CONTROL OF POLLUTION IN THE CHEMICAL INDUSTRY

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Summary

In the present chapter a brief review of chemical industries producing basic bulk chemicals and having strong impact on environment is presented. It is shown that the best way to combat environmental pollution is to prevent it. The traditional manufacturing processes such as production of sulfuric acid, nitrate-based fertilizers, soda and caustics, cement, as well as pharmaceutical and organic chemicals are discussed. It is demonstrated, that new efficient technologies and processes, which save raw materials and energy, as well as those involving by-product use and recycling are beneficial for both processes efficiency and environment protection by reduction of emissions in air, water, and soil.

This approach is known as the environmentally sustainable industrial development (ESID), leading to reduction of consumption of natural resources and to lessen damage to environment during raw material extraction. ESID leads also to lower energy demands and consequent indirect decrease in fuel consumption and environment pollution, to reduction of emissions in all of the components of environment and therefore to reduction of waste treatment costs.

1. Introduction

Chemical industry is recognized as one of the most powerful sources of environmental pollution. Since all of the chemical manufacturing processes use raw materials and consumables from each component of environment, it is clear that damages resulting from the activities in chemical industry are not due to the very industrial processes only, but because to exhaustion of natural resources too. In the 20th century oil, coal, minerals, wood, etc. have been extracted at extremely high rates, thus affecting the ecological balance in the nature and damaging the landscape. The primary effect of chemical industry on environment and on the lifestyle as well, is due to the pollution, arising from the industrial activities, resulting in gas emissions, wastewater polluting the natural ponds and underground water, solid and slurry waste, polluting the soil and underground water, if not treated. However, even the complete control of emissions yields additional pollution as waste to be treated or disposed. Moreover, since any industry requires energy supply for mechanical processes, heating and electricity, chemical industry indirectly charges the environment with emissions of sulfur dioxide, nitrogen oxides and particulate due to energy production in heat power stations. Production of oil and coal used as fuels and raw materials in chemical industry also charge the environment by destroying fertile land due to mining activities and oil extraction.

The extension of chemical industry in the 20th century throughout the world lead to dangerous trends: acid rains, greenhouse effect, ozone layer depletion, global climate changes, exhaustion of fresh water, damaging fertile lands, etc.

It was clear, therefore, that global solutions have to be found to restrict the adverse impact of industry on environment and to restore nature's conditions as far as it is possible.

A well defined approach is focused on environmentally sustainable industrial development (ESID), considered in the development programs of the United Nations and being the basic concept in the document approved at the Earth Summit in Rio-de-Janeiro, 1992.

For chemical industry this approach is associated with pollution prevention as a first step, saving of raw materials and energy, whenever possible and introduction of clean technologies to avoid impacts on environment with pollution and treatment facilities. Other options are to adjust manufacturing in a way to generate less waste or those compatible with the self-regenerating capabilities of environment.

In what follows we shall consider some of the bulk chemical production processes with the possibilities for environment protection based on pollution prevention principles and on environmentally sustainable industrial development.

2. Production of Sulfuric Acid

Sulfuric acid is one of the basic chemicals with extremely large scale of annual production throughout the world. Its applications cover different areas of human activity, starting with fertilizers and ending with explosives. It is applied mainly in chemical industry as acid, dehydrating and sulfonating reagent. Its annual production per capita is an indicator for the industrialization level of a certain country. For example, its annual production in the developed countries is between 50 and 200 kg/capita, whereas for the developing countries these figures are below 5 kg/capita.
During the last decades its world production is large enough to maintain its low prices. However, its production is associated with a severe pollution of the environment, therefore deserving special attention.

2.1. Manufacturing

There are two main groups of methods for sulfuric acid manufacturing: the contact and the chamber one. Both methods are based on the catalytic oxidation of sulfur dioxide to sulfur trioxide.

$2SO_2 + O_2 = 2SO_3$

Usually a four-stage catalytic converter is used which is an equilibrium and exothermic process. Formation of nitrogen oxides is possible too. On the other hand, sulfur trioxide is a strongly hygroscopic substance. To avoid formation of stable mists of sulfur trioxide, the reacting gases are washed in absorbers by dilute sulfuric acid, thus obtaining more concentrated product (oleum, respectively).

