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4.10 Responsible water use – The example of BASF AG Ludwigshafen

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SUMMARY: *BASF places a high priority on the responsible use of water resources. Efficient processes as well as optimised treatment of wastewater minimise emissions into the Rhine. This is achieved by using a combination of process-integrated technologies in the production process (prevent, reduce and reuse), decentralised wastewater pretreatment processes, and downstream wastewater purification in the central treatment plant (end-of-pipe). The success and constant improvement of this system are illustrated by the example of wastewater generation trends, as well as by the reductions in the pollution loads of TOC, ammonium-nitrogen and EDTA.*

This article presents the main options and processes available for the reduction of wastewater pollution levels, and provides specific examples of the measures implemented. One example is provided of each of the following: a process-integrated wastewater prevention measure, a recovery process for potentially recyclable materials, a decentralised wastewater pre-treatment process, and centralised end of pipe treatment in the treatment plant.

Water is essential for chemistry. Water serves as a reactant and solvent in chemical processes, is used for cooling and to generate steam, and is of great importance when it comes to supplying our locations with raw materials and shipping our products.

The sections that follow provide a description and explanation of how water resources are used responsibly, using BASF AG's Ludwigshafen production site as an example.

Ludwigshafen Verbund site of BASF Aktiengesellschaft

The Ludwigshafen Verbund site is the largest integrated chemical manufacturing complex of BASF. About 8,000 commercial products are manufactured at the site for delivery to customers in over 170 countries.

World-wide, BASF operates six integrated sites and over 100 production sites near to its clients. At our integrated sites, production operations, power use, waste flows, logistics and infrastructure are all integrated into networks. This system makes it possible to conserve resources during chemical manufacturing processes by optimising energy consumption and maximising production. The integration of production plants within this type of complex results in efficient value chains from basic chemicals to highly refined products such as paints or crop protection products. In addition, the by-products from one plant can be used as raw materials in another. The production facilities are connected by a dense network of pipelines. These pipelines are an environmentally friendly way of transporting raw materials and energy sources quickly and safely to their destination.

Production-related

Environmental Pollution Integrating the Ludwigshafen site creates favourable environmentally friendly production conditions. The chemical manufacturing process generates emissions and waste. For every metric ton of sales product manufactured by BASF AG in 2005, an average of 4.8 kilograms of emissions and waste was generated. Comparison with the data for 1996 reveals that constant improvements have led to a 47% reduction in production-related environmental pollution (*Fig. 4.10-1*).

Environmental pollution is estimated from the amount of non-reusable waste which has been properly disposed of, the organic effluent pollution load, and the air pollutants emitted. In 2005, BASF AG manufactured about 8.9 million tonnes of sales product.

In the past, the reduced levels of production-related

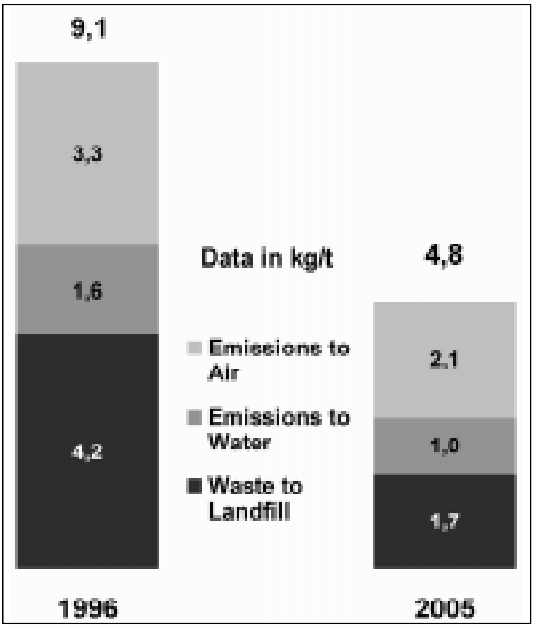

Fig. 4.10-1: Production-specific environmental impact per metric tonne of sales product (BASF AG, Ludwigshafen, 1996 and 2005).

