

CHAPTER 20

WASTE WATER FROM THE INORGANIC CHEMICALS INDUSTRY

CHARACTERISTICS OF THE WASTE WATER

The waste water from the inorganic chemicals industry obviously varies greatly from plant to plant. This makes it very difficult to give any general picture. The mineral acid industry and the fertilizer industry will be dealt with in this chapter. These two industries have special problems since the waste water of the former has a very low pH and that of the latter industry high concentrations of nutrients such as nitrate, ammonium and phosphate. However, it is possible to distinguish three general cases:

1. The waste water contains relatively harmless pollutants in acceptably low concentrations. In this case the waste water can be discharged into the receiving water without any treatment. For example, it is harmless to discharge 1% sodium chloride solution into a river with a water flow 100 times greater than the waste water flow.
2. The concentration of pollutants in the waste water is too high to permit direct discharge but, on the other hand, the concentration is too low to allow recovery of the components of the waste water.
3. The concentration of the impurities is sufficiently high to make recovery profitable. In this context it should be considered that recovery gives three advantages:
 - a) The recovered materials have a certain value.
 - b) The waste water treatment costs less.
 - c) A proportion of the water can be recycled, which decreases the cost of the process water.

Survey of the methods of treatment

As the composition of the waste water varies considerably, it is necessary to have a wide range of methods for treatment of waste water from the inorganic chemicals industry.

The most important methods are as follows:

1. Flocculation is used to remove colloidal impurities.
2. Precipitation is used for the removal of almost all types of metal ions except the alkaline earth metals.
3. Sedimentation is used in conjunction with flocculation and precipitation.
4. Neutralization is a rather simple, but absolutely necessary treatment process when the waste water has a pH other than 6-8. Often the addition of acid or alkali is automatically regulated. The most commonly used alkali is calcium hydroxide and the acid, sulphuric acid or carbon dioxide.
5. Reverse osmosis or other membrane processes are often used for recovering valuable materials.
6. Oxidation-reduction processes are used when the waste water contains compounds such as cyanide, chromate, sulphite etc.

Fig. 20.1 shows a treatment which includes the recovery of valuable chemicals.

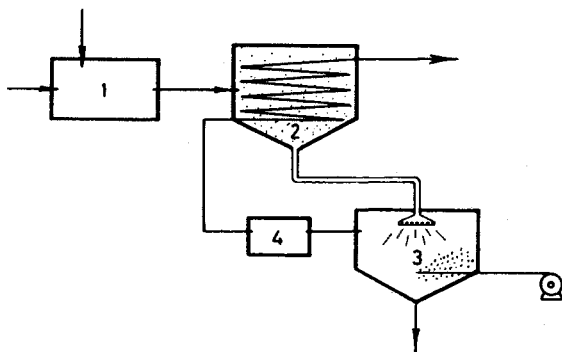


Fig. 20.1. Recovery of chemicals: After the waste water has been neutralized (1), it is concentrated in a drying chamber(2). (3) is a spray dryer. The heat capacity of the evaporated water is used (4) in the drying chamber (2).

After the waste water has been neutralized by sulphuric acid or sodium hydroxide it is concentrated in a drying chamber until the concentration of dry matter is approximately 50%. It is then spray-dried in an incinerator where the organic impurities are combusted. Molten inorganic chemicals will be deposited on the wall of the incinerator and can afterwards be collected and re-used. If the waste water contains only a relatively small concentration of the valuable components, it might be possible to make the recovery profitable by use of a heat exchanger before the drying chamber.

Waste water from the production of sulphuric acid

The degree of acid pollution from a sulphuric acid plant depends in principle on the efficiency and condition of the coolers, particularly the cooling water flows under pressure through lead pipes. In addition to the cooling waters the wastes may contain water from the rinsing and washing of various pieces of equipment and rooms. They may also contain pollutants from washing the gases from ore roasting.

The average composition of the total waste water from a sulphuric acid plant is shown in Table 20.1.

