SUSTAINABLE ENERGY

PART B
CLEAN COAL TECHNOLOGY
- Course -

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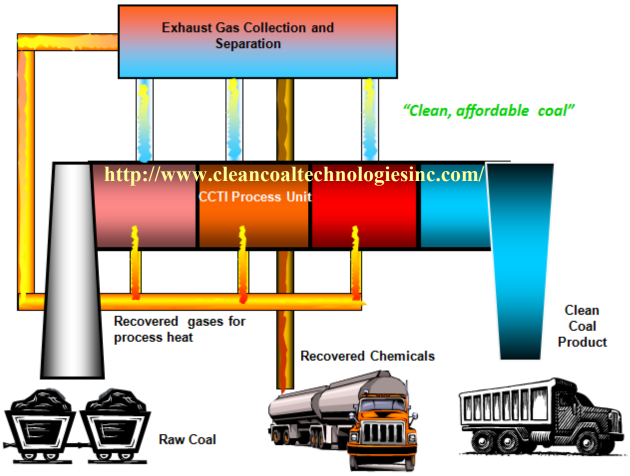

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CHAPTER 1

THERMAL POWER PLANTS AND THE ENVIRONMENT

The energy sector, worldwide, by the complexity of installations and technological processes, characteristics of raw materials and waste in number and size of occupied land area, is one of the most important industries, with major impact on the environment.

Implications of EU environmental legislation alignment, and other regulations to which Romania is party, are, in particular, economic and technical nature and require significant efforts to comply with new legislative requirements. But even the power plants face significant environmental problems whose solution depends on the authorization environment operating under conditions imposed by the European Union.

1.1. Power plants as pollution sources

Producing electricity is not a process fully effective, in terms of the impacts to the environment. Thus, any power generation techniques involve environmental aggression.

Hydroelectric plants during their operation, determine the zoning changes of microclimate, with effects on flora and fauna. If, for ordinary species the effects of these changes can be minor, the impact on endemic species can be major. A major disruption of ecosystems is recorded at the stage of realization of investment in hydropower. Deforestation, impressive excavations, dam construction are all major environmental impact factors.

Nuclear plants, the classical part, are a minor pollutant and their pollution may come from the installation cooling circuit, from the heat treatment circuit or from operating and maintenance operations. If the cooling circuit is opened, heating of cooling water reflects pollution and if the cooling circuit is closed, the pollution is reflected by water evaporation from the cooling towers. Regardless of the technical solution adopted for the cooling circuit, should not neglect the impact that it can have chlorination, operation necessary for destruction of microorganisms that can multiply themselves excessive in plant's equipments.

On the nuclear reactor, radioactive pollution is low, not exceeding the naturally, background radiation. On the other hand, nuclear power plants pollution must be considered from the point of view of the risk of radioactive contamination. Another possible approach, relative to nuclear energy as a source of pollution, could take into account all technological processes, from extraction of nuclear fuel to the storage of radioactive waste. Even under these conditions, nuclear energy is far cleaner and safer than the thermal power.

Production of electricity in solar or wind plants is a clean technique. There can not be neglected, however, changes occurring in the air currents distribution and in evaporation volume, with effects on local microclimate. It should also be analyzed pollution induced in order to produce electricity needed for the construction of unconventional plants, especially since all materials used are intensive. Deliberately, listed last is the classical power system based on burning fossil fuels, due to its major impact on all environmental factors.

The assault on the environment is due to both the combustion process and all related processes, from extraction to waste storage. It is very important that this process, highly pollutant, holds the weight in the total amount of energy produced worldwide. Environmental impact is even more aggressive as the fuel is lower quality, energy coal combustion exceeding the quantities of pollutants generated by human activities. A prime example in this sense can refer to emissions into the atmosphere. Thus, the process of burning fossil fuels, worldwide, gives the following pollutants, the quantities being given in relation to the total anthropogenic emissions of those pollutants: 90% sulfur oxides, 30 ÷ 50% carbon monoxide, 40% particles matter, 55% volatile organic compounds, 15 ÷ 40% methane and 55 ÷ 80% carbon dioxide.

In figure 1.1 is presented the chemical balance of a thermal power plant operating with coal.

Chemical balance entries are: fuel; limestone - required for SO_2 emission control; water - needed to produce steam, to heat and cool the circuit; ammonia and catalysts - required for NO_x emission control; various chemicals used in treatment processes, water softening and neutralization, as in maintenance operations.

Coal contains carbon and various organic combinations, which are burned during combustion, certain amounts of sulfur, and a wide range of combinations of chemicals, organic and inorganic, including heavy metals.

Limestone contains essentially calcium carbonate, possibly magnesium carbonate and small amounts of other chemicals.

In the power plants can be identified more sources of pollution, such as:

- ✓ transporting installations, fuel preparation and storage,
- ✓ combustion installations,
- ✓ water supply installations,
- ✓ installations for the treatment of process water,

- ✓ wastewater treatment and neutralization systems and the sewage related,
- ✓ deposits of slag, ash and by-products of neutralization reactions.

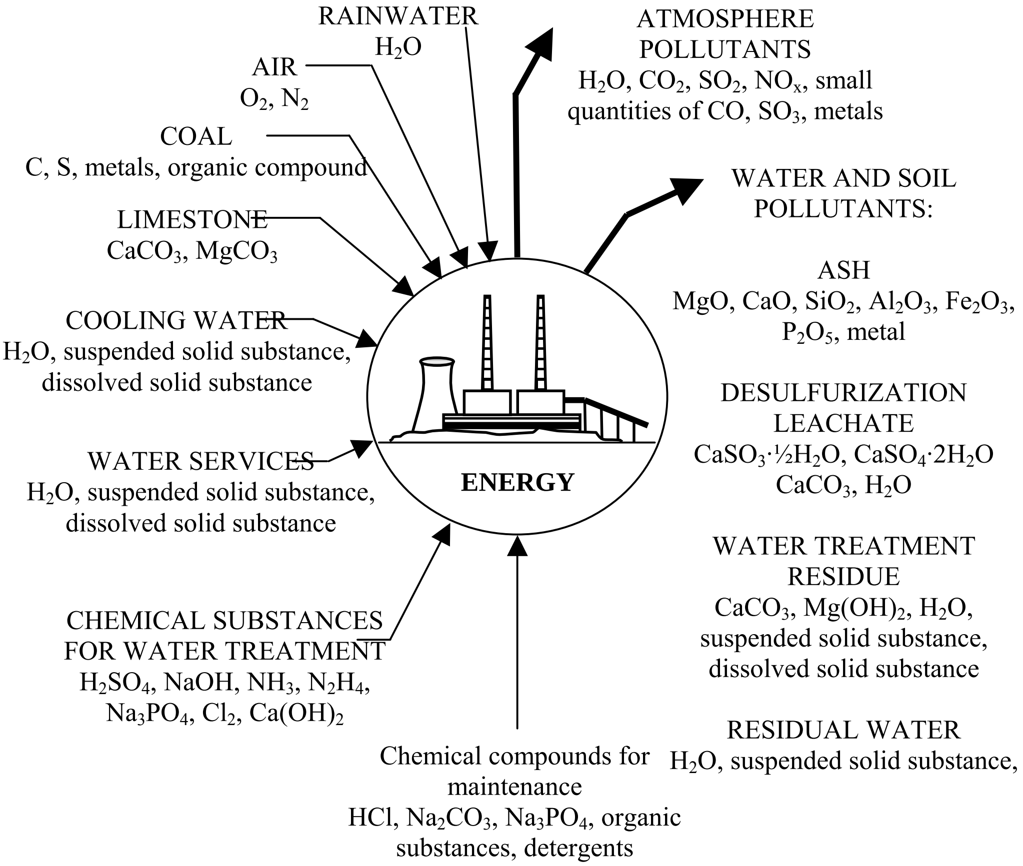


Fig.1.1. Chemical balance, overall, of a thermal power plant operating with coal

Water, depending on its origin, can contain a wide range of substances, usually inorganic, in dissolved state or in suspension.

Chemicals used in process water treatment are: lime and coagulants - to pre-treatment operation; sulfuric acid, hydrochloric acid and sodium hydroxide - ion exchangers in neutralization and regeneration processes; ammonia, hydrazine and sodium phosphate – for water conditioning in water-steam circuit; silting and erosion inhibitors, chlorine and sulfuric acid – for cooling water conditioning. A number of other chemicals, acids, alkalis and organic compounds are used for maintenance installations.

Multitude of chemical reactions that occur in all technological processes inside the power plant modifies the characteristics of materials in the configuration, generating residues, which must be stored or released into the environment.

Quantitatively, the main soil's contaminants are ash, slag and calcium-sulfur compounds resulting from the flue gas desulfurization. However, it cannot be neglected the infiltration of liquid fuels, lubricants and transformer oil.

Liquid residues result from several technological processes. The main source of pollution is the water treatment process. The water resulting from this process will be used in the water-steam circuit. The cooling process of thermal agent represents another important source of liquid residues. It pollutes by evaporation, by heating the envoy, as well as by discharging chemicals. The processes of flue gas desulfurization and transportation of slag and ash represent a third major source of water pollution. It should not be neglected the fact that power plants are large industrial installations that require constant maintenance, large amounts of liquid residues resulting from cleaning operations of various equipment. Also, should not be neglected leakage of lubricants and wastes from plumbing.

Rainwater can contribute to the transfer of pollutants through dissolution of chemical compounds.