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environmental pollution were primarily attributable to the use of retrofitted environmental protection systems such as waste gas and wastewater purification equipment and waste incinerators. In the 1990s, effective use was made of the concept of »prevent, reduce and reuse« to supplement these retrofit systems by aiming to reduce the generation of waste and emissions while processes and facilities were still in the planning stages. This concept of so-called »production-integrated environmental protection« will continue to gain in significance in the future and to enhance the end-of-pipe processes. BASF's goal is to limit environmental impact through the most effective possible combination of these two approaches.

Water requirements, use, and discharge

Of particular importance when examining how the Ludwigshafen site obtains its water supply and discharges its wastewater is its location on the river Rhine. As a water resource, the Rhine is one of the most vital lifelines of the site. In addition, since purified wastewater is discharged into the Rhine, the river is an important point of interface between chemical manufacturing operations and the environment.

BASF AG's water requirement in 2005 was 1.369 billion cubic metres, 98% of which was river water taken from the Rhine. Most of this water is used in sealed piping systems for cooling during manufacturing processes and is discharged uncontaminated back into the Rhine. Internal cooling circuits also make it possible for 485 million cubic metres of water to be used repeatedly, and thus for the amount of water taken from the river to be reduced.

A smaller amount of the water (7%) is used directly in the production process. Polluted water from production operations, municipal sewage and site domestic sewage are sent for purification to BASF's own central wastewater treatment plant (WWTP).

The amount of groundwater consumed is less than 2% of the total water requirements. The groundwater is pre-processed, and equal amounts are then used to generate steam and for production processes. The requirement for potable water is less than 0.2% of the total amount of water used.

Wastewater equipment and management

Background

Until the start of the 1970s, BASF discharged wastewater from the Ludwigshafen site untreated into the Rhine. Polluted production wastewater and unpolluted cooling water were mixed and discharged via a common drainage network.

In 1974, the wastewater treatment plant was brought into service. This was preceded by a great deal of planning, testing, and design work. In order to ensure a manageable hydraulic loading rate, the polluted and uncontaminated water had to be separated and carried in a split drainage system, with the contaminated water carried to the treatment plant for purification and the unpolluted water discharged directly into the Rhine.

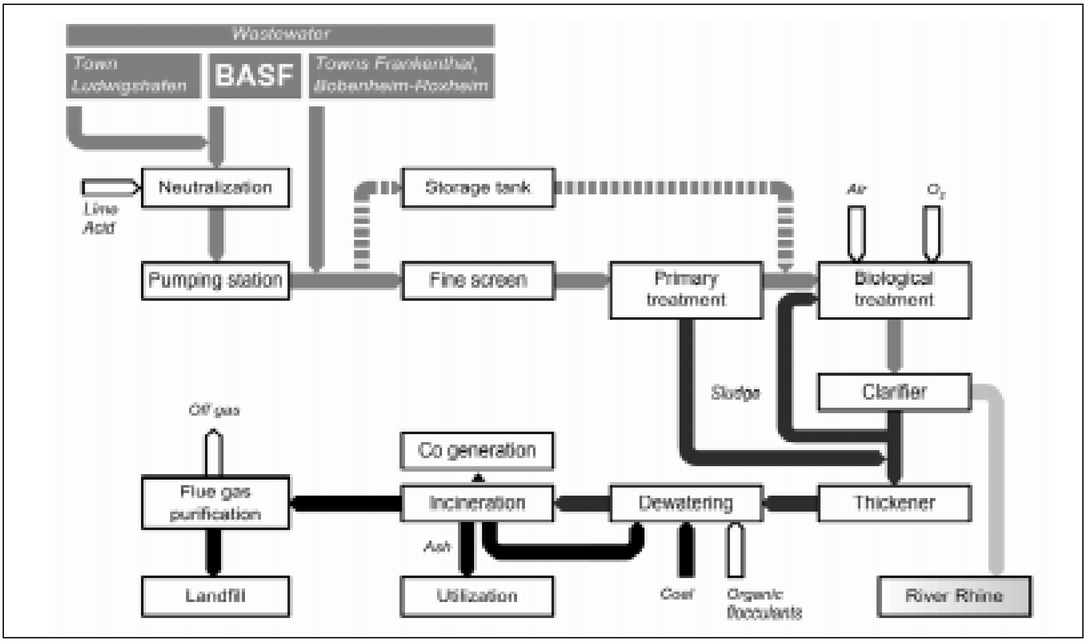

Fig. 4.10-2: Process flow chart of the central wastewater treatment plant (BASF AG, Ludwigshafen).