TABLE 20.1

Composition of waste water from sulphuric acid production

Property	Tower process	Contact process
pH	3-7	3-7
Alkalinity	1-2	1-2
Acidity	6-8	10-16
Total solid (mg/l)	200-500	200-600
BOD ₅ (mg/l)	15-25	4-15
Suspended solid (mg/l)	5-50	30-120
Colour	yellowish	yellowish

The primary effect of the discharge of the waste water will be the pH reduction. The limiting values for pH are between 6.0 and 6.5, which for the majority of freshwater organisms is too low. If the appropriate pH of the receiving water is not maintained there is a definitely unfavourable effect on the rate of the self-purification processes in the water, which again limits their utilization for municipal purposes.

Acidic waste water must not be discharged into the common sewer system unless it has been neutralized. Concrete pipes are particularly susceptible to corrosion (Taylor et al., 1947).

The neutralization method is generally used to eliminate the harmful effect of acidic waste water. Because of the variation in acidity the pH should be controlled automatically. Instead of adding alkali it is also possible to carry out the neutralization on a basic bed (limestone, dolomite) (Gehm et al., 1944).

Waste water from production of hydrochloric acid

The effluent from the production of hydrochloric acid generally contains 2-10 mg HCl/l. Small amounts of sulphuric acid may also be present and certain quantities of mineral oils. The amount of water is 10-15 m³/ton of acid produced. Neutralization of the waste water which contains hydrochloric acid as main constituent should not create great difficulty.

The removal of suspended matter should precede feeding the waste water to the basic bed (limestone or dolomite).

The fertilizer industry: nitrogen compounds

Waste water from plants producing nitrogen fertilizers includes cooling water (80-90% of the total quantity of water) coming into direct contact with the process gases, waste water which has not had such contact, and waste water from washing of floors and equipment, garages, auxiliaries, shops, etc.

The cooling and purification of gases from the synthesis of ammonia contains carbon dioxide, hydrogen sulphide and suspended solid as the chief pollutants. The quantity of waste water is 40-50 m³/ton of ammonia.

The waste water from the manufacture of nitric acid contains nitric and sulphuric acids as the main pollutants, about 3 g/l. Between 80 and 90 m³ of waste water are produced per ton of acid.

The chief pollutant in the production of ammonium sulphate is ammonia, and the quantity may reach 3 g/l of ton of ammonium sulphate produced.

Nitrate (200-250 mg/l) and ammonium (10-20 mg/l) are the chief pollutants from the production of calcium nitrate. Here the consumption of water is 5-15 m³/ton of salt produced.

A general feature of the composition of the waste water from the fertilizer industry is that it has a low BOD_5 , but it has an extremely high concentration of nitrogen compounds. Table 20.2 gives an analysis of waste water from a factory producing ammonium nitrate, urea and ammonia (Foster, 1969).

TABLE 20.2

Analysis of waste water from a factory producing nitrogen fertilizers

pH	8
Ammonium nitrogen (mg/l)	2500
Nitrate nitrogen (mg/l)	10000
P (mg/l)	2
COD (mg/l)	100

The treatment methods for this type of waste water must take into consideration the large concentration differences which characterize this waste water.

Since the concentration of nitrogen and the nitrogen/ BOD_5 ratio is much higher than generally met with in municipal waste water plants, biological treatment is less attractive.

The LF value (see chapter 11) for waste water from the manufacture of nitrogen fertilizers is 0.25-0.32. Furthermore, the biological activity of an activated sludge plant decreases with a decreasing BOD_5 /nitrogen ratio.

The application of biological treatment methods to these types of waste water is not to reduce the BOD_5 number, but rather to reduce the concentration of nitrogen, particularly ammonia. In other words, the biological treatment method utilizes the nitrification process. Two main parameters play an important role in determining the efficiency of the nitrification process (Johnson et al., 1964).

1. The LF value, which should be less than 0.4. This value can be achieved by maintaining a low flow. Generally, there is a linear dependence with negative slope between the efficiency of the nitrification process and the logarithm of the flow rate. This is demonstrated in Fig. 20.2.
2. The ratio between carbon and nitrogen in the waste water plays an important role in the efficiency of the nitrification process. This can also be seen in Fig. 20.2 by comparing plots 1 and 2 (Barth et al., 1968).