Burning fossil fuels is a major source of atmospheric pollution, with direct effects on the population, as well as indirect effects, materialized in the increased acid rain and greenhouse effect. In addition, to the main pollutants in the combustion process, results new pollutant gases from the process of gaseous pollutants treatment. Under these conditions, analysis of pollution from power plants should consider the following issues: air pollution with solid particles, toxic gases (SO_2, NO_x, CO, CO_2, NH_3, HCl etc) and by evaporation; pollution of wastewater discharge areas with chemicals, dissolved and suspended, thermal pollution of envoy; pollution of soil, groundwater and the envoys with various chemicals; pollution caused by hydraulic circuits, which can become sources of air pollution at the level of cooling towers, through evaporation; pollution caused by ash and slag deposits, which contaminate, first, the soil and groundwater through seepage, and second, the air, by solid particles driven by wind; noise due to circular aggregates exhaust into the atmosphere; aesthetic pollution due to electrical and thermal networks, chimneys and cooling towers, electromagnetic pollution caused by the high and very high voltage plants.

Air pollution causes practically the most aggressive environmental impact, not only because of the quantity and variety of pollutants, but also due to damage over large geographical areas, so that, air pollution is no longer a local problem, but has a global character. Through effects and by their geographical and temporal extending, atmospheric pollution can be classified into one of the following categories:

- ✓ **proximity pollution** at local level, whose time scale is the order of hours; the main air pollutants (SO_2, NO_x, CO, O_3, Pb, powders) have immediate effects on human health and ecosystems;

- ✓ **distributed pollution**, at regional level, whose time scale is the order of days, the main effects of such pollution are acidification, eutrophication and photochemical pollution;
- ✓ **global pollution**, at planetary level, whose time scale is of the order of years, the results of this kind of pollution are increased greenhouse effect and stratospheric ozone layer depletion.

An overview of air pollution, by human activities, and its evolution in recent decades, is presented in the following tables. These data are valid for metropolitan areas of France. From these information results the distribution of emissions of the main pollutants (SO_2, NO_x, CO, volatile organic compounds) in the areas of human activities.

Table 1.1. **SO_2** emissions, in kt, for the metropolitan areas of France

Year	Energetics	Industry	Tertiary sector	Agriculture	Transports		TOTAL
					By Road	Others	
1960	638	689	298	13	31	105	**1774**
1970	1179	911	535	32	81	41	**2779**
1980	1743	938	349	32	127	24	**3214**
1990	591	426	133	21	139	16	**1326**
1995	425	322	87	15	114	14	**978**
2000	308	197	77	11	22	12	**627**
2001	256	192	76	11	23	13	**570**
2002	244	181	64	11	24	13	**537**
2003	262	174	61	11	24	13	**544**

Table 1.2. NO_2 emissions, in kt, for the metropolitan areas of France

Year	Energetics	Industry	Tertiary sector	Agriculture	Transports		TOTAL
					By Road	Others	
1960	155	268	51	109	177	90	**848**
1970	226	411	117	230	445	93	**1523**
1980	358	370	116	264	827	89	**2024**
1990	150	236	94	253	1093	71	**1897**
1995	133	192	96	225	987	71	**1704**
2000	153	174	95	216	728	66	**1431**
2001	127	180	105	217	695	71	**1395**
2002	133	173	94	228	649	74	**1352**
2003	139	170	91	211	603	75	**1289**

Table 1.3. CO emissions, in kt, for the metropolitan areas of France

Year	Energetics	Industry	Tertiary sector	Agriculture	Transports		TOTAL
					By Road	Others	
1960	65	4038	2115	669	2422	181	**9489**
1970	69	5275	2086	686	6573	165	**14852**
1980	65	4627	1783	637	8542	156	**15810**

1990	35	1973	1932	655	6258	94	**10947**
1995	28	1908	1781	605	4477	115	**8913**
2000	30	1565	1658	633	2607	132	**6624**
2001	31	1410	1726	609	2351	134	**6261**
2002	28	1565	1557	654	2001	149	**5954**
2003	28	1540	1553	631	1732	149	**5633**

Table 1.4. The emission of volatile organic compounds (VOCs), in kt, for the metropolitan areas of France

Year	**Energetics**	**Industry**	**Tertiary sector**	**Agriculture**	**Transports**		**TOTAL**
					By Road	**Others**	
1990	176	601	401	226	1051	44	**2499**
1995	120	522	382	232	802	50	**2107**
2000	96	511	368	210	479	55	**1719**
2001	88	489	371	218	425	57	**1648**
2002	83	480	338	216	364	61	**1542**
2003	80	479	338	210	313	61	**1481**

From tables 1.1 ÷ 1.4, we can see that the main pollutants of the atmosphere, resulting from the processes of power generation are sulfur oxides (as SO_2 equivalent) and nitrogen oxides. Emission of carbon monoxide and volatile organic compounds is practically insignificant in relation to pollution from other industries and road transport. There should not be ignored the fact that energy sector is an important pollutant with airborne particles.

Spectacular reduction of SO_2 and NO_x emissions in France, after 1980, is due to the vast nuclear program, through which about 80% of the electricity is produced in nuclear power plants and to activities supported by efficient energy management. Such a structure of power generation is not found in other countries, where is prevalent fossil-fuel energy production. In these circumstances, the share that holds power engineering in air pollution is similar to that of France in the early '80s: SO_2 - 54%, NO_x – 17,7%. Thus, for Germany and the United States of America, in the year 1995, the production of electricity holds the following predominance: SO_2 - 6%, NO_x - 25%, airborne particles - 15%, CO - 1%.

Romania has set the strategy for environment protection, priority directions for power engineering being the following:

✓ use of coal and fuel oil with low sulfur content;
✓ increase yields of power generation by rehabilitation and retrofit works;
✓ improving processes of control and combustion in the same time with the maintenance, rehabilitation and retrofit works;
✓ increase the performance of electrostatic precipitators;
✓ introduction of low NO_x emission burners;
✓ installation of desulfurization systems;
✓ improving energy-environment management;
✓ disposal of the installations with advanced physical and moral ageing.

1.2. Pollutant's toxicity

From an environmental perspective, there are important distinctions between different categories of pollutants. Thus, it can be identified:

- ✓ pollutants with direct action on the human body, such as nitrogen oxides, sulfur oxides, carbon monoxide and some heavy metals;
- ✓ pollutants with direct action on vegetation, such as sulfur dioxide and combinations of hydrogen with chlorine;
- ✓ pollutants that underlie the formation of acids, such as SO_2, SO_3, NO and NO_2;
- ✓ pollutants that influence the climate, such as CO_2, NO_2 and N_2O, and important factors in enhancing the greenhouse effect and contributing ozone layer depletion.

1.2.1. Volatile Organic Compounds

The most representative volatile organic compounds are petroleum products: gasoline, petroleum ether, benzene, acetone, chloroform, ether, phenol, carbon disulfide, etc. Internal combustion engines generate the biggest quantities. However, cannot be neglected the quantities produced in thermoenergetics or in waste incineration.

Environmental impact is similar to that caused by troposphere ozone because the VOCs and NO_x contributes decisively to the formation of ozone.

In some countries like USA, concentrations of volatile organic compounds and NO_x are not standardized, but their harm is highlighted by the ozone concentration, being imposed severe limits on the pollutant. In Germany, there are standardized concentrations of hydrocarbons, as well as in our country, where, by STAS 12574-87 are set maximum allowable concentrations for phenol, benzene, etc.

1.2.2. Toxicity of Carbon Oxides

Carbon monoxide is an odorless and colorless gas, arising mainly from burning different fuels. CO is one of the deleterious emissions widespread in industrialized urban environments, the main source of pollution being internal combustion engines. Stationary sources can generate significant emissions of CO only under incorrect combustion process.

Once inhaled CO replaces oxygen in the blood, causing blurred vision, reduced mental and physical capacity and severe effects on the nervous system, cardiovascular and lung.

According to 12574-87 standard, the maximum permissible concentrations of CO are 6 mg/m^3 for short-term average (30 min.) and 2 mg/m^3 for 24 hours. In the U.S., maximum concentration is 10 mg/m^3 for 8 hours.

Carbon dioxide is toxic only in very high concentrations (over 5000 ppm). CO_2 influences climate through increased greenhouse effect, the contribution that is being assessed is about 50%.

So far, there are not viable solutions, technically and economically, for eliminating CO_2 emissions. The only feasible solution, at this stage is that of increasing the efficiency of production processes, transformation and use of electricity or development of nuclear power plants and generation through unconventional techniques.

1.2.3. Toxic effects of sulfur compounds

The main source of atmospheric pollution with sulfur oxides is the thermal power plants that burn coal and heavy fuel and whose emissions exceed 60% of the total emissions of sulfur oxides.

In the combustion process, most sulfur content of fuel (95%) is converted into SO_2 and the rest in SO_3. SO_2 to SO_3 conversion occurs in the flame, but only after burning with high oxygen excess. SO_2 further oxidation can occur in the flue gas channels in the presence of vanadium and iron oxides, which act as a catalyst for the oxidation reaction of SO_2 to SO_3. This reaction may have a high kinetic in denitration system's reactors, disturbing their operation.

Discharged into the atmosphere, SO_2 reacts in proportion of 1 ÷ 2 ‰/h with oxygen, under the action of ultraviolet radiation, generating SO_3. This gas reacts with water vapor to form sulfuric acid. In periods of fog and very wet days, it is reached a level of transformation up to 15,7 %.

SO_2 is a colorless gas with pungent and stifling smell. Enhancing the effects of chronic respiratory diseases reflects SO_2 gas environmental impact. In low concentrations, causes spasm and contraction of upper airway and at high levels, causing respiratory and conjunctively mucosa burning, difficulty breathing, choking.

The harmful effects of SO_3 are presented in Table 1.5, for different concentrations of the gas in the air.

The presence of sulfur oxides in the environment is marked both by directs damage to plants and by altering water and soil composition. Thus, SO_2, in higher concentrations, destroys chlorophyll, his action being amplified through synergism with NO_2.

Sulfur oxides as sulfur dioxide and sulfuric acids resulting from their hydration, causes corrosion, discoloration of different materials and reduced resistance and elasticity of organic compounds.