Central treatment plant

Centralised biological wastewater treatment remains the heart of the wastewater purification process at the Ludwigshafen site.

BASF's treatment plant is one of the largest in Europe. The plant could be used to purify wastewater for 6–7 million people. As the flow chart in *Fig. 4.10-2* shows, after neutralisation solids are first removed in a primary treatment. The wastewater then comes into contact with the activated sludge in the biological treatment tanks and is aerated with air and pure oxygen. The pollutants in the wastewater are broken down by microbes or adsorbed to the surface of the sludge. Feeding in a large amount of oxygen also makes it possible for nitrifying bacteria to grow. These bacteria oxidise ammonium-nitrogen to nitrate, which is also eliminated in a further step. In a subsequent separation step (clarifier), the activated sludge is settled out of the purified wastewater and the water is discharged into the river Rhine.

The activated sludge is recirculated in the treatment process. Excess amounts are separated out (thickener, dewatering) and disposed of in the treatment plant's own activated sludge incinerator. By co generation electricity and heat is gained from the incineration process.

Patterns in the emission of various materials in wastewater discharged into the Rhine

Since the central wastewater treatment plant began operating in 1974, the treatment process at the Ludwigshafen site has undergone a variety of modifications and upgrades. *Fig. 4.10-3a-d* contain data for some representative parameters, and show how successful this process has been. Thus, it can be seen from the above figures that the wastewater flow rate requiring treatment in the central treatment plant was reduced from 675,000 m³ per day in 1987 to 333,000 m³ per day in 2005.

The total amount of organic compounds released into the Rhine via the outflow of the treatment plant measured as TOC (Total Organic Carbon) was cut from over 40 tonnes per day in 1978 to 8 tonnes per day by 2005. The level of ammonium-nitrogen discharged into the Rhine was also drastically reduced. While 63 tonnes was being discharged per day in 1976, the current level is 0.6 tonnes per day.

We selected EDTA (Ethylenediaminetetraacetic acid) to provide an example of how the pollution load of a compound that is difficult to biodegrade can be reduced. It has also been possible to reduce the EDTA emission to the Rhine significantly, from 1,830 kg per day to 51 kg on an average per day.