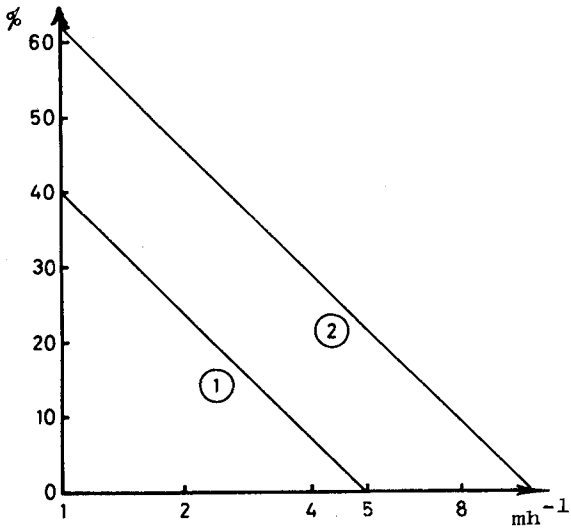


Fig. 20.2. Efficiency of the nitrification process plotted to the flowrate by (1) 1500 mg/l HCO_3^- and (2) 3000 mg/l.

However, the amount of nitrogen which can be removed per m^3 is limited. This is illustrated in Fig. 20.3, where it is seen that it is not possible to remove more than 21 mg/l per 24 h even the ammonium concentration in the inflow is increased to about 1000 mg/l.

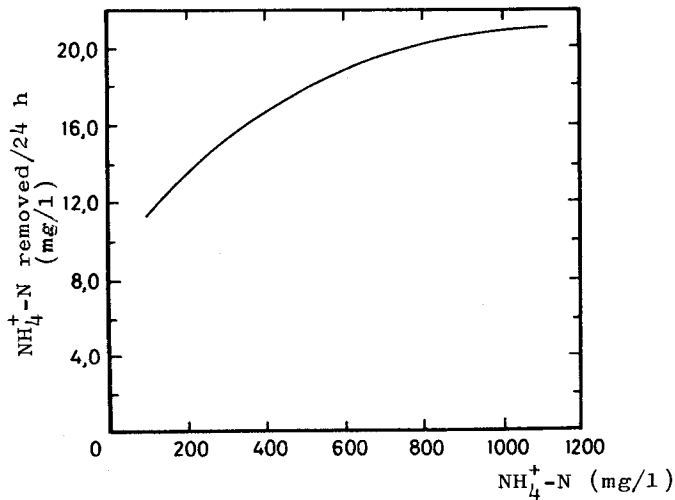
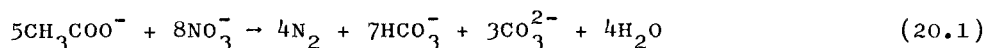


Fig. 20.3. Ammonium removal per 24h plotted to concentration.

By using denitrifying bacteria it is possible to remove nitrate. If acetate is used as carbon source the process is:



This process requires anaerobic conditions since nitrate is the oxygen source. As there is not sufficient carbon present in the waste water from the fertilizer industry, it is necessary to add a carbon compound, methanol or acetate often being used.

Fig. 20.4 illustrates the influence of the $\text{COD}/\text{NO}_3\text{-N}$ ratio on the denitrification efficiency. The plots shown in this figure are based on experiments for the denitrification of waste water from the manufacture of nitrogen fertilizers.

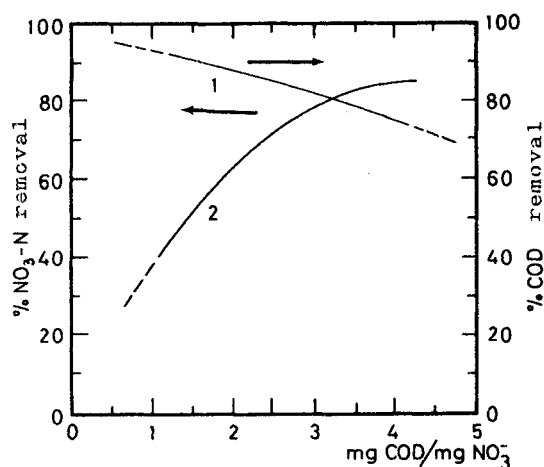


Fig. 20.4. Efficiency plotted to the ratio $\text{COD}/\text{NO}_3\text{-N}$.

