encrustations) will change the evaporation characteristics considerably. Problems of corrosion must be attended to.

If undissolved substances occur in the aqueous medium, evaporator designs with low tendency to encrustation (e.g. thin film evaporators) are suitable. Constituents which form volatile substances, encrustations or resinous deposits due to thermic decomposition can mostly be handled by adopting short residence times or small temperature difference between the heating-up and boiling space (forced circulation evaporator). Special separator designs (centrifugal separators with tangential inlet of the boiling solution) or the use of defoamers are necessary if surface-active substances are contained in the water.

The different evaporator types available can be roughly broken down as follows:

- circulation evaporators (with natural or forced circulation)
- thin film evaporators
- agitation evaporators
- immersion heater evaporators

Forced circulation evaporators are employed, for example, in the evaporation of residues such as obtained in the production of citric acid or ethanol by fermentation, the production of yeast or the production of pulp from wood by the sulfite process. The proportion of evaporable substances here ranges from 3 to 10 %. The residue on evaporation containing, for example, 65 % solids, can mostly be utilized, for instance as animal feed.

In the production of titanium dioxide from ilmenite, iron (II) sulfate solutions in sulfuric acid (21-24 % H_2SO_4) are obtained which are concentrated in immersion heater evaporators.

In all evaporation processes optimum energy utilization is of paramount importance, so that suitable application must be seen in conjunction with the works as a whole where waste heat from adjoining plants can be used to advantage.

6. WASTE WATER COMBUSTION

The term "waste water combustion" is understood to mean the process by which organic waste water constituents are converted as completely as possible into inorganic combustion products by oxidation with atmospheric oxgen at a high temperature, the water itself being completely evaporated.

The air, which is usually preheated, is mixed with fuel - waste water or energy source - and burnt in a flame. Low-energy waste water is injected into the flame of an auxiliary burner.

The shape of the surrounding chamber is adapted to the combustion problems muffle furnaces, rotary furnaces, multiple hearth furnaces or fluidized bed furnaces being used. The energy of the fumes can be used for producing steam or for heating or preheating the air for combustion.

If the content of organic constituents in waste water exeeds 10 %, waste water combustion should be considered as an economically interesting alternative. However, if corrosion and erosion problems are to be expected or, if because of the emission or pollutants, expensive off-gas cleaning is necessary, the specific costs rise steeply. Above all in the case of dilute waste water containing nontoxic, biodegrable constituents, biological waste water treatment can represent a less expensive alternative.

For judging whether a particular type of waste water is suitable for combustion or not, it is advisable to determine the upper calorific value. If the energy requirement for converting a waste water into the gas phase is covered - this applies from calorific value of 2,900 kJ/kg (700 kcal/kg) upwards - this water by first approximation,will not require additional energy for the case being burnt together with other energy sources.

Combustion without additional fuels (supporting fire) is possible in the case of waste water with a calorific value of 8,000 to 12,000 kJ/kg. If air preheating is employed, the energy content can be as low as 6,000 kJ/kg.

Statements about the energy balance of a waste water incineration plant do not in themselves provide a complete survey of the cost situation. It is absolutely essential to check the consequences arising from the presence of the following groups of waste water constituents.

- high-boiling organic compounds generally preclude feeding of the water in vapour form. These compounds have to be introduced in liquid form into the combustion chamber and vaporized there;

- if inorganic salts are present, emission, encrustation and compo-
  sition of the materials of the plant will raise problems. For
  removing aerosols, wet fabric filters, for example, are used.
  Ashes, slag or salt melts must be eliminated in an environmentally
  acceptable way for instance by disposing in a special tip;

- problems of corrosion play an increasingly important role if acids
  or alkalis are active;

- suspended solids have to be taken into consideration when deciding
  on the metering equipment;

- relatively large sums have to be spent on fume cleaning if the
  waste water constituents contain sulfur, nitrogen or halogens,
  whose oxidation products have to be removed under the existing regu-
  lations governing emissions. This applies also to dust. The follo-
  wing emission limit values, related to a content of 11 percent by
  volume oxygen in the fumes are prescribed in the Federal Republic
  of Germany: carbon 50 mg/m^3; dust 100 mg/m^3; carbon monoxide 100
  mg/m^3; inorganic chlorine compounds as chloride 100 mg/m^3; inorganic
  fluorine compounds as fluoride 5 mg/m^3.