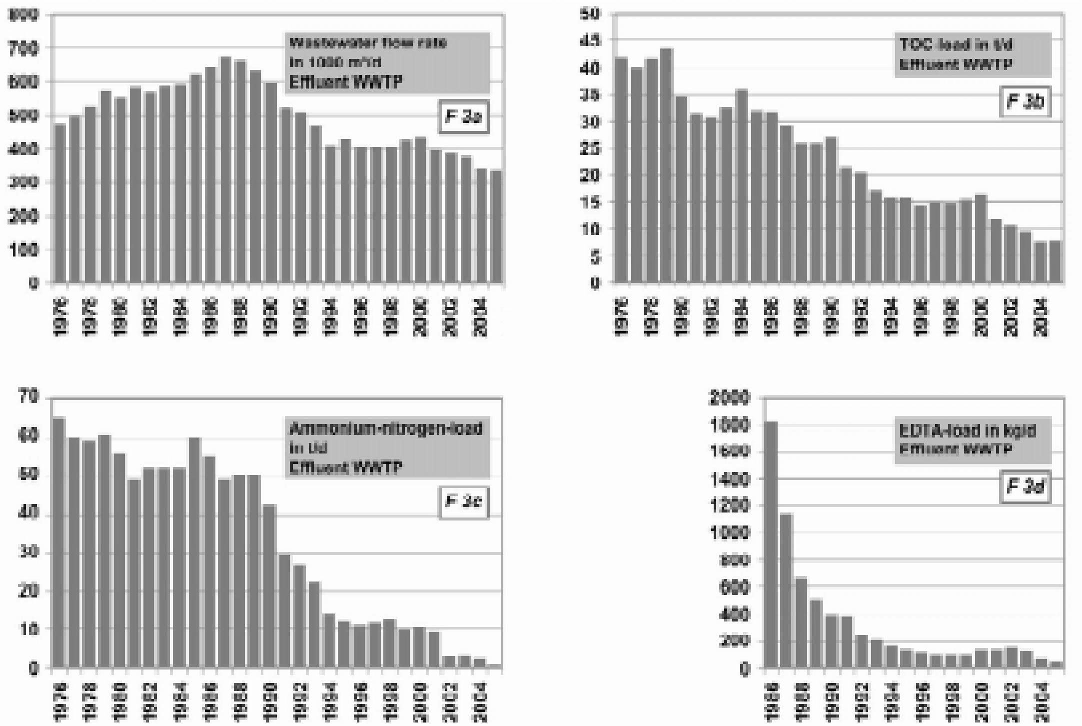

Fig. 4.10-3a–d: Trend of wastewater key parameters at the effluent of the central waste water treatment plant of BASF AG, Ludwigshafen (Wastewater flow rate, TOC-load, Ammonium-nitrogen-load and EDTA-load).

Measures to prevent and reduce water pollution

Overview, principles and examples of processes

The success in reducing the amount of water requiring treatment and cutting pollution loads discussed in Section 6 are the result of tailored combinations of measures starting with the production process and including the targeted, decentralised pre-treatment of individual wastewater streams and the centralised treatment of the wastewater as a whole in the treatment plant (end-of-pipe). *Fig. 4.10-4* summarises the possible combinations of the various processes.

Of particular importance are process-integrated measures, the use of which will ideally prevent any polluted wastewater at all from being generated (wastewater-free production processes). However, for chemical and technological reasons, these types of processes are only an option in some cases. They often require a great deal of research and development.

Very close to the production process and therefore still regarded as process-integrated are those procedures that make it possible for potentially recyclable materials to be directed back into production. This includes all of the physical procedures used to concentrate and/or recover and if necessary, to purify potentially recyclable materials. Examples of these so-called »concentration processes« include adsorption to and desorption from suitable adsorbents, distillation and extraction, filtration or membrane processes. A typical example of this type of process is the recovery and recycling of solvents.

Any wastewater materials that cannot be directed back into the production process must be tested for sufficient elimination in a biological treatment plant. If they cannot fulfill the requirements, pre-treatment may be an option. Pre-treatment involves chemically transformation the compounds in wastewater in order to improve their biodegradability. Pre-treatment processes include methods using high temperatures and pressure, such as thermolysis, wet oxidation, or oxidation using powerful oxidants such as ozone and hydrogen peroxide with catalytic activation. Under these circumstances, laboratory testing and half-scale pilot plants are used to select the processes to be used and determine the optimal process conditions. In making these decisions, primary consideration must be given to the overall effect of the combined pre-treatment and end-of-pipe treatment process.

If the required target level of purification cannot be achieved even using a combination of pre-treatment and end-treatment, the method of last choice for wastewater treatment is incineration, either directly or after an upstream concentration process.

Clearly, the development of a suitable and optimal conceptual design for wastewater prevention and treatment