In Romania, l2574-87 standard normalizes the maxim concentrations of SO_2 as follows: 0,75 mg/m^3- average for 30 min., 0,25 mg/m^3- 24-hour average and 0,01 mg/m^3 annual average. U.S. standard indicates for SO_2 emissions resulting from power plants and industry, an amount of 0,365 mg/m^3- 24-hour average.

Table 1.5. SO_3 harmful effects in the air

Concentration (ppm)	Physiological effects	Observations
0,3 ÷ 1,0	It is felt by smell	Tolerable concentrations in workshops and work areas.
1 ÷ 10	Is possible eye and respiratory irritation	Ways of standing decreasing until one hour with increasing concentration.
10 ÷ 100	Pronounced irritation of the eyes and upper respiratory tract.	Same as above.
150 ÷ 650	Attack of the respiratory system.	A half-hour to an hour of exposure can be life threatening depending on the individual.
10000 or 1%	Progressive respiratory paralysis	Rapidly lethal concentration. A lively irritation of the wet skin, which appears after a few minutes, is an indication of intoxication.

Hydrogen sulfide is a colorless gas with unpleasant odor, toxic, soluble in water, perceptible only in very small quantities and concentrations. The main source of H_2S emissions is the petrochemical industry, but also some energetic processes, heavy water production and coal gasification.

H_2S toxicity determines an aggressive impact on living organisms. Inhaled, in high concentrations, it kills by forming some combinations with hemoglobin and through paralysis of nervous center which controls breathing. In low concentration, is less dangerous because the body can break down over time, certain quantities of H_2S. In very low concentrations (0,0014 ÷ 0,0028 mg/l), it has a very unpleasant odor, which warns the presence of the pollutant.

H_2S concentrations indicated in STAS 12574-87, are as follows: 0,015 mg/l - the average for 30 min. and 0,008 mg/l - for 24 hours.

1.2.4. Toxicity and corrosive action of nitrogen compounds

The main polluters of the atmosphere with nitrogen oxides (NO_x) are mobile sources, however, cannot be neglected pollution from stationary sources, such as power plants, industrial enterprises, housing with proper heating.

Through their aggressiveness and toxicity, nitrogen oxides and nitric acid are extremely dangerous for humans. They attack the mucous membranes, respiratory system and transform the oxihemoglobin in metahemoglobin, which can lead to paralysis. A longer exposure to the action of nitrogen oxides, even at very low concentrations (only 0,5 ppm), weakens the human body, which became sensitive to bacterial infections. This kind of influence is greater in children. In addition, it should be noted that the toxicity of nitrogen oxides greatly increases through synergism with other toxic substances.

Nitric acid, formed by the reaction of NO_2 with H_2O, causes several types of corrosion, seriously affecting metal construction. H_2NO_3 forms nitrogen in the reaction with various cations present in the atmosphere. They have a corrosive action on copper, brass, aluminum, nickel, etc., destroying electrical and telecommunication networks. These processes can take place even at very low concentrations of oxides of nitrogen in atmospheric air (0,08 ppm).

The strength character of oxidizing and nitrated of nitrogen oxides and nitric acid is the main cause of destruction of plastics, paints and varnishes, used as safety covers in industrial plants. NO_x acts destructive on the building materials from the carbonates (marble) group. Nitrogen oxides penetrate the micro cracks of these materials, form nitrates, which, by crystallization, increase the cracks.

Primary and secondary measures applied to reduce emissions of nitrogen oxides are always accompanied by production of secondary emissions of CO, N_2O and NH_3. This way, it is recorded an increase, up 10% of annual N_2O concentration in the troposphere.

Harmful effect of N_2O is twofold. First, it should be mentioned his contribution in the enhancement of greenhouse effect. The most harmful effect of the presence of N_2O in the atmosphere is destruction of the protective ozone layer. Thus, N_2O is part of the inert gases in the troposphere, but harmful in the stratosphere, because of its catalytic effect in the photochemical reactions that develop active radicals that destroy ozone. The phenomenon is strongly enhanced by the fact that the lifetime of N_2O is very high (up to 180 years).

The 12574-87 standard provides for NO_2, maximum allowable concentrations of 0,3 mg/m^3- average 30 min.; 0,1 mg/m^3- 24 hour average and 0,01 mg/m^3- annual average.

Ammonia is a hydrogenated compound of nitrogen, colorless gas with strong odor and choking. Ammonia dissolves easily in water. Thus, one liter of water at a temperature of 0 ^oC dissolves ll50 l of ammonia. Ammonia solutions have lower density than water and a basic reaction.

The main source of pollution with NH_3 is its manufacturing process. Another source of NH_3 emission is the technological processes of production of nitric acid, ammonium nitrate and urea. Finally, another NH_3 pollution source results from the agricultural areas with intensive vegetation.

Anthropogenic emissions of NH_3 represent 80% of such emissions at the global level. Not be neglected the NH_3 emission from the NO_x emissions treatment systems of power plants.

NH_3 effect on organisms is stifling. At long or repeated exposure, the airways are severely affected. Because ammonia present in the air dissolves easily in water, it is driven by precipitation and reach surface waters, participating in their eutrophication.

1.2.5. Airborne toxic substances

Metal foundries, refineries, fuel burning stationary sources emit airborne inorganic substances such as lead, cadmium, arsenic, chromium, mercury, beryllium, and organic substances (vinyl chloride, benzene). Airborne toxic emissions get into the atmosphere, directly or indirectly, through the exhaust gas from the high stacks of different industries.

Exposure to these toxic substances can be directly, by inhalation, but also indirectly, by consuming contaminated food and water. These substances are accumulated in the body and affect health. Thus, beryllium causes diseases on lung, liver, kidney, spleen and lymph glands; arsenic causes malignancies; benzene causes leukemia; vinyl chloride causes liver and lung cancer. Many other toxic airborne substances affect the airways, lungs and cause nervous system disorders.

For some toxic substances maximum permissible airborne concentrations are indicated in STAS 12574-87. Thus, the maximum permissible concentrations, as daily averages are: 0,007 mg/l - for lead, 0,003 mg/l - for arsenic and 0,8 mg/l - for benzene.

In airborne substances, are also included dusts, both deposited and in suspension. The difference between them is only the gravitational deposition velocity, which is strongly related to the size and density of particles.

Anthropogenic sources of pollution with particulate matter are: asbestos cement factories, steel mills, metals foundries, power plants fueled with solid fuels, plants based on cotton decortications, diesel engines, elevators for grain handling, construction sites etc.

On short or long term, dust, aerosols and smoke may have negative environmental effects. Regarding the human health the effects are: irritation of the eyes and throat as well as reduced resistance to infection. Suspended particles exhausted from diesel engine can cause lung cancer. Some dust can damage the flora and fauna or cause corrosion of buildings.

Fly ash, evacuated by the stacks of combustion installations, fine ash driven by wind and coal dust from the stockpiles of coal, have the effect of environmental contamination and long-distance circulation of harmful gases in relation to the emission site. One such example is the carbon monoxide that can reach long distances to where it was issued.

Increased toxicity of air pollutants determinate the World Health Organization to impose the maximum allowable limits for various pollutants, depending on the duration of exposure. For the main air pollutants of combustion processes, these limits are given in Table 1.6.

Table 1.6. Maximum allowable values imposed by the World Health Organization, for a range of air pollutants

Pollutant	Maxim quantity ($\mu g/m^3$)	Exposure time
Sulfur dioxide (SO_2)	500	10 minutes
	350	1 hour
	100 ÷ 150	24 hours
	40 ÷ 60	1 year
Nitrate dioxide (NO_2)	400	1 hour
	150	24 hours
Carbon monoxide (CO)	30	1 hour
	10	8 hours
Particles in suspension in the black smoke	100 ÷ 150*)	24 hours
	40 ÷ 60*)	1 year
Total amount of airborne particles	150 ÷ 230	24 hours
	60 ÷ 90*)	1 year
Small particles (less than 10 m) that enter the lungs	70*)	24 hours
Lead	60 ÷ 90	1 year

*) – Guideline values for simultaneous exposure to sulfur dioxide and particulates, these values can not be applied when it is present only one of the two components.

1.3. Environmental legislation; Regulations

Environmental pollution is a contemporaneous social and economic problem, pollution alarming proportions requiring stringent legislative measures.

Environmental status is a concern of United Nations Organization, who has proposed the development of joint activities in protecting and preserving the environment, especially through the introduction of national and international legislation.

Environmental legislation in Romania is in full compliance with European law. European regulations, for the environment, can be classified into the following categories:

1 An environmental legislation, a set of 300 acts (directives, regulations, decisions, and recommendations); European environmental legislation can be classified into:
  - horizontal legislation, such as that relating to environmental management;
  - sectorial legislation, focused on specific problems such as air quality, waste management, water quality, nature protection, industrial pollution control and risk management (for chemicals and organic substances for noise pollution, generated by vehicles and machinery, nuclear safety and radiation protection);

2 Documents with political character, a package of five action programs, sectorial policies and strategies, communicates and statements; all these documents are not legally binding;

3 EU environmental treaty, which is a small package of regulations, with 70 directives and 11 regulations adopted under the constituent treaty, international treaties signed by the Council of Europe and the principles derived from European Court of Justice.

Since the combustion of classic fuels ranks among the first places in terms of environmental pollution, it is expected to exist special regulations, limit values of harmful emissions at the stack. Such standards were developed in all industrialized countries in the world, being more or less severe depending on the specifics of each country, the fuels used, the installed capacity per unit for energy groups, the duration of remaining life of installations, the level of development for burning and flue gas purification technologies etc. In this sense, in Romania it is in force the Government Decision (GD) no. 541/2003, laying down measures for the limitation of emissions of certain pollutants arising from large combustion installations.