The combustion chamber is generally preferred in the chemical industry.
It can be horizontal, inclined or vertical. Fuel and waste water are intro-
duced into the chamber by burners (multi-fuel burners or lances), if ne-
cessary at several points of the chamber, whilst the air can be introduced
both into the burner (primary air) and in the form of secondary air (e.g.
annular pipe). The size of the chamber should be such that the residence
time of the fumes is sufficient for complete combustion. Temperatures
over 800°C are necessary to achieve this.

The fluidized bed furnace is distinguished by rapid and intensive exchange
of materials which takes place in a layer of granulated, inert heat car-
riers. Fresh air, partly also the fumes formed during combustion, keep
the particles in suspension. Inorganic salts in the waste water can result
in the formation of melts on the fluidized bed which lead to adhesion,
caking and finally the collapse of the fluidized bed. An important appli-
cation of fluidized bed furnaces is the combustion of concentrated spent
wood pulp liquors.

The rotary furnace is employed for the incineration of heterogeneous mat-
ter. Complete combustion is ensured in a subsequent combustion chamber by
way of the residence time, excess oxygen and temperature.

7. WET OXIDATION

Organic waste water constituents are also oxidized by the so-called wet oxidation process. This is understood to mean the oxidation of organic substances in aqueous phase with dissolved atmospheric oxygen at temperatures from 150 to $370^{\circ}C$ and pressures between 10 and 220 bar. Thus no water has to be converted to the gas phase in this process.

The waste water is transferred by means of high-pressure pumps via heat exchangers into a reactor and mixed with compressed air, usually in one of the heat exchangers. The heat given off during oxidation is utilized for heating the starting materials (waste water and air). The gas and liquid phase are separated in a separator.

In the low-pressure process temperatures of 150 to $170^{\circ}C$ and pressures of 10 to 20 bar are used, but only low degrees of oxidation from 5 to about 15 % are achieved. The process is also used for the conditioning of sludge in the industrial sector. Besides the difficulties described below there are additional problems of a nuisance due to strong smells.

The high-pressure process takes place at temperatures between 200 and $300^{\circ}C$ and pressures between 100 and 220 bar. High degrees of oxidation of 80 to 90 % are only attained at higher temperatures, approximately between 250 and 300 $^{\circ}C$. The efficiency depends on the type of waste water constituents, the pH and the use of catalysts, if any. The residence time in the reactor is normally between 30 minutes and one hour, depending on the type of waste water and the desired cleaning effect.

Wet oxidation facilities have so far been used in the industrial sector only for a few special types of waste water. A plant for the cleaning of black liquor from pulp production by the sodium hydroxide process has been in operation for 10 years. The degree of oxidation is some 90 % at $300^{\circ}C$ and 220 bar. Waste water types from acrylonitrile production that are difficult to treat biologically are purified by wet oxidation in Japan.

When designing a wet oxidation plant, problems of corrosion, encrustations in heat exchangers and the desired efficiency are the decisive criteria. Only heavily polluted waste water types are suitable for wet oxidation, with a COD of above 30,000 mg/litre. As wide temperature fluctuations are difficult to control, the pollution and quantity of waste water entering the plant must be uniform. For this reason sufficiently large buffer vessels are provided.

In the project planning stage a wet oxidation plant may appear to be a very favourable solution on account of high throughputs and a low energy requirement. However, because of the high temperatures required, problems of corrosion have to be kept under safe control. This means in most cases that high-quality materials have to be used, such as special steels (steel 316), Hastelloy C or titanium.

Often no reliable statement can be made about service lives. Corrosion may occur not only in the reactor but also on the surfaces of the heat exchangers which are several times as large. Thus the risk of using this process in the presence of salts, particularly chlorides in the waste water, is rarely accepted.