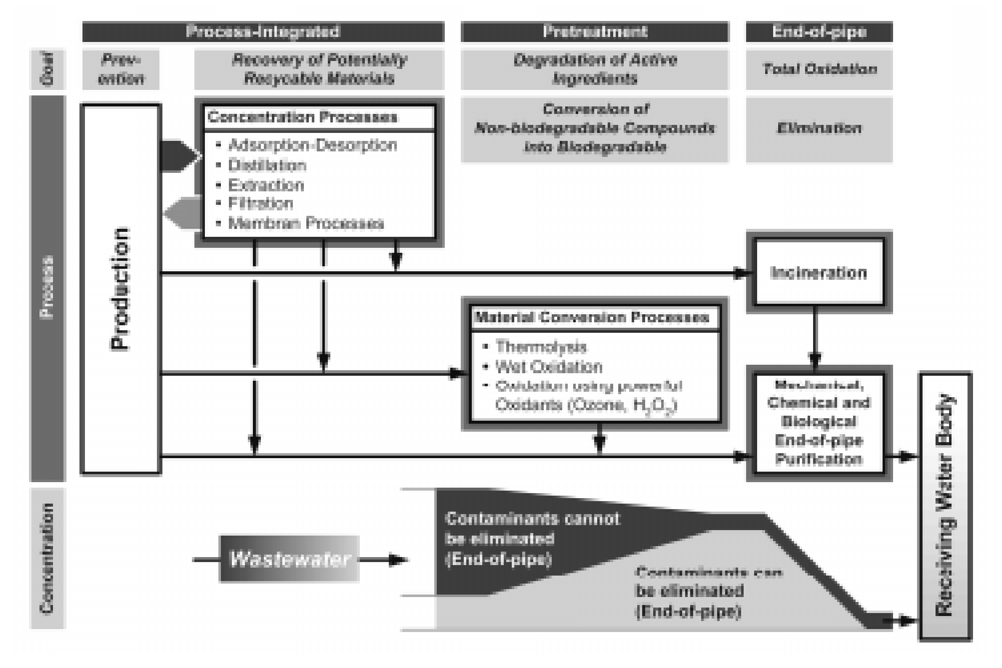

Fig. 4.10-4: Overview scheme for process integrated steps concerning recovery, decentral pretreatment and end-of-pipe treatment of waste water.

from the production process to end-of-pipe treatment is a complicated undertaking, requiring the balanced assessment not only of technical feasibility, but also of economic and environmental factors. In the case of complex processes with a number of possible options, the »eco-efficiency analysis« tool (KERN et al. 2006) could help to identify the best solution.

It would definitely be beyond the scope of this article to list all of the possible wastewater prevention and reduction processes available to the chemical industry and provide details for each. The reader must rather be referred to the relevant technical literature.

In order to describe in more detail the processes and process combinations summarised in *Fig. 4.10-4*, the following sections provide some examples of the measures that have been implemented at the Ludwigshafen site.

Example of a process-integrated solution: Wastewater-free production process for isooctene

Isooctene, an important product used in the chemical industry in the production of plasticizers, was previously manufactured by homogeneous catalysed synthesis. In this process, the catalyst was dissolved in the reaction medium, and was then released together with the converted raw product. The catalyst could no longer be used for further synthesis, and was mixed with water to exclude any risk of fire. This procedure caused a highly wastewater pollution.

By further developing the technology, a heterogeneous (i.e. solid) catalyst was found that remains in the reaction chamber. The generation of wastewater contaminated with a high concentration of organic material is thus prevented. The wastewater load of the plant was reduced by more than 97%. Waste generation was also reduced since the solid catalyst could be used for longer periods.

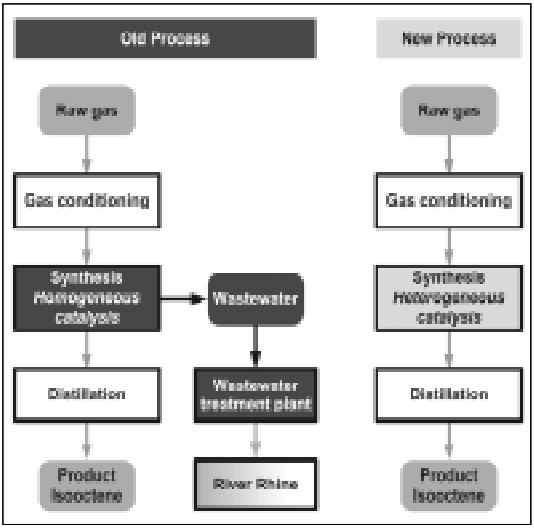

Fig. 4.10-5: Process modification for Isooctene production to avoid wastewater.