GD nr.541/2003 is actually the European Council Directive 2001/80/EEC transposed into Romanian legislation and amends Directive 88/609/EEC being in close correlation with acts such as: GEO 34/2002, the Ordinance on the prevention, reduction and integrated control of pollution approved with some amendments by law no. 645/2002; GEO 243/2000, Atmosphere Protection Ordinance, approved by Law no. 655/2001, GD 142/2003, Decision on limiting the sulfur content of liquid fuels (sets the maximum sulfur content of fuel oil and diesel, other than that covered by GD 1336/2000, to limit the sulfur content of diesel and GD no. 732/2001, laying down conditions for the marketing of gasoline and diesel, the most relevant one is the provision for heavy fuel, that the maximum sulfur content in percent by mass, should not the step 1% from 1 January 2007.

Government Decision no. 541/2003 applies to combustion installations whose nominal thermal power of 50 MW, irrespective of the type of fuel used. These provisions do not apply to large combustion installations that use directly, the products of combustion in technological processes, such as: reheating or direct heating, drying, treatment of objects or materials (reheating furnaces, furnaces for heat treatment); post-combustion installations; installations used for regeneration of cracking catalysts; installations for the conversion of hydrogen sulfide in sulfur; reactors used in the chemical industry; coke oven batteries; any installation used for propulsion; gas turbines used offshore.

Summary of emission limits for large combustion installations, provided by GD nr.541/2003 is given in Table 1.7.

According to the GD nr.541/2003, large combustion installations are classified in three categories: Class I and II with those installations whose emissions are not within the emission limits, and in category III installations complying with the limit pollutant emissions.

Table 1.7. Summary of emission limit values provided in GD nr.541/2003.

Pollutant	**Fuel type**	**Emission limit values (Note 1)** mg/Nm^3			
		50 ÷ 100 MW$_t$	100 ÷ 300 MW$_t$	300 ÷ 500 MW$_t$	> 500 MW$_t$
SO_2	Solid (Notes 2; 3)	2000	2000 ÷ 400, linear variation		400
	Liquid	1700		1700÷400 linear variation	400
	Gaseous	35 - generally, 5 - liquefied gas, 800 - low calorific power, derived from gasification of refinery residues, coke oven gas and blast furnace gas with low calorific power.			
NO_x	Solid (Notes 4; 5)	600			500, and from 1.01.2016-200
	Liquid	450			400
	Gaseous	300			200
Dust	Solid	100			50 (Note 6)
	Liquid	50 (Note 7)			
	Gaseous	5 - General; 1 - furnace gas, 50 - gas from steel industry, which can be used elsewhere			
SO_2, NO_x and dust	Big installations with mixed outbreak	(Note 8)			

Notes:

1. Emission limit values are considered as the mass of substance reported to the volume of waste gas, considering the oxygen content of 3% in volume, for liquid and gaseous fuels, 6% for solid fuels and 15% for gas turbines.
2. Units with a nominal thermal power ≥ 400 MWt, which doesn't operates more than
   - 2000 hours per year, until December 31, 2015,
   - 1500 hours per year, starting with January 1, 2016

   (calculated as the average working hours over a period of 5 years) it applies a limit of 800 mg/Nm^3 for SO_2.

3. If the emission limit value can not be respected due to fuel characteristics, the following rates of desulfurization must be respected:

- at least 60% for large combustion installations with thermal power ≤ 100 MWt,
- at least 75% for large combustion installations with thermal power of 100 MWt and 300 MWt,
- at least 90% for large combustion installations with rated thermal power > 300 MWt
- at least 94% for large combustion installations with rated thermal power > 500 MWt.

4. Until 31 December 2015, the NOx emission limit is 600 mg/Nm^3 for plants with nominal thermal power > 500 MWt, whose annual use (averaged over the last five years) does not exceed 2000 hours, from 1 January 2008. From 1 January 2016 such plants, whose annual duration of use does not exceed 1500 hours (averaged over a period of five years) must comply with NOx emission limit value of 450 mg/Nm^3.
5. By 1 January 2018, large combustion installations that operated during the 12 months preceding the date of January 1, 2001 and thereafter, continues to operate, using solid fuels with less than 10 % volatile organic compounds, must comply with emission limit value of 1200 mg/Nm^3.
6. An emission limit value of 100 mg/Nm^3 can be applied to existing installations with a thermal power ≥ 500 MWt, which uses solid fuel with a lower calorific value of 5800 kJ/kg, higher moisture content of 45% content moisture and ash more than 60% and calcium oxide content greater than 10%.

7. Emission limit value of 100 mg/Nm^3 can be applied to large combustion installations with thermal power less than 500 MWt using liquid fuel with an ash content > 0,06%.
8. Installations burning two or more fuels simultaneously, as specified in Article 13 are applicable limit values calculated according to Annex 8 of GD. 541/2003.

Normal limit values of concentrations of pollutants are not immutable, those being the result of an evolution towards more restrictive levels. Tighter restrictions are expected, with the development of clean combustion technology and flue gas cleaning. Illustrative in this sense are the EURELECTRIC (Union of the Electricity Industry) proposals, in order to reduce emissions from combustion of solid fuels, being also specified the treatment technologies to be used (Table 1.8).

Table 1.8. EURELECTRIC suggestions for reducing emissions in coal combustion installations

Fuel	**Installation type**	**Combustion technique**	**Purification technique / standard emission in dry gases to 6% O_2 (mg/Nm^3)**		
			Dust	SO_2	NO_x
Bituminous coal	New	pulverized coal	Electrostatic precipitators 20 ÷ 30	wet cleaning 140 ÷ 400	Catalytic systems 170 ÷ 200
					Basic methods 900 ÷ 2000
Lignite	New	pulverized coal	Electrostatic precipitators 20 ÷ 30	dry absorber 140 ÷ 400	Basic methods 170 ÷ 200
				wet cleaning 140 ÷ 400	
Bituminous coal, lignite	New	fluidized	Electrostatic precipitators 20 ÷ 30	Calcium product injection 140 ÷ 200	Basic methods 170 ÷ 200
Bituminous coal	Existent	pulverized coal	Electrostatic precipitators 30 ÷ 200	wet cleaning 200 ÷ 400	Basic methods 150 ÷ 250
				Fuel with less sulfur 900 ÷ 1000	Catalytic systems 200 ÷ 400
				dry absorber 400 ÷ 600	
Lignite	Existent	fluidized	Electrostatic precipitators 50 ÷ 200	Fuel with less sulfur 200 ÷ 400	Basic methods 200 ÷ 400
Bituminous coal	Existent	fluidized	Electrostatic precipitators 30 ÷ 200	Calcium product injection 300 ÷ 450	No reduction measures 150 ÷ 700
Lignite	Existent	fluidized	Electrostatic precipitators 50 ÷ 200	Calcium product injection max. 400	-

Emission's limit values in flue gases are standard in European Union's countries through the troposphere ozone concentration. Thus, in the EU Directive regarding the ozone in ambient air and by Decree no. 2002-213 there are limited the allowable emissions values, as is shown in Table 1.9.

Table 1.9. Values imposed by the European regulations

Limit values of pollutants in ambient air for protecting human health **The** European Directive relating to ozone $^{(1)}$ and Decree no.2002-213/2002$^{(2)}$								
Pollutant	**Ozone**$^{(1)}$	**SO$_2$** $^{(2)}$		**Fine particulate matter** $^{(2)}$		**NO$_x$** $^{(2)}$		
Pollution type	background	punctual	punctual	punctual	background	punctual	punctual	background
Limit values	120 µg/m^3 but not more than 25 days per calendar year averaged over three years	350 µg/m^3 but not more than 24 hours per calendar year	125 µg/m^3 but not more than 3 days per calendar year	50 µg/m^3 but not more than 35 days per calendar year	40 µg/m^3	200 µg/m^3 but not more than 175 hours per calendar year	200 µg/m^3 but not more than 18 hours per calendar year	40 µg/m^3
Date of application	1.01.2010	1.01.2005	2002	1.01.2005		Until 31.12.2009	1.01.2010	1.01.2010
Exceeding margin	2001	120		20	6		90	18
	2002	90		15	4		80	16
	2003	60		10	3		70	14
	2004	30		5	1		60	12
	2005						50	10
	2006						40	8
	2007						30	6
	2008						20	4
	2009						10	2

1.4. Determination of emissions

Emissions of pollutants are expressed, usually in mass concentration (C_m), measured in mg/m^3 or mg/Nm^3, and volume concentration (C_v), measured in parts per million (ppm). Because 1 ppm = 1 cm^3/m^3 the relation of transformation volume concentration in mass concentration is of the form:

$$C_m = C_v \cdot \frac{M_G}{22{,}41383}\left(mg / Nm^3\right), \qquad (1.1)$$

where, M_G is the molecular weight of harmful gas (kg/kmol) and 22,41383 is the molar volume (m^3/kmol) in normal environmental conditions (0 $^{\circ}$C, 1013 mbar).