8. ULTRAFILTRATION AND REVERSE OSMOSIS

Ultrafiltration and reverse osmosis are process steps for concentrating dilute solutions with the aid of membranes which, depending on the pore size, retain larger particles in the concentrate and permit the solvent water with a proportion of smaller particles to pass through the permeable layer. In the ideal case the process is reversible and the energy consumption consequently minimal.

Reverse osmosis is the enrichment of electrolytes or low molecular weight organic compounds at pressures up to about 100 bar and particle sizes from about 5×10^{-7} to 10^{-6} mm; by means of ultrafiltration high molecular weight substances with particle sizes approximately from 10^{-6} to 10^{-2} mm are concentrated at low pressures - preferably 3 bar. In practice in the field of waste water treatment only ultrafiltration has been used.

By the application of pressure in ultrafiltration the raw solution is applied to the ideally very large surface of a very thin membrance. The membrane itself has a thickness of 0.2 to 0.5 μm, rests on supporting fabrics and is housed in exchangeable units, so-called modules. Pipe, tube or plate modules are currently preferred in ultrafiltration. The membranes are usually made of cellulose acetate, polyamide and polysulfone.

The facilities consist of a pump, which raises the pressure of the waste water to the desired value, a fine filter for removing particles which would clog the membrane, mostly of several modules and a control valve which regulates the discharge of the concentrate while maintaining the operating pressure. The solution, which is under pressure, can be circulated by means of separate pumps, providing high flow rates so as to prevent deposits and polarization due to high concentrations.

The economics of the process are decisively influenced by high capital expenditure, repair costs and the service life of the modules. Thus the process must not be judged unilaterally from the aspect of its favourable energy consumption.

In electrodeposition of paints, spent baths used to be obtained which had to be purified by precipitation before discharge into the sewer. Nowadays by means of ultrafiltration it is possible to concentrate the bath liquors, while simultaneously recovering a substantial proportion of the paint, namely up to 15 % of the amount used. In addition, by using the permeate the paints are returned from the treated parts to the electrodeposition tank.

Oily emulsions containing approximately 1 % emulsified oil can be concentrated with the aid of ultrafiltration to a content of 40 to 50 %; the concentrates are usually burnt.

Whey is produced during cheese manufacture; by means of ultrafiltration it can be converted into animal feedstuff with a protein content of 20 to 30 %.

9. EXTRACTION

Substances can be separated from waste water by means of extraction techniques, the favoured solubility of these substances in the solvent being utilized . Besides the extract with the concentrated substance, a depleted solution - the refined product.- is produced, which contains the extractant in a proportion corresponding to its solubility in water. The solvent can, if required, be recovered for example, by stripping.

It is essential for extraction that the extractant and waste water are intimately mixed, namely until the solubility equilibrium has come about, that separation of the two phases into an extract layer and a refined product layer proceeds without disturbances and that the substances to be extracted have as high as possible a distribution coefficient in the solvent.

There is no known case of an extraction unit having been used as the final step of a waste water treatment facility in practice.

A multi-stage counter-current extraction unit is commonly used as an inexpensive variant.Extractors based on the mixer-settler principle, extraction centrifuges or packed extraction columns are used as alternatives for this purpose.

The extraction of phenol from gas condensates of coking plants - an example from practice - can be considered a true waste water treatment process, since the phenol produced does not provide a profit but only partially covers the costs. The benzen-alkali process is preponderantly used and in some plants the Phenosolvan process.

In the former process benzene as the solvent is used in packed columns in counterflow to the waste water and the extract regenerated with sodium hydroxide solution. The benzene is recycled. The efficiency of the phenol extraction ranging from 92 to 94% can be increased to 98 % by means of a Podbielniak extractor (extraction centrifuge).

Diisopropyl ether is currently used in the Phenosolvan process.After a ten-step extraction the extract is distilled. The efficiency is about 99 %.

Gas condensates contain only up to 50 % phenols alongside 50 % other organic substances, such as cyanides, pyridines, rhodanides, ammonium and sulfur compounds which remain in the water and have to be eliminated in a

biological waste water treatment plant.

In addition to phenol extraction, the extractive recovery of chlorophenol from waste water has been employed; trichloroethylene is used as the extractant for this purpose.