Example of a material conversion process: Pre-treatment of wastewater from the EDTA production process by catalytic oxidation with UV-Light

EDTA is an important additive used for complexation of interfering metal ions in cleaning agents, in electroplating processes, printed circuit manufacture, and in the leather, paper and textile industries. It is not a toxic chemical, but it is not readily biodegradable. As a manufacturer of EDTA, BASF has expended considerable effort on operational measures aimed at minimising the environmental impact of the chemical. As *Fig. 4.10-3d* shows, the amount of EDTA discharged into the Rhine has been significantly reduced over the past 20 years.

The most recent cut in discharge levels was achieved by introducing a decentralised process for the pre-treatment of the contaminated wastewater resulting from production operations (see *Fig. 4.10-6*). In the new plant, which commenced operations in 2004, EDTA molecules are broken down by targeted UV light activation and the addition of a catalyst, resulting in EDTA being converted into biodegradable compounds (WIRSING & SÖRENDEN 2004). These compounds are then eliminated in the central treatment plant.

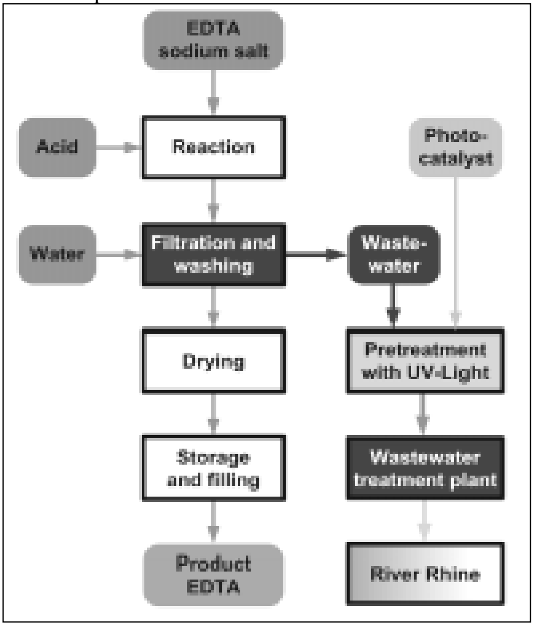

Fig. 4.10-6: Pretreatment of EDTA containing wastewaters with UV light, combined with the central waste water treatment plant.

Example of a process-integrated measure involving the reuse of recyclable materials: Recovery of ammonia by distillation

As *Fig. 4.10-3c* shows, prior to 1989, some 50–60 tonnes of ammonium-nitrogen were being discharged from the Ludwigshafen site into the Rhine every day. Because of the product portfolio, BASF caused for 6% of the total ammonium load in the Rhine, the largest amount of ammonium being discharged into the Rhine from any single location. Since the mid 1980s, BASF has actively sought to reduce the ammonium load in the Rhine.

Based on detailed analysis involving all of the significant wastewater flows that contain ammonium, processes were developed to prevent or reducing the discharge of ammonium from a number of production facilities. A total of 60 million Euros was invested in ammonium reduction measures at the Ludwigshafen site between 1990 and 1994. Thanks to these measures, the level of ammonium-nitrogen emissions into the Rhine was cut from about 60 tonnes per day to about 12 tonnes per day, an 80% reduction.

The biggest share of this reduction was achieved by introducing processes that involve recovering ammonium from wastewater with an ammonium content of 1–5% by steam stripping or distillation at various pressure levels. The ammonium recovered from the wastewater is in the form of either a 25% aqueous solution or (after pressure distillation) pure liquid ammonia, and is reused as a raw material in the manufacturing process.

Fig. 4.10-7 shows the situation with regard to ammonium emissions prior to 1990, before the implementation of the ammonium recovery distillation process. Five production facilities (E1–E5) discharged a total of 31.5 tonnes per day of ammonium-nitrogen into the treatment plant, and thus into the Rhine. The majority of this amount was generated in plant E1 as a reaction product. By constructing a two-stage distillation facility with pressure levels of 4.5 bar and 12–14 bar in plant E1, and by combined reconditioning of the wastewater from all five production plants (and thus the amount of ammonium discharged into the Rhine) was reduced by 30.5 tonnes per day to less than 1 tonne per day (see *Fig. 4.10-8*).