The denitrification efficiency as a function of the retention time is shown in Fig. 20.5. As seen, a minimum of 10 days retention time is required for the anaerobic denitrification process. However, the ratio between COD and the nitrate, which is removed, decreases with increasing retention time (see Fig. 20.6).

Ammonium ions can also be removed from waste water by a stripping process. On addition of air the following process occurs:



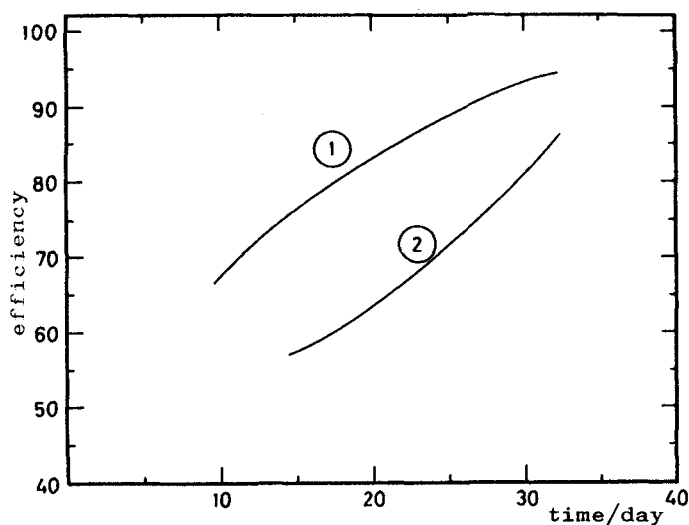


Fig. 20.5. Denitrification efficiency plotted to retention time. (1) COD removal and (2) denitrification.

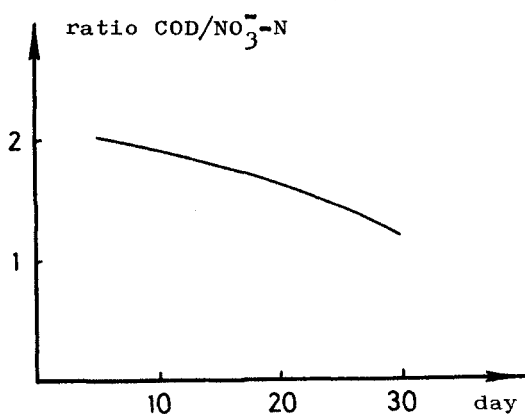


Fig. 20.6. Ratio COD removal per unit of time to NO₃⁻-N. Removal per unit of time plotted to retention time.

As the pK_s for ammonium is about 9.3, a pH of about 10.5 or above is required for complete transformation of ammonium ions to ammonia.

The efficiency of the ammonia removal increases with increasing quantity of air, as discussed in chapter 10.

Fig. 20.7 shows the results of reverse osmosis applied to the waste water, analyzed in Table 20.2. Polyacetate membranes are used.

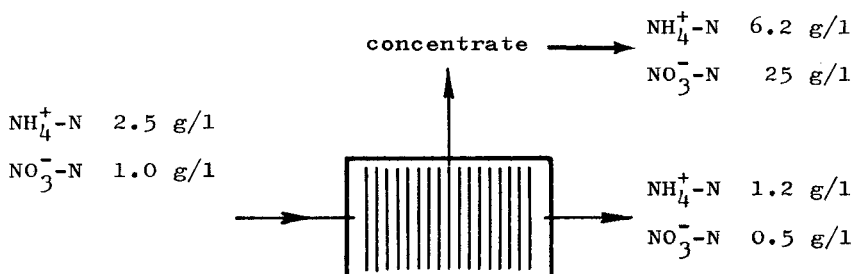


Fig. 20.7. Results of reverse osmosis.

The results are in most cases not acceptable and reverse osmosis is probably not the right answer to the waste water problems of the nitrogen fertilizer industry.