In the first group of methods the catalysts are solid, being platinum or vanadium oxide - based ones. Nowadays, platinum catalysts are abandoned, because of their higher prices and their vulnerability to catalytic poisons, like arsenic and its compounds.

In the second group nitrogen oxides serve as catalysts (homogeneous catalysis).

Sulfur dioxide is produced by combustion either of elemental sulfur or of metal sulfides, e.g. pyrites.

The main disadvantage of the use of sulfides as a source of sulfur for sulfuric acid production is the content of arsenic, which cannot be removed successfully from the product with the associated problems with environment protection (particulate, arsenic, etc.). Therefore, sulfuric acid is usually a by-product in non-ferrous metallurgy in the process of emissions control, where sulfide ores are the basic raw materials.

The equilibrium constant of sulfur dioxide to sulfur trioxide oxidation shows, that at lower temperatures the equilibrium is shifted towards higher yields of sulfur trioxides but at lower reaction rate and vice versa. Therefore this catalytic reaction is carried out in practice in a four-stage reactor with intermediate cooling of the reaction mixture. Using this technique a 98 per cent conversion is attained. Afterwards the obtained sulfur trioxide is absorbed in concentrated sulfuric acid to produce oleum. Later it is diluted according to the needs.

2.2. Emissions in Air

The possible emissions in exhaust gases are due to different reasons.

First, it could be the non-reacted sulfur dioxide. One method for reduction of the content of sulfur dioxide in the exhaust gases is the optimization of the ratio sulfur dioxide to oxygen in the gas, entering the catalytic converter. Additionally, the residence time of the reacting gases could be extended, by increasing the length of the catalytic bed, or by reduction of the gas superficial velocity. The reduction of sulfur dioxide content in the exhaust gases could be improved by adding an intermediate cooling and absorption of the obtained sulfur trioxide, prior to the conversion in the fourth stage. In this case the equilibrium is shifted towards formation of sulfur trioxide and hence, the remaining sulfur dioxide is converted more completely.

Next, it is the mist formed by small droplets of sulfuric acid in the gases leaving the absorbers. The mist may be formed due to the presence of water vapor in the feeding air. This source of humidity could be neutralized by washing the inlet air with concentrated sulfuric acid. When the acid is not concentrated enough additional mist formation could take place. Mist formation is usual also when the sulfuric acid plant is set on run. Reduction of these emissions could be attained by washing with water or ammonium hydroxide in a scrubber. The produced ammonium sulfate is a by-product, which could cover partially the costs of the emission control. However, the most exploited equipment for mist removal is the Brinck’s demister, containing fabrics of glass fibers. The demister could be applied not only for mist removal from exhaust gases, but also at intermediate air drying with sulfuric acid and of the sulfur-containing gases after the step of intermediate absorption. The efficiency of the demisters reaches 97-98 per cent, thus reducing the mist concentration in exhaust gases from 850-1275 mg/m^3 to 18-21 mg/m^3. Washing scrubbers are also frequently used, situated just after the demisters.

On the other hand, the heating of the metal surfaces in the catalytic reactor may enhance the formation of nitrogen oxides (NOx), thus charging the environment additionally. However, their concentration is much lower, than it is the case of combustion processes. Release of particulate from the used catalyst is possible too.

2.3. Solid Waste

The main source of solid waste in sulfuric acid production is the spent catalyst, containing vanadia. The first layer of catalyst is mostly subjected to destruction and contamination with dust. The regular cleaning and replacement of the spent catalyst is considered as sufficient for the maintenance of stable operations. The spent catalyst and its dust are collected and shipped for extraction of vanadia and recycling. Scrubbing of the non-reacted SO_2 is usually accomplished by water and ammonia solution. The obtained ammonium sulfate as a by-product could cover partially the costs for the pollution control.

3. Production of Nitrates-Containing Fertilizers

Nitrates-containing fertilizers were the most frequently used ones in the past. Mainly they are potassium, sodium and ammonium salts of nitric acid. The natural resources of these salts are large, but not sufficient to meet the demands of agriculture, and therefore, their industrial manufacturing has become inevitable.