The recovered ammonia is delivered via a pipeline as liquid ammonia with the required level of purity to facilities V1 and V2, where it is used as an ingredient in the production process. In this way, the demand of fresh ammonia resulting from ammonia synthesis in these plants was reduced by 30.5 tonnes per day.

This integrated ammonium recovery process and the reuse of the ammonium in production operations is a typical example of the advantages of BASF's Verbund.

However, the ammonium recovery process does have its limitations. For example, the recovered ammonia must consistently meet specific purity requirements in order to be reused in the production process. Depending on the composition of the ammoniacal wastewater, this is not always possible. The recovery of ammonia from wastewater flows with a low ammonium load is not economically feasible, nor is it environmentally justifiable due to the large amount of energy required. For the Ludwigshafen site, this means that it is not possible to cut the load on the central treatment plant to less than 12 tonnes per day using recovery processes given the current range of products manufactured. The possibility of recovery must be considered each time production operations generate new sources of wastewater.

After the process-related ammonium-reduction

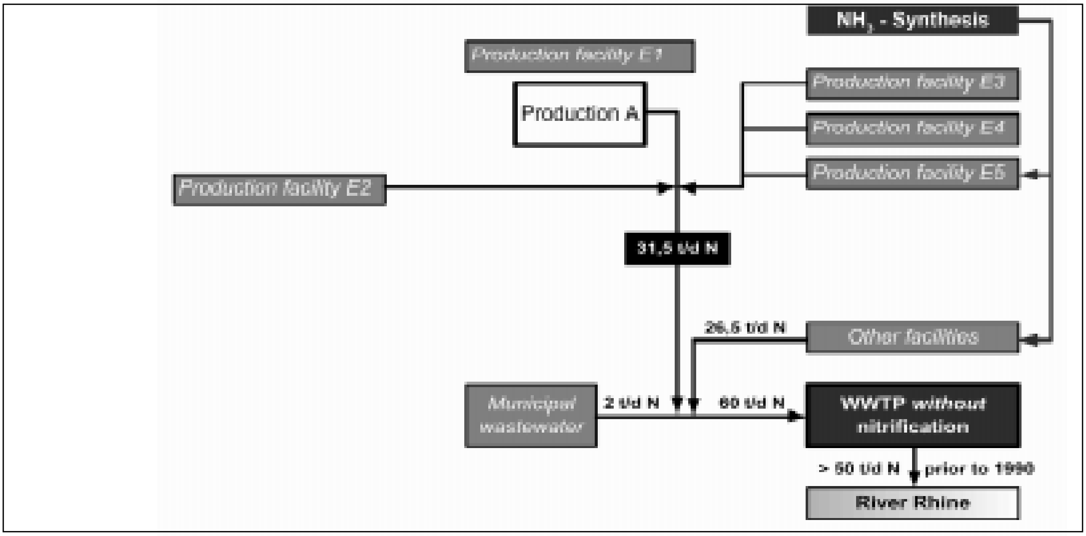

Fig. 4.10-7: Ammonium situation at BASF AG, Ludwigshafen prior to 1990.