The relations between volume and mass concentrations, for different gaseous pollutants are of the form:

$$\begin{cases} 1ppm\ SO_2 = \dfrac{M_{SO_2}}{22{,}41383} = \dfrac{64{,}059}{22{,}41383} = 2{,}858\ mg/Nm^3 \\ 1ppm\ NO_2 = \dfrac{M_{NO_2}}{22{,}41383} = \dfrac{46{,}0055}{22{,}41383} = 2{,}0525\ mg/Nm^3\ , \\ 1ppm\ CO = \dfrac{M_{CO}}{22{,}41383} = \dfrac{28{,}02}{22{,}41383} = 1{,}25\ mg/Nm^3 \end{cases} \qquad (1.2)$$

Typically, nitrogen oxides concentrations (C_i) becomes equivalent concentration of NO_2 ($C_{e\ NO2\ i}$), which relates to the normal oxygen content in flue gas. Transformation relation is as follows:

$$\frac{C_i}{C_{eNO_2i}} = \frac{M_i}{M_{NO_2}}. \qquad (1.3)$$

For example, initial concentration of NO (C_{NO}) equivalent as NO_2 (C_{NO2}) concentration, is calculated as follows:

$$C_{NO_2} = (46/30) \cdot C_{NO}. \qquad (1.4)$$

Thus, if concentrations of nitrogen monoxide, protoxide and dioxide are experimentally determined (C_{NO} , C_{N2O}, C_{NO2}), at a certain temperature and certain oxygen content, then it can be calculated the NO_2 total concentration reported in an outbreak situation which work with coal dust for various temperatures in the range (0 ÷ 1000) °C. For input data: C_{NO} = 391,4 ppm, C_{N2O} = 3,6 ppm, C_{NO2} = 45,1 ppm, at a temperature of 27 °C and 4 % O_2 content, will result the data presented in Table 1.10.

Table 1.10. Results of the calculation of total equivalent concentration of NO_2

Temperature (K)	**The concentration of nitrogen oxides equivalent in NO_2**		
	ppm, at 4 % O_2	ppm, at 6 % O_2	mg/Nm^3, at 6 % O_2
273	590,600	521,117	1069,592
300	649,011	572,656	1175,370
500	1081,685	954,427	1958,961
800	1730,696	1527,084	3134,340
1000	2163,370	1908,856	3917,926
1300	2812,381	2481,613	5093,300

Emissions of pollutants can be expressed as a ratio of pollutant mass and lower calorific value of fuel.

According to EU methodology, CORINAIR/SNAP (**COR**e **I**nventories **AIR**/ **S**ystem of **N**omenclature for **A**ir **P**ollution/), emissions of a given activity can be expressed by a general formula, as is the following:

$$E_{s,a,t} = C_{a,t} \cdot e_{s,a}\ , \tag{1.5}$$

where:

$E_{s,a,t}$ – relative emission of substance s, released by activity a, for a period of time t;
$C_{a,t}$ – quantity of products of activity a, for a period of time t;
$e_{s,a}$ – emission factor relative to substance s, released by activity a.

For a set of activities, the relation determines the total emission relative to a given pollutant:

$$E_{s,t} = \sum_{a=1}^{a=n} E_{s,a,t}\ , \tag{1.6}$$

where, n represents the number of pollutant activities taken into account.

If the volume of production ($C_{a,t}$) is not very difficult to be determinate, the emission factors, corresponding to specific pollutants, released in certain circumstances, for certain types of raw materials, basically, can not be calculated in a deterministic manner. Experience in environmental inventories allowed to establish, by statistical way, the emission factors for a wide range of human activities. In fact, to estimate does not mean applying a relation of the form (1.5), the terms of the expression must be determined in a restricted activity inside a technology or an operation. In these circumstances, a more accurate estimation of the emission of a substance in a given period of time, for a given geographical area is given by a relation of the form (1.7), adapted to fuel combustion:

$$E_{s,t,z} = \sum_{a,i,f}\left[C_{a,i,f,t,z} \cdot \sum_{p}\left(e_{s,a,i,f,p} \cdot P_{a,i,p,f} \right)\right], \tag{1.7}$$

where, C represents amount of energy delivered by process, e represents the emission factors, and P a factor dependent on activity, fuel type and combustion technology. Indices have the following meanings:

a – relative index to the source of pollution (activity);
f – relative index to the fuel type;
i – relative index to the economic sector;
p – relative index to the combustion process;
s – relative index to the pollutant substance;
t – relative index to the duration of analysis;
z – relative index to the geographic area.

The complexity of phenomena is necessary to establish specific models for different pollutants, the most difficult to address being the models for distributed sources of pollution (transport, biogenic emissions, etc.).

In the case of thermal power plants, the relation of the form (1.7) is applied to the components of the process, usually two of these components being analyzed:

$$E = E_1 + E_2\ , \tag{1.8}$$

where,

E_1 – emission resulted from the combustion process;
E_2 – emission resulted from other activities, as extractive and preparation process, water treatment, treatment processes for solid, liquid and gaseous pollutants.

If E_2 refers to control processes of pollutants, in (1.8) this quantity is taken with negative sign. Always $E_1 \geq 0$, while E_2 can take positive or negative values (smaller, in absolute, than E_1). If measurements results are not sufficient and the processes of flow of fuel are not know, the emission estimation method, involves the use of a relation like:

$$E_{s,t} = \sum_{f=1}^{f=n} Q_f \cdot H_f^i \cdot e_{s,f} \,, \tag{1.9}$$

where:
$E_{s,t}$ – emission of substance s, in range t;
Q_f – total fuel consumed f
H_f^i – lower calorific value of fuel f;
$e_{s,f}$ – emission factor of substance s, for fuel f.

The method requires knowledge of emission factors, strictly dependent on the type of fuel. In Table 1.11 are given the emission factors of fuels and European codes of these fuels – code NAPFUE (**N**omenclature for **A**ir **P**ollution of **FUELS**).

Table 1.10. Emission factors specific for combustion

Fuel	**Cod** NAPFUE	**Emission factor** (g/GJ)			
		SO_2	NO_x	CO	CO_2
Brown coal	101 ÷ 103	623	160$^{1)}$; 200$^{2)}$; 340$^{3)}$; 280$^{4)}$; 95 ÷ 150$^{5)}$.	200	$96\cdot10^3$
Mixtures of bituminous coal	104	506			$95\cdot10^3$
Lignite	105	*			$100\cdot10^3$
BKB	106	*	*	*	$98\cdot10^3$
Bituminous coal coke	107	578	*	*	$107\cdot10^3$
Peat	113	500	*	*	$110\cdot10^3$
Household Waste	114	385	*	*	$109\cdot10^3$
Heavy fuel	203	1430/885/ 478/240	170 ÷ 190	15	$79\cdot10^3$/ $77\cdot10^3$
Light fuel oil	204	95	100	15	$75\cdot10^3$
Gasoline car (without / with lead)	208	6,8/54	*	*	$73\cdot10^3$
Natural gas	301	0,5	60 ÷75	19	$57\cdot10^3$
LPG	303	2,2/8,7	*	19	*
Petroleum coke	304	530	42	19	$47\cdot10^3$

Note: * - specific values
1) – classical grill furnace;
2) – pulverized coil furnace;
3) – front burner furnace;
4) – tangential furnace;
5) – fluidized combustion furnace.

The amount of pollutant discharged into the atmosphere, in a certain period of time, is determined with a relation obtained by customizing the relation (1.9):

$$E = Q_c \cdot H^i \cdot e\,, \quad \text{(kg)} \tag{1.10}$$

where: Q_c is the amount of fuel consumed, during that period (kg), H^i - initial fuel calorific power (kJ/kg), and e is the emission factor, for a certain pollutant (kg/kJ).

Lot, based on primary records for the period under consideration, determines quantities of fuel and calorific power.

In precise calculations for coal combustion it is introduced a correction on the amount of fuel consumed (Q_c), excluding the content of the slag and ash unburned. When using several types of fuel, the total amount of pollutant is determined by adding the emission of each of them.

For forecasting calculations, the mass concentration of pollutants E_m can be determined with the relation:

$$E_m = \frac{e}{F_V}\,, \quad \text{(mg/Nm}^3\text{)} \tag{1.11}$$

where, emission factor (e) is measured in mg/GJ, and F_V represents the volume factor, defined as the ratio of total volume of combustion gases and heat related to the fuel burned in the boiler, measured in Nm^3/GJ. For the volume factor are indicated the following values:

$F_V = 480\ Nm^3/GJ$ – for lignite,
$F_V = 380\ Nm^3/GJ$ – for bituminous coal,
$F_V = 290\ Nm^3/GJ$ - for heavy fuel,
$F_V = 320\ Nm^3/GJ$ – for natural gas.

✓ SO_2 pollutant

The relation determines emission factor for sulfur dioxide:

$$e_{SO_2} = \frac{\frac{M_{SO_2}}{M_S} \cdot \frac{S}{100}}{H^i} \cdot (1 - r)(kg/kJ), \tag{1.12}$$

where:

M_{SO_2} - molecular mass of SO_2, in kg/kmol;
M_S – molecular mass of sulfur, in kg/kmol;
S - amount of sulfur in fuel, in %;
H^i - lower calorific value of fuel, in kJ/kg;
r - degree of sulfur retention by ash and slag.

In the current calculations, it is recommended:

$r = 0{,}2$ - for lignite,
$r = 0{,}05$ - for bituminous coal,

$r = 0$ - for heavy fuel and natural gases.

For forecasting calculations are recommended the values:

$r = 1{,}15$ - for lignite,
$r = 2{,}15$ - for mixture bituminous coal and silt,
$r = 1{,}0$ – for internal production heavy fuel,
$r = 3{,}0$ - for import heavy fuel.

✓ NO_x pollutant

To calculate the NO_x emission there are used the emission factors indicated in 1.11 to which it was applied the correction corresponding to the oxygen content in flue gas. Those factors are dependent on the fuel type, the boiler's effective power and correspond to the nominal charge of combustion installation. The values of emission factors are close to those used in the European Economic Community countries (Table 1.10), especially for smaller than 300 MW_t power plants.

A big difference is observed for combustion of natural gas, due to the lack of secondary systems of NO_x emissions control. For coal combustion, should be considered in comparison with pulverized coal, technique used mainly in power plants from Romania.