3.1. Ammonia Synthesis

The overall technology for nitrates production is based on the synthesis of ammonia. The most widely used process is the catalytic synthesis from the very elements, nitrogen and hydrogen developed from the work of Haber and Bosch:

$N_2 + 3H_2 = 2NH_3$

It is accomplished at high pressure, in order to shift the equilibrium towards the product formation and at higher temperature, to attain fast enough reaction. Pressures are extremely high: 100 - 300 bars at 450-500^{0}C (according to Haber&Bosch); 750 bars (Claude&Cassal, Italy); 900 bars (Claude&Cassal, France). Hence, the equipment for this manufacturing is quite expensive. Reduction of temperature could be admitted, when appropriate catalyst is used. Haber has discovered that magnetic ferrous-ferric oxide, promoted by alumina and potassium oxide is very efficient. Now all of the catalysts used for this manufacturing are based on iron compounds.

The nitrogen required for the synthesis is produced by distillation of liquid air or by controlled combustion of fuels for the selective oxygen consumption.

When nitrogen is produced by liquid air distillation, the hydrogen necessary for the synthesis is usually obtained as a by product of electrolytic production of chlorine and sodium hydroxide, or petrochemical industry (by-product at cracking-processes or at synthesis of olefins), coal, natural gas, as well as from water gas.

According the original Haber&Bosch method, hydrogen is taken from water gas, produced by coke, combusted in air, and then air is replaced by water steam:

$$C + H_2O \overset{1000^0C}{=} CO + H_2$$

Then the heated gas mixture is fed to the converter, where a catalytic oxidation of carbon monoxide takes place:

$$CO + H_2 \overset{\sim 500^0C}{\underset{\text{catalyst } FeO+Cr_2O_3}{=}} CO_2 + H_2$$

The resulting carbon dioxide is removed by absorption.

The necessary nitrogen is taken from one part of the gaseous mixture, containing no oxygen and obtained at coke combustion. The use of coal and coke relatively is more expensive, because of the increased capital costs, compared to natural gas. On the other hand, the environmental problems are significant. When natural gas is available, reforming and secondary reforming is preferred. These processes consist in the controlled combustion of natural gas in presence of water steam and shortage of air to produce a mixture of hydrogen, nitrogen and carbon dioxide.

$$CH_4 + H_2O = CO + H_2$$

The produced CO_2 could be removed by scrubbing with water, mono-ethanolamine, etc. The rest could be treated by hydrogen to obtain methane again.

The main problem arises, when gas or oil derivatives are used in desulfurization, because of the content of sulfur compounds which give rise to catalytic poisoning in the considered case.

Once ammonia is synthesized, it could be easily removed at high pressure by condensation or by absorption. The non-reacted substrates could be recycled for complete conversion. However, the main contamination (argon and methane) has to be removed to avoid dilution of the synthesis-gas or possible explosion.

3.2. New Development in Ammonia Synthesis

Natural gas is considered as the main source of hydrogen in ammonia synthesis. Therefore, the new developments in ammonia production are associated with the improvement of energy efficiency and the hydrogen utilization.

Organization of the heat streams in the equipment is the new development, thus saving 18 per cent of the required energy. Another improvement is the intermediate indirect cooling of the gases between the separate catalyst layers in the synthesis column. In this case much higher concentrations of ammonia are attained.

The efficiency in hydrogen utilization was enhanced considerably by diminishing the ratio of the steam to hydrogen in the reforming step from 4.5 to 3, and by improving the system of separation of carbon dioxide.

The control of inert components in the synthesis of gaseous mixture reduces the losses of nitrogen and hydrogen in the feed, as well as the losses of ammonia, when the latter is combusted as a fuel for the reforming.

3.3. Emission Control at Ammonia Synthesis

3.3.1. Air Emissions

One source of pollution is the sulfur dioxide, resulting from the combustion of coke, oil products or natural gas, when desulfurization is not sufficient. Since it is catalyst poison, careful desulfurization is required.

