

AIR PROTECTION FROM POWER INDUSTRY EMISSIONS

1.1. Nitrogen oxide emission reduction

1.1.3. Flue gas cleaning from nitrogen oxides

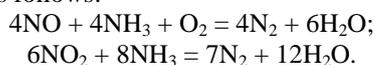
1.1.3.1 Selective Catalytic Reduction (SCR)

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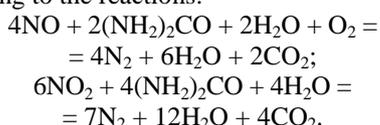
This method is currently the most effective tool for NO_x emission reduction, applied at the large power boilers. The method has been used for a long time at power plants in Europe, USA and Japan (Fig. 1.19).

The reducing agent (for that purpose ammonia or urea is usually used) is injected into the flue gas stream before the catalyst. Near the catalyst surface in the temperature range of 170 ... 510°C at a different level of intensity, the reducing reactions, resulting in nitrogen oxide transformation into the molecular nitrogen, occur [20].

When using ammonia (ammonia water), the main reactions are as follows:



In case more expensive reagent—urea is applied, the reduction occurs according to the reactions:



At power plants ammonia is stored, as a rule, in the form of an aqueous solution or in a liquefied state at a pressure of 1,7 MPa (17 bar) at 20°C. For small systems urea in the form of white crystalline granules that dissolve in water before their injection into the flue duct, is often used. This urea is more expensive but safer to transport and store.

An aqueous ammonia before entering the flue duct is heated in the electric heater. To heat the ammonia solution, steam or hot water can be used, as well. To improve the efficiency of NO_x recovery, and reduce the ammonia slip, it is necessary to ensure even distribution of the injected reagent. Only when the desired relationship of NH₃/NO_x around the duct cross section before the catalyst is ensured, it's possible to reduce the ammonia slip to its concentration in the flue gases before 2 ppm (0,0002% by volume). Otherwise, the sale of ash, caught from coal-fired boilers, becomes impossible for the construction industry in accordance with technical requirements for dry ash supplied to consumers.

Another reason, compelling to achieve the minimal ammonia slip, is a dangerous interaction between NH₃ and SO₃ in flue gases at cooling the latter to a temperature of 220°C. The resulting ammonium bisulfate increases a risk of contamination and corrosion of the heating surfaces.

Of course, much depends on the catalyst itself, including a shape of the catalyst lattice, through which flue gases pass together with ammonia. Catalytic reactors of plate or cell types are more likely to occur in practice.

All kinds of materials that are used as catalysts for flue gas cleaning, can be divided into four groups [20]:

- carrier - metal oxides (for example, TiO₂) with the active components: vanadium, molybdenum or tungsten. V₂O₅ is often used with a small quantity of WO₃ (which is added to extend the temperature window frames) or SiO₂ (to increase in the structure stability), or MoO₃ (to reduce a risk

of "poisoning" the catalyst with flue gas components);

- zeolites - crystalline natural substance with a highly developed porous or synthetic aluminum silicates that are used at temperatures of 350 to 600°C;

- iron oxides in the form of particles coated with a thin crystal film of iron phosphate;

- activated carbon, consisting of the crushed stone and brown coal, mixed with an inert material and processed to agglomerated pellet state. The catalyst can operate in the temperature range of 100 ... 220°C.

When choosing the size of holes for the flue gas passing, a number of catalyst layers and other parameters, a characteristic of the dust flow, the required degree of NO_x emission reduction, allowable pressure drop of the catalytic reactor, etc should be considered. An experience of SCR plant operation abroad testifies that duration of the catalyst applied at the coal-fired boilers is 6 ... 10 years, and for the oil-gas it changes from 8 to 12 years. A frequency of the catalyst replacement is not only determined by a characteristic of the fuel, but also by other indicators of the installation: input NO_x concentration, efficiency of nitrogen oxide reduction, allowable ammonia slip, etc.

When choosing a connection scheme of the catalytic reactor in the gas path of the boiler, it's necessary to consider not only the boiler cost, but also the desired duration of the treatment plant without changing the catalyst. There are three layouts with different SCR units (Fig. 1.20).

Layout **A** is the easiest and the most common option, in which the catalytic reactor (DENOX) is set after economizer, before air heater of the boiler plant. A temperature in this zone of the gas system allows to use the majority of catalysts. However, the reactor operating at the untreated flue gases, creates significant problems. Firstly, measures for erosion reduction should be taken. Secondly, the products of combustion and fly ash can "poison" the catalyst, reducing its activity. This decreases the efficiency of cleaning of flue gases from NO_x (particularly, this effect could be noticed at slag-tap boilers). Another disadvantage of this layout is that for its implementation at the existing boilers the space is needed in the immediate vicinity of the boiler, which is not always possible to find. This layout is called "high-dust" because the catalyst operates at the dusty flow.

Option **B**, in contrast to the first one, is called "low-dust", because in this layout the catalyst is set after the high dust collector (but, again, before the air heater that solves a problem of providing the gas temperature in the zone of DENOX reactor).

This layout reduces a mechanical impact on the catalyst, thereby increasing its service life. A disadvantage of this option is a need to install inefficient "hot" ash collector and the difficulty of its mounting at implementation of SCR method at the operating boiler. In addition, a risk of ammonium bisulfate formation in the air heater zone at ammonia slip, remains.