Table 1.11. Emission factors $e_{100}^{NO_x}$

Fuel	**NO_x emission factors, at boiler's nominal charge**					
	Boiler thermal power (MW_t)$^{*)}$					
	50 ÷ 100		100 ÷ 300		> 300	
	kg/kJ	g/GJ	kg/kJ	g/GJ	kg/kJ	g/GJ
Lignite	$2{,}0 \cdot 10^{-7}$	200	$2{,}2 \cdot 10^{-7}$	220	$2{,}6 \cdot 10^{-7}$	260
Bituminous coal	$3{,}8 \cdot 10^{-7}$	380	$4{,}2 \cdot 10^{-7}$	420	$4{,}5 \cdot 10^{-7}$	450
Heavy fuel	$1{,}9 \cdot 10^{-7}$	190	$2{,}1 \cdot 10^{-7}$	210	$2{,}8 \cdot 10^{-7}$	280
Natural gases	$1{,}3 \cdot 10^{-7}$	130	$1{,}5 \cdot 10^{-7}$	150	$1{,}7 \cdot 10^{-7}$	170
Note: $^{*)}$ it is determined the wedge between the fuel inserted into the boiler and the fuel's lower calorific power .						

To calculate the emission factor of the boiler at partial load, but more than 50%, it is introduced the following correction:

$$e_x^{NO_x} = e_{100}^{NO_x} \cdot \left[a + (1-a)\frac{L-50}{50} \right] \quad \text{(kg/kJ)}, \qquad (1.13)$$

where:

$e_x^{NO_x}$ - emission factor of charge x;

$e_{100}^{NO_x}$ - emission factor at nominal charge;

L - partial load of boiler (between 50 % and 100 %);

a – coefficient dependent on the fuel type and may have the following values:

0,85 – for pulverized coal
0,75 – for heavy fuel,
0,50 – for natural gases.

NO_x emission strongly depends on the oxygen content in the combustion gases. If the measured values for O_2 differs from standard specifications (6 % for coal combustion and 3 % for natural gases and heavy fuel combustion in dry gases), the NO_x emission values are corrected according to:

$$E_{NO_x}^{corect} = E_{NO_x}^{masurat} \cdot \left[\frac{21 - O_2^{s\tan dard}}{21 - O_2^{masurat}} \right]. \tag{1.14}$$

In more rigorous calculations, which take into account the temperature and humidity of flue gas can be used correction:

$$E_{NO_x}^{corect} = E_{NO_x}^{masurat} \cdot \left[1 + \frac{22{,}4 \cdot W}{18 \cdot 10^3} \right] \cdot \left[\frac{273 + t_m}{273} \right] \left[\frac{20{,}9 - O_2^{s\tan dard}}{20{,}9 - O_2^{masurat}} \right], \tag{1.15}$$

where:
W – combustion gases humidity, measures in g H_2O / m^3 of dry gases;
t_m – average temperature of combustion gases, in ^oC.

✓ Fly ash pollutant

Emission factor is determined with the relation:

$$e_{cenusa} = \frac{A \cdot (1 - \eta_f)(1 - \eta_e)}{H^i} \text{ (kg/kJ)}, \tag{1.16}$$

where:
A - coal ash content (%);
η_f - degree of retention of the ash in the furnace (in mass %);
η_e - Dust retention installation efficiency (electrostatic precipitator), in %;
H^i – fuel's lower calorific power (kJ/kg).

For post calculation are used average values, results from operation, and for forecast calculations is recommended to use the following values:

$A = 40$ % - for lignite,
$A = 30$ % - for bituminous coal in the country,
$A = 20$ % - for imported bituminous coal,
$\eta_f = 15$ %;
$\eta_e = 97$ % - if electrostatic precipitators rehabilitation do not exceeded 50% of program,
$\eta_e = 99$ % - to finish the electrostatic precipitator's rehabilitation program.

Usually, when burning heavy fuel, emission of particles is neglected. Usually, when heavy fuel is burned, the emission of particles is neglected. For rigorous calculations, it can be an ash content of heavy fuel A = 0,1%, ash which is fully discharged to the stack.

✓ CO_2 pollutant

CO_2 emission factors adopted by all European Community countries are used to forecast calculations. These values are given in Table 1.10, for most fuels used for energy purposes.

For accurate calculations can be used the relation:

$$e_{CO_2} = \frac{\frac{M_{CO_2}}{M_C} \cdot \frac{C}{100}}{H^i} \quad \text{(kg/kJ)}, \qquad (1.17)$$

where:

M_{CO_2} - CO_2 molecular mass in kg/kmol;
M_C – carbon molecular mass in kg/kmol;
C – amount of carbon in the fuel in mass %;
H^i - fuel's lower calorific power in kJ/kg.

For fuels used in power plants in Romania, in 1992, it results the following average values of emission factors for CO_2:

109000 g/GJ – for lignite;
100000 g/GJ – for bituminous coal;
81000 g/GJ – for heavy fuel;
59000 g/GJ – for natural gas.

These values are only slightly higher than those adopted by the European Economic Community countries (Table 1.10), the largest overflow is at lignite combustion.

To illustrate the emission evaluation methodology, in Box 1.1 is given a computational application.

Box 1.1. Computational application of emission evaluation methodology for the thermal power plant

Application

Assess pollutant emissions discharged into the atmosphere of a steam boiler, with the following characteristics:

- thermal power higher than 300 MW_t;
- average charge = 80 %;
- works with pulverized lignite and heavy fuel with the following:

1. lignite – lower calorific power H_l^i = 6700 kJ/kg, sulfur content of 1,15 %, carbon content 18 %;

2. heavy fuel - lower calorific power H_2^i = 38456 kJ/kg, sulfur content of 3 %.
The total amount of lignite consumed is Q_1 = 100 t, and heavy fuel Q_2 = 10 t.

Issue
Emissions are calculated for the considered period, separately, for each fuel used. The total emission results by summing those quantities. Emission factor for sulfur dioxide, in lignite case, is:

$$e_{1SO_2} = \frac{\frac{M_{SO_2}}{M_S} \cdot \frac{S_1}{100}}{H_1^i} \cdot (1 - r_1) = \frac{\frac{64}{32} \cdot \frac{1,15}{100}}{6,7 \cdot 10^3} \cdot (1 - 0,2) = 2,74 \cdot 10^{-6} \text{ kg/kJ}$$

Sulfur dioxide emission, generated at lignite combustion is:

$$E_{1SO_2} = 100 \cdot 10^3 \cdot 6,7 \cdot 10^3 \cdot 1,56 \cdot 10^{-6} = 1,8 \text{ tonnes}$$

For heavy fuel combustion results:

$$e_{2SO_2} = \frac{\frac{M_{SO_2}}{M_S} \cdot \frac{S_2}{100}}{H_2^i} \cdot (1 - r_2) = \frac{\frac{64}{32} \cdot \frac{0,03}{100}}{38,456 \cdot 10^3} \cdot (1 - 0) = 1,56 \cdot 10^{-6} \text{ kg/kJ}$$

$$E_{2SO_2} = 10 \cdot 10^3 \cdot 38,456 \cdot 10^3 \cdot 1,56 \cdot 10^{-6} = 580 \ kg = 0,58 \text{ tonnes}$$

Total emission of sulfur dioxide is

$$E_{totalaSO_2} = E_{1SO_2} + E_{2SO_2} = 1,80 + 0,58 = 2,40 \text{ tonnes}$$

NO_x emissions are calculated similarly:
For lignite combustion:

$$e_{100}^{NO_x} = 2,6 \cdot 10^{-7} \text{ kg/kJ,}$$

$$e_{80}^{NO_x} = e_{100}^{NO_x} \cdot \left[a_1 + (1 - a_1) \frac{L - 50}{50} \right] = 2,6 \cdot 10^{-7} \cdot \left[0,85 + (1 - 0,85) \frac{80 - 50}{50} \right] =$$

$$= 2,5 \cdot 10^{-7}$$

$$E_{1NO_x} = 100 \cdot 10^3 \cdot 6,7 \cdot 10^3 \cdot 2,5 \cdot 10^{-7} = 0,17 \text{ tonnes.}$$

For heavy fuel combustion

$$e_{100}^{NO_x} = 2,8 \cdot 10^{-7} \text{ kg/kJ,}$$

$$e_{80}^{NO_x} = e_{100}^{NO_x} \cdot \left[a_2 + (1-a_2)\frac{L-50}{50}\right] = 2{,}8 \cdot 10^{-7} \cdot \left[0{,}75 + (1-0{,}75)\frac{80-50}{50}\right] =$$

$$= 2{,}52 \cdot 10^{-7},$$

$$E_{2NO_x} = 10 \cdot 10^3 \cdot 38{,}456 \cdot 10^3 \cdot 2{,}52 \cdot 10^{-7} = 97 kg = 0{,}097 \text{ tonnes.}$$

The cumulated NO$_x$ emission is:

$$E_{totalNO_x} = E_{1NO_x} + E_{2NO_x} = 0{,}17 + 0{,}097 = 0{,}27 \text{ tonnes.}$$

Dust emission is calculated only for lignite, and could be accepted that the emission factor, in heavy fuel combustion, is invalid:

$$e_{ash} = \frac{A_1 \cdot (1-\eta_f)(1-\eta_e)}{H_1^i} = \frac{0{,}40 \cdot (1-0{,}15)(1-0{,}97)}{6700} = 1{,}5 \cdot 10^{-6} \text{ kg/kJ}$$

The ash that is evacuated into the atmosphere is

$$E_{ash} = 100 \cdot 10^3 \cdot 6{,}7 \cdot 10^3 \cdot 1{,}5 \cdot 10^{-6} = 1 \text{ tonne}$$

Carbon dioxide emission is calculated:

For lignite, the emission factor, for CO$_2$, is 98•10^{-6} kg/kJ, so the emission

$$E_{1CO_2} = 100 \cdot 10^3 \cdot 6{,}7 \cdot 10^3 \cdot 98 \cdot 10^{-6} = 65600 kg = 65{,}6 \text{ tonnes;}$$

For heavy fuel, the emission factor, for CO$_2$, is 72•10^{-6} kg/kJ, so the emission

$$E_{2CO_2} = 10 \cdot 10^3 \cdot 38{,}456 \cdot 10^3 \cdot 72 \cdot 10^{-6} = 27688 kg = 27{,}7 \text{ tonnes.}$$

Carbon dioxide cumulated emission is

$$E_{totalaCO_2} = E_{1CO_2} + E_{2CO_2} = 65{,}5 + 27{,}7 = 93{,}3 \text{ tonnes.}$$

CHAPTER 2

SULFUR OXIDES EMISSIONS CONTROL

Natural emissions of sulfur oxides (SO_x), the result of volcanic activities and fumaroles, are huge, between $(78 \div 284)\cdot 10^6$ t SO_2 equivalent per year and impossible to be reduced or controlled. Simultaneously with the natural emissions, large quantities of SO_x are released into the atmosphere from human activities (about 150 – 200 Mt SO_x equivalent per year). Thus, in large urban areas, concentrations of SO_x can be achieved between $0{,}01 \div 0{,}1$ ppm (at 25 degree and 1 atmosphere pressure, 1 ppm = 2620 $\mu g/m^3$), values that can achieve and even exceed the daily-allowed emissions. Most of human SO_2 emissions result from combustion processes in power energy. Unlike natural emissions, human emissions can be controlled, but with considerable efforts technical and economical.