Ammonium ions can be removed by ion exchange as demonstrated in chapter 7. Table 20.3 gives the result of cation and anion exchange on waste water containing nitrate and ammonium ions.

TABLE 20.3

Ion exchange

	NH_4^+ nitrogen (mg/l)	NO_3^- nitrogen (mg/l)
Inflow	360	250
Outflow	10	1

A zeolite type cation exchanger is used while the anion exchanger is a strong basic macro-porous anion exchanger.

The eluate from the combined ion exchangers can be directly used as fertilizer. Ammonium nitrate is produced by evaporation of the solution. The product can partly pay for the cost of the ion exchange process.

Ammonium ions can be precipitated as heavy, soluble magnesium ammonium phosphate. The stoichiometric amount of phosphorus must be present and magnesium sulphate is added as precipitant.

Fig. 20.8 shows the efficiency for the removal of ammonium by precipitation of magnesium ammonium phosphate at different pH values. A pH of 10.0 is preferred.

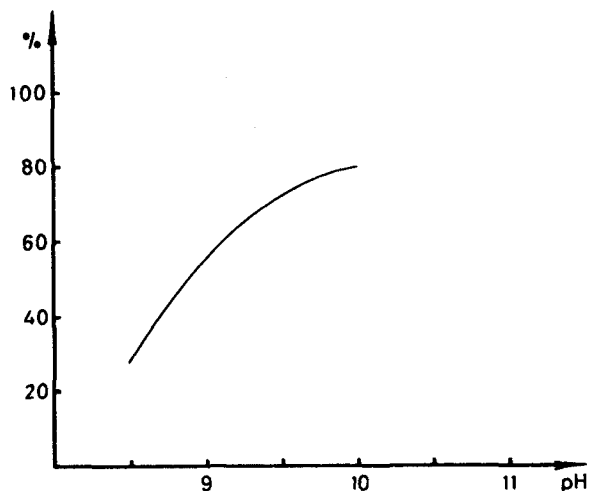
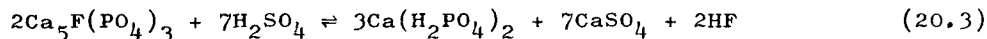


Fig. 20.8. Efficiency of ammonium removal by precipitation as a function of pH.

The fertilizer industry: phosphorus compounds

The production of superphosphate is based upon the following reaction:



Hydrogen fluoride and silico fluoric acid are evolved during the process of dissolving the phosphorite. These constituents are removed from the acidic highly toxic gases by washing the water and drying in a closed condenser. The waste water from these processes is usually acidic, clear and colourless.

If the superphosphate production is combined with the manufacture of sodium fluorosilicate, the amount of waste water is larger. However, sodium fluorosilicate is easily separated from the precipitated silicic acid gel by sedimentation, because the fluorosilicate settles almost ten times as quickly as silicic acid.

The characteristics of waste water after the recovery of sodium silicofluoride are illustrated in Table 20.4.

Table 20.4

Analysis of waste water from superphosphate production

pH	8-9
NH ₄ -nitrogen (mg/l)	10
NO ₃ -nitrogen (mg/l)	0
P } (mg/l)	800
COD (mg/l)	150

Since biological treatment only removes smaller amounts of phosphorus, it is not feasible to treat waste water from the manufacture of phosphorus fertilizers by biological treatment methods.

The methods used for this type of waste water are mainly precipitation and ion exchange.

Phosphorus can be precipitated from waste water by using aluminium sulphate, iron(III)chloride and calcium hydroxide (see chapter 3). An efficiency of 90% can easily be achieved.

Apart from the phosphorus compounds found in municipal waste water all the phosphorus is present exclusively as orthophosphate, which can easily be removed effectively from this type of waste water, since aluminium phosphate, iron phosphate and calcium phosphate have a very small solubility.

Table 20.5 shows the efficiency which can be obtained by use of ion exchange on waste water from the manufacture of phosphorus compounds.

Table 20.5

Ion exchange

Inflow	800 mg P/l
Outflow	15 mg P/l

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