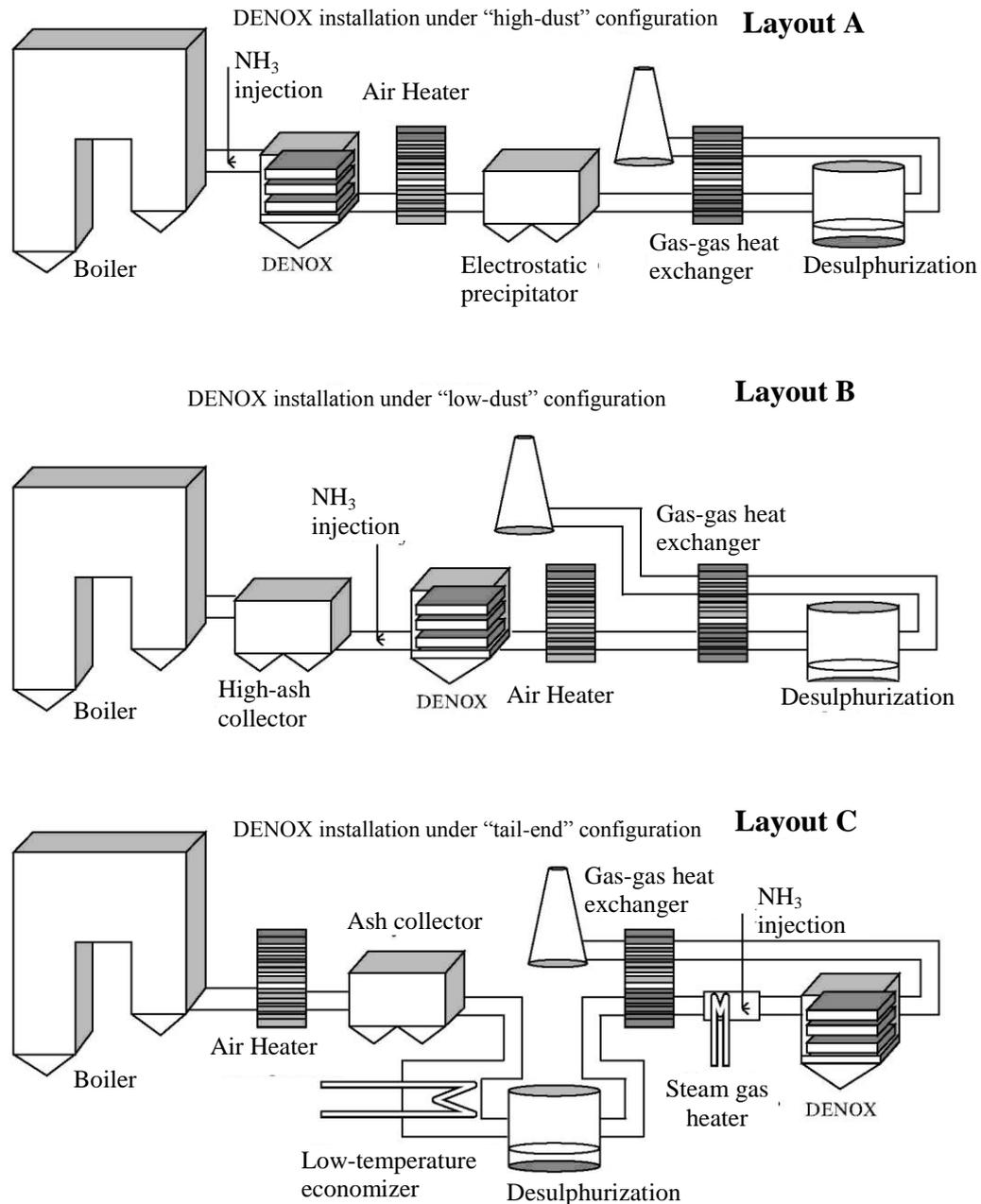


Fig. 1.20. Different layouts of SCR process arrangement

In the option C, installation of DENOX reactor after all the heating surfaces, i.e. at the end of the boiler, is supposed (hence, it is called tail-end configuration). This layout more suits for its implementation at other operating boilers as the catalyst undergoes less wear, corruptions, and deactivation.

The catalyst volume can be also reduced in comparison with the "high-dust" option (by reducing the lattice spacing). A disadvantage of this option is a need for the gas-gas heat exchanger and for an additional gas heater in order to provide the desired gas temperature in DENOX reactor.

The main risk in using SCR system is ammonia slip, which is possible with a decrease in the catalytic activity and high NH₃/NO_x ratio. Ammonia slip can cause the following:

- formation of ammonium sulfate with its subsequent depositing at the elements of gas system;
- occurrence of ammonia in the wash water while washing the air heater and in the desulfurization wastes;
- increase in the ammonia concentration in fly ash.

Despite of these difficulties, SCR plants are applied increasingly, as the catalyst use gives a number of

advantages:

- the method is suitable for burning all types of fuel - from natural gas to coal;
- NO reduction is not accompanied by formation of other pollutants;
- effectiveness of such plants can reach 90% or even more;
- SCR method can be combined with any technology (primary measures).

An obstacle to wider adoption of SCR method is rather high capital costs for its implementation. According to foreign data [20], the catalyst costs from 10 to 15 thousand euros per 1 m³. But if all expenditures are considered (design, installation, auxiliary equipment, including pipelines, pumps, fans, etc.), the costs will be many times more. Even in case the cheapest "high-dust" option for the power unit of 200 MW is selected, it requires from 12 to 20 million euros. And if the most expensive "tail-end" option is accepted, for the same unit 37,5 million euros will be needed. For power units of 500 MW, the capital cost for SCR

installation using "tail-end" layout, will make 60...75 million euros.

According to other reports [21], for the coal-fired power unit of 200 MW, SCR plant will be of 16,9 million dollars,

the boiler itself – 84,0 million dollars, and SCR plant operation – 0,86 million dollars/year. Similar figures for the coal-fired power unit of 500 MW will be the following: 30,7; 210,0 million and 1,89 million dollars/year.