2.1. Sulfur oxides forming in the combustion processes

It is assumed that a large amount of SO formed in the main combustion area at beginning of combustion. SO is oxidized to SO_2 first and then to SO_3. The main reactions that lead to the formation of SO_2 are:

$$SO + O_2 \rightarrow SO_2 + O\ ; \tag{2.1}$$

$$SO + OH \rightarrow SO_2 + H\ . \tag{2.2}$$

It is outstanding that these reactions lead to the appearance of free oxygen and hydrogen atoms, chemically very active and which will interfere in subsequent reactions. Besides, it should not neglect the fact that sulfur oxidation reactions occur simultaneously with the oxidation of hydrocarbon fuels, obtaining large quantities of radicals O, H and OH, which will occur in the sulfur oxidation reactions.

Reactions of SO_3 formation and a third component (M), which can be represented even by an additional consumption of energy:

$$SO_2 + O_2 + M \rightarrow SO_3 + M\ . \tag{2.3}$$

Reactions of this type, involving a third component have a lower kinetic than reactions involving only two components. However, due to the high temperature from combustion chamber, reactions of the type (2.3) evolve quickly. At the same time, in combustion chambers, the concentration of oxygen atoms is maxim, so that SO_3 is converted in SO_2 through a sequence of reactions like:

$$SO_3 + O \rightarrow SO_2 + O_2 \ , \qquad (2.4)$$

$$SO_3 + H \rightarrow SO_2 + OH \ , \qquad (2.5)$$

$$SO_3 + M \rightarrow SO_2 + O + M \ , \qquad (2.6)$$

the last stage being actually a process of thermal dissolution. In the high temperature area from furnace, where the concentration of free oxygen atoms is high, reactions of type (2.3) and (2.4) are predominant and when the hydrocarbon concentration from flame is high, reaction of type (2.5) become predominant.

When the flue gases enter into the colder areas of the boiler, the free atoms concentration drops rapidly due to recombination processes. In these conditions, formation and decomposition of SO_3 through reactions of type (2.3) ÷ (2.5) is much slower. A part of SO_3 can be thermally decomposed by reactions of the type (2.6), but when the temperature drops significantly, the amount of $SO_{3,}$ which is thermally decomposed, became insignificant.

In the industrial combustion installations, reactions sequence involving sulfur and sulfur oxides evolve so much that SO_3/SO_2 ratio is between 1/40 ÷ 1/80. If the excess fuel from the primary pyrolysis area is significant, amount of SO_3 can be omitted. It can be concluded that the main sulfur compound in the flue gas is SO_2, despite the fact that the thermodynamics of oxidation reactions, could tip the balance towards the formation of SO_3. Conversion of SO_2 into SO_3 in free atmosphere is a slow process due to the low temperature, however, the conversion rate may be increased in the presence of compounds in airborne particles, compounds that catalyze the conversion reaction of SO_2 to SO_3 and formation of aerosols sulfates with high toxicity.

2.2. Desulfurization techniques

Burning of solid and liquid fuels can pollute the atmosphere harmfull with SO_2 emissions. The large volume of emissions make necessary desulfurization of flue gases, thus SO_2 control can be achieved in the next stages of technological process:

- ✓ before combustion, by treating the fuel;
- ✓ during the combustion, at the furnace level;
- ✓ after the combustion, by cold gases treatment.

The first category of techniques called pre-combustion techniques aims in one form or another reduction of sulfur quantity that is introduced into the furnace. The methods used in combustion are called the primary or intra-combustion methods and are based on neutralization reactions of pollutant, using alkaline compounds that are injected into the furnace. The highest rate of desulfurization is achieved when the combustion gases are treated on their exhaust path to the stack. Post-combustion or secondary techniques can be dry, semi-dry and wet type, after predominant processes that can be adsorption or absorption.

2.2.1. Pre-combustion control of SO_x emissions

In coal, sulfur exists as a organic and inorganic combinations. Inorganic combinations are mainly pyrites (FeS_2) in the form of granules, which can be removed by physical washing with water or denser medium and gravity separation. This technique is called the enrichment of coal. Because the organic compounds of sulfur are chemically connected in fossil fuels, for concentration reduction must to use chemical processes that are more complex and more expensive. This type of processes may be the gasification of coal or their conversion into synthetic liquid fuels.

Desulfurization of heavy fuel to reduce the sulfur content below 1% is a process known and applied in most oil refineries in the world, but which involves considerable costs. High production cost of heavy fuel is the reason that, on the world energy market, exists two categories of heavy fuel: one more expensive - with sulfur content below 1% and another one - sulfur heavy fuel (in many cases with a sulfur content higher than 2%).

Industrial activity has demonstrated that, respecting SO_2 admissible limit emissions, it is more economical to burn heavy fuel with low sulfur content than to do the desulphurization of flue gases burning sulfur heavy fuel. This is one of the reasons why, in Romania, since 1996, is not permitted sulfur heavy fuel trade for energetic purposes.

2.2.1.1. Coal enrichment

Some economic studies have concluded that warranted only a summary of coal enrichment, substantial enrichment did not have a major effect on reducing the emission, even if, in some varieties of coal, pyrite form can exceed 40% of the total amount of sulfur.

Typically, through coal enrichment may be reduced to 60 ÷ 70% of the sulfur that exists in inorganic compounds. Advanced enrichment of sulfur coal with high concentration of inorganic and sterile can lead to high desulfurization concurrent with direct and indirect costs reducing of power plants operation. Thus, reducing the amount of sterile decreases the cost of transportation and handling of fuel. Reduction of the abrasive silica increases installations' efficiency and reduces power plant's shutdowns.

Reduction of sulfur concentration decreases the rate of acid corrosion of installation components and hence, the operational and maintenance costs.

Schematic diagram of a line of advanced enrichment technology with high-sulfur coal is shown in Figure 2.1. Treatment involves coating, multi-stage separation (sieving gravity, flotation and magnetic), filtration and partial removal of the water.

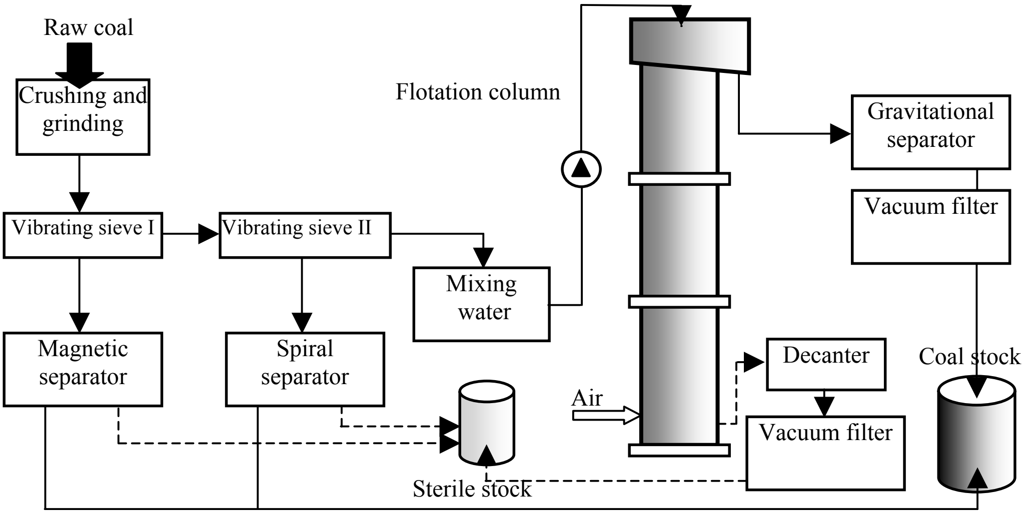


Fig. 2.1. Schematic diagram of the technological line for advanced enrichment of sulfur coal

After its crushing and spraying, coal is passed through two stages of separation by sieving of the vibrating grills. To retain large pyrite grains and other ferromagnetic materials, in the first stage it used a magnetic separation.

In the second stage of mechanical separation by sieving, skimmers with spiral transporters separate pyrite particles. Fine particles resulting from the second stage of sieving, are mixed with water, sludge process being conducted to the principal element of enrichment line - flotation column. The treated coal is passed through a high efficiency centrifugal and gravity separator then dried in a vacuum filter and conduced to the coal stock. The process sludge is passed through a decanter and then dried in a vacuum filter for storage of sterile.

The higher efficiency of advanced enrichment is determined mainly by the combination beetwen flotation column and gravitational-centrifugal filter.