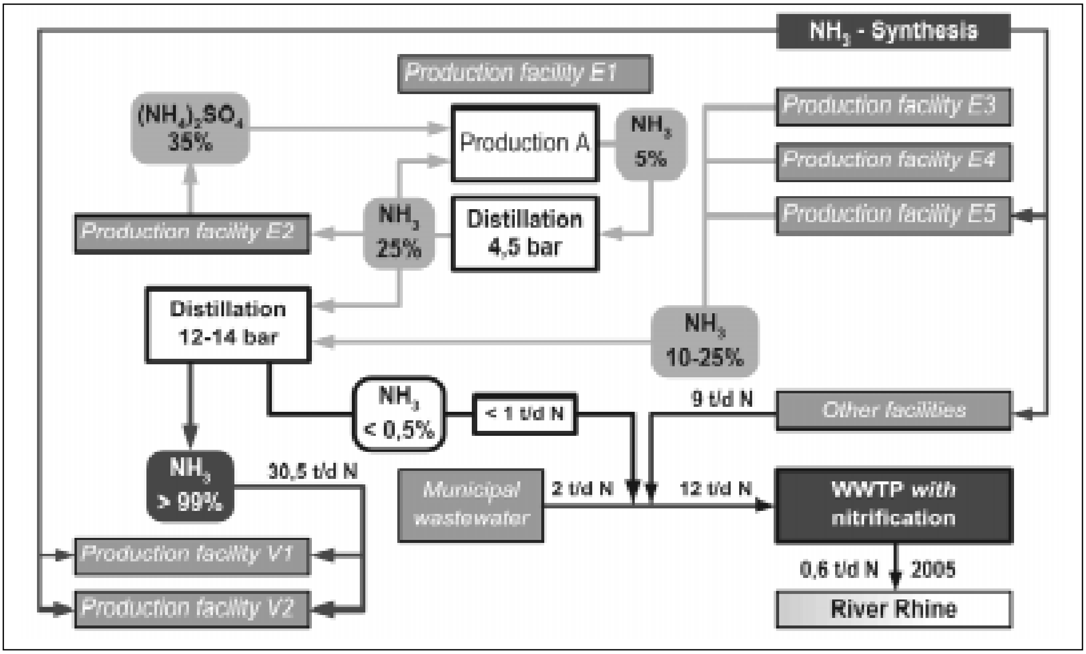

Fig. 4.10-8: Ammonium situation following implementation of the recovery processes and the nitrification-denitrification step at the central wastewater treatment plant.

measures had been successfully implemented, in 1995, BASF gave voluntary assurances to the State of Rheinland-Pfalz that the company would further reduce the amount of ammonium discharged into the river Rhine by converting the central treatment plant from denitrification to nitrification-denitrification.

Example of end-of-pipe treatment: Central elimination of nitrogen by nitrification-denitrification in the wastewater treatment plant at BASF AG Ludwigshafen

The central wastewater treatment plant at BASF Ludwigshafen was designed and operated from 1974 to function based on the denitrification process step. Denitrification involves bacteria in the non-aerated part of the activated sludge tanks reducing nitrate-nitrogen to elemental nitrogen, which is discharged as gas from the wastewater. By appropriately combining this process with the so-called nitrification process (which uses oxidising bacteria to convert ammonium to nitrite, and nitrite to nitrate), ammoniacal nitrogen can be converted via nitrate-nitrogen to elemental nitrogen.

In order to implement this combined process at the central treatment plant, the existing aeration system with surface aerators was upgraded by adding a pure oxygen gas injection system to provide the additional oxygen required to oxidise the ammonium to nitrate. In addition, the sludge age had to be increased, the primary treatment process optimised, a constant, adequate supply of phosphorus nutrient for the bacteria assured, a conceptual design for controlling oxygen supply developed, and targeted measures implemented to reduce the amount of nitrification-inhibiting constituents in the wastewater, to name just the most important steps required. The costs associated with this project were around 15 million Euros.

After the nitrification process was brought online at the end of 2001, the ammonium load was reduced from of 10–12 tonnes per day to about 2 tonnes per day, a cut of over 80% (see *Fig. 4.10-3c*). Further improvements resulted in the amount of ammonium discharged into the Rhine being further cut to 0.6 tonnes per day by 2005. When compared with the discharge level of 60 tonnes per day in the 1980s, this represents a 99% reduction.

The reduction of ammonium levels by nitrification alone (i.e., without the decentralised recovery processes) would effectively have been impossible. The volume of the existing tanks would have been far less than would have been needed. Neither would it have been possible to cut ammonium emissions from 60 tonnes per day to 0.5 tonnes per day using only decentralised, production-integrated recovery processes. This case clearly illustrates the advantages offered by an economically and environmentally feasible combination of various wastewater purification processes♦