Another source of pollution is nitrogen dioxide, resulting from partial oxidation of atmospheric nitrogen at combustion of reforming fuel, as it happens at the combustion of any fuel. Additional part of nitrogen dioxide is obtained from partial oxidation of the produced ammonia. This problem can be minimized, when the reforming process is optimized, i.e. to reduce the excess of the air and to improve the process control.

Release of produced ammonia is possible too. Measures for restriction of this process are taken, consisting in removal of these products from the exhaust gases, better feeding and compressing of ammonia, as well as an improved control on evaporation in the reservoirs. Realistic amounts of released ammonia are 1 - 1.5 kg/tons.

3.3.2. Water Emissions

The main water pollutants, resulting from ammonia production are the heated water effluents, and diluted ammonia-containing waters. Organic compound could also be present. The latter is a result of condensation.
The solution of these problems is in the secondary use of the heated effluents for heat utilization. Ammonia could be stripped by steam, or used directly as fertilizer.

3.4. Production of Nitric Acid

Nitric acid has a wide practical application, like a base chemical for fertilizer manufacturing and for production of explosives. Nowadays catalytic oxidation of ammonia and the consequent absorption of the nitrogen oxides in water accomplish its production.

The substrate mixture of ammonia and air is passed through a multi-layer catalyst of platinum net:

$4NH_3 + 5O_2 = 4NO + 6H_2O$

It the first step NO is formed and then consequently oxidized to NO_2. The latter is reversibly dimerized to N_2O_4 (two monomer molecules form a dimer; many monomer molecules form a polymer ;Dimerization - polymerization). The last step is the absorption of NO_2 in water, thus giving nitric acid:

$3NO_2 + H_2O = 2HNO_3 + NO$

For this purpose liquid ammonia is evaporated by indirect heating and then filtration to remove the particles that may block the catalyst. The air is compressed to the same pressure as ammonia (i.e. 8 bars) and then filtered. The gases are mixed and passed through the catalyst bed at high temperatures. The product is a mixture of NO, water steam and the initial gases with 95per cent yield.

The hot gases are cooled prior to absorption and steam for regeneration of the catalyst is produced. The high- pressure oxidation to produce nitric acid is associated with losses of the catalyst. Then the gas mixture is filtered, rapidly cooled, and subjected to absorption in water in a column, where nitric dioxide dissolves in water, yielding nitric acid and NO, which additionally oxidized. The final product is nitric acid with a concentration of 60-62per cent.

The release of the waste gases is used to move a turbine for energy utilization. Hence, about 40 per cent of the energy demand for air compression is covered in this way.

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Biographical Sketch

Venko N. Beschkov was born in 1946 in Sofia, Bulgaria. He obtained his M. Sc. degree in inorganic and physical chemistry in the University of Sofia "St. Clement Ohridski" (1969). He obtained his Ph.D. degree in the Central Laboratory of Chemical Engineering at the Bulgarian Academy of Sciences in Sofia Bulgaria (1978), and his D.Sc. degree in 1996. He was promoted as associate professor in 1984 and as a full professor in 1997. He is Director of Institute of Chemical Engineering at the Bulgarian Academy of Sciences (since 1993).

The scope of his scientific activity is on mass transfer operations in chemical and biochemical engineering, bioprocess engineering and environment protection (fine chemicals production, waste water treatment, gas pollution removal, etc.). He has over 60 scientific papers and 1 monograph (*Boyadjiev Chr., V.Beschkov, Mass Transfer in Liquid Film Flow, Publishing House of the Bulgarian Academy of Sciences, Sofia, 1984*) published. He is an editor-in-chief of the scientific journal *Bulgarian Chemical Communications* (since 1996). He was also an editor of textbooks on chemical technology in Bulgarian (1986).

His teaching activity consisted in delivering courses in hydrodynamics in the Faculty of Chemistry, University of Sofia “Climent Ohridski" as a assistant professor and a reader (1976-1984); in biochemical engineering in the Faculty of Biology, University of Sofia “Climent Ohridski" as a reader (1987-1989); in technology in bioconversion as a reader in the University of Chemical Technology & Metallurgy, Sofia, Bulgaria (since 1999).

He was Deputy-minister of The Ministry of Environment Protection in the Government of The Republic of Bulgaria (1991/92), consultant and trainer in different international projects on environment protection (since 1993).