U.S. Company VPISU made flotation column that provide the highest separation of pyrite and other sterile combinations, in the so-called Microcell™ technology. Schematic representation of a flotation column is shown in Figure 2.2.

The mixture of coal powder and water, prepared outside the flotation column is introduced into the main area of the column, where the solid suspension is maintained in a violent agitation condition by compressed air flow and, especially, by a flow of air bubbles very low. These bubbles are obtained in a static generator, where is mixed the flotation medium with compressed air.

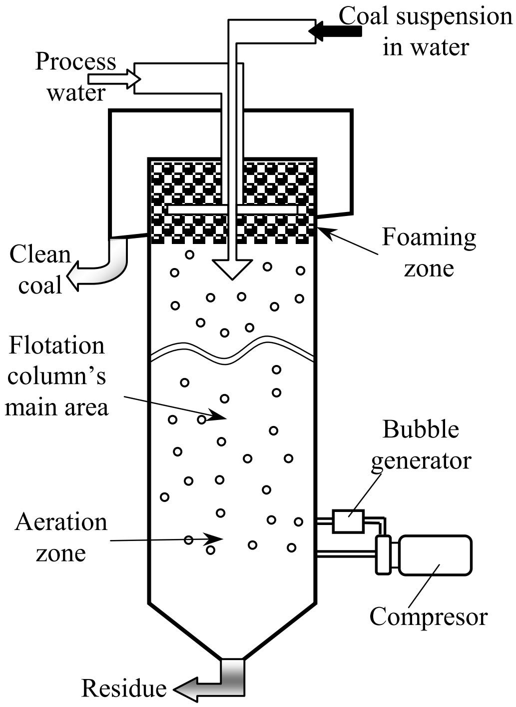


Fig. 2.2. Functional diagram of a Microcell™ flotation column

Due to the large difference between coal densities (about 1200 kg/m^3) and pyrite (about 5000 kg/m^3), pyrite sulfur particles moving to the area at the bottom of the column flotation, where are discharged, and coal particles are handled to the foaming area at the top of the column, where are washed by fresh water flow and are extracted from the flotation column.

In some coal particles it may exists very fine pyrite inclusions. Even if the difference between the densities of those two materials is high, these cannot be separated in the flotation column, but are separated in the gravitational-centrifugal separator downstream of the flotation column.

The higher efficiency of separation in the flotation column is given by the very large number and small size air bubbles that adhere to the surface of coal particles, increasing their buoyancy. This type of column, compared with mechanical flotation columns, ensure the separation of very fine particles of coal.

The separation rate of this technology for sulfur coal, where sulfur in inorganic combination is predominant, is that given in Table 2.2.

This technology is very effective in sulfur reduction, sulfur found in inorganic combination, in reduction of sterile concentration as well as concentration of arsenic and mercury from coal energy. This process of physical separation, does not remove sulfur found in organic combinations. For this reason, it is preferable to be associated with one of the secondary desulfurization techniques. If the concentration of pyrite sulfur is high, marked enrichment can reduce SO_2 emissions to levels below the maximum allowable, being usable as a single desulfurization technique for flue gases emitted by the power plants.

Table 2.2. The degree of separation of coal's enrichment advanced technology

Coal concentrations (%)						**Purification degree** (%)		
Raw coal			Enriched coal					
Ash	Total sulfur	Pyrites sulfur	Ash	Total sulfur	Pyrites sulfur	Ash	Total sulfur	Pyrites sulfur
25	4	3,2	10	1,25	0,5	75	80	90

Emphasized enrichment of coal with high sulfur content, which is in inorganic combination, has the effect of reducing direct costs of desulfurization compared with intra-combustion and after combustion techniques, as well as reducing operating and maintenance costs of power plants. Reducing total costs result from:

- ✓ reduction of own technological consumption - typically, the thermal power plants which operate with pulverized coal, consume 2 to 5% of the electricity produced in its own technological process; the reduction of coal ash amount from 24% to 8%, determine the reduction of own consumption with 10%;
- ✓ thermal efficiency - the use of coal with diminished content of sterile make to decrease the amount of heat losted through sterile heated, heat which is difficult to recover in most cases; to reduce the amount of ash from 24% to 8% thermal efficiency of the boiler is increased by 1.5% (USD 135 million savings per year, for a 500 MW power plant, which burn 450 million tons of coal annually at an average price of 20 USD/t);
- ✓ rising the total efficiency of the power plant - superior quality coal use improves the efficiency of power plant, including that of the boiler by 8 ÷ 12%; in this way can save some resources for new investments;
- ✓ the reduction of the maintenance costs - using a smaller quantity of clean coal, which were eliminated abrasive silicates and pyrite sulfur, corrosive after combustion, it provides a reduction of up to 5,000,000 USD/year maintenance costs of a 500 MW power plant;
- ✓ rising the plants' availability - the use of clean coal will reduce the period of interruptions, necessary for current and capital repairs, so that the power plants' availability can be increased by up to 5%;
- ✓ the reduction of the transport costs - coal from the mine mouth contains 20 ÷ 30 % sterile and 10 ÷ 20% water; through coal enrichment is reduce the amount of sterile

and humidity of coal, treatment at the mouth of the mine determining coal transport cost reduction to the power plant, reducing costs for using the railway;

✓ the reduction of the airborne particulate pollution risk - coal-silicates are the main cause of the air pollution with particulate matter; reducing the amount of the silicates is reduced the cost of pollution control in transport and preparation stage as well as in flue gases treatment stage in electrostatic precipitator.

A comparison in terms of investment, operation and maintenance costs in case of pre-combustion treatment is given in Table 2.3. The data are valid for a 500 MW power plant operating with pulverized coal with calorific value of 5600 kcal/kg, an ash content of 25% and 4% total sulfur, sulfur content in inorganic combinations having a concentration of 3.2%.

Table 2.3. Economic evaluation of precombustion desulfurization

Expenditure type	Secondary desulfurization - Unique step		Hybrid, precombustion and secondary desulfurization					
			Precombustion component		Secondary component		Total	
	10^6 \$/an	10^{-3} \$/kWh	10^6 \$/an	10^{-3} \$/kWh	10^6 \$/an	10^{-3} \$/kWh	10^6 \$/an	10^{-3} \$/kWh
Annual investment	26,60	9,33	4,79	1,68	19,40	6,81	24,19	8,49
Exploiting and maintenance – fixe costs	11,45	4,02	0,76	0,26	8,35	2,93	9,11	3,20
Exploiting and maintenance – variable costs	10,42	3,66	1,91	0,67	2,68	0,94	4,59	1,61
Total	48,47	17,01	7,46	2,62	30,43	10,68	37,89	13,30
Global investment	229052218 $		36952003 $		167043438 $		203995441 $	

Data analysis shows that for coal with high-inorganic sulfur, is more economical a hybrid treatment than classical post-combustion treatment in a single stage.

Tests have shown that the costs' reduction is achieved by hybrid desulfurization for all sorts of sulfur coal having the inorganic sulfur content higher than 1.2%, as is shown in Figure 2.3.

2.2.1.2. Coal gasification

In principle, gasification involves converting coal into a gas mixture, some of them combustible, using a quantity of coal for thermal treatments involved in such a process.

There are many industrial processes for coal gasification different by coal type, mode of processing, the flow of air and steam introduced into the conversion installation (gasificator), thermodynamic parameters, process productivity, as well as calorific power of synthesis gases obtained.

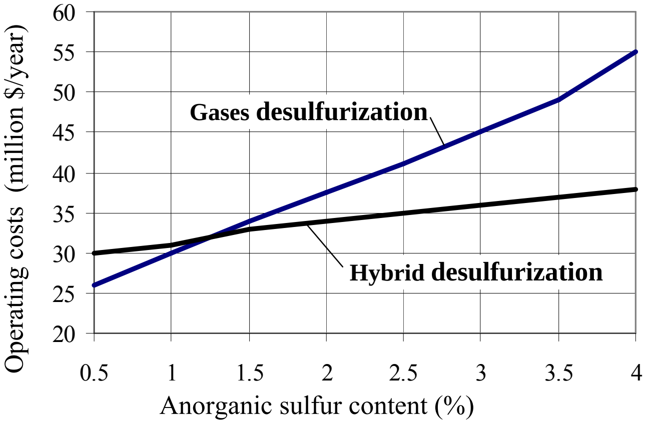


Fig. 2.3. Annual operating cost of a 500 MW power plant

If oxygen is introduced over the dry fuel, „airy gas" is achieved. The main chemical reactions are:

- ✓ the oxidation of carbon, highly exothermic reaction

$$C + O_2 = CO_2 + 408000\ kJ/kmol\,; \qquad (2.7)$$

- ✓ reducing carbon dioxide through an endothermic reaction,

$$CO_2 + C = 2CO - 160000\ kJ/kmol\,, \qquad (2.8)$$

the last reaction processing at temperatures higher than 630 °C.

Overall, the two reactions processing simultaneously, the global reaction from gasificator coresponds to incomplete combustion.

$$C + \tfrac{1}{2}O_2 = CO + 124000\ kJ/kmol\,, \qquad (2.9)$$

the liberated heat attending to fuel warming and to heat loss compensation. Some of the energy released in exothermic reaction is recovered as heat, temperature of synthesis gas being significantly higher than ambient temperature. If in the gasificator is introduced the air instead of oxygen, gas composition is 33.2% CO and 66.8% N_2 and calorific power is 560 kJ/Nm3.

When over incandescent carbon is introduced water vapours, „water-gas" is obtained. In this case the reaction is only endothermic and requires energy input from the combustion of some part of treated coal. The reaction is of the form:

$$C + H_2O = CO + H_2 - 119700\ kJ/kmol, \qquad (2.10)$$

„water-gas” containing, theoretical, 50 % CO and 50 % H_2. „Water-gas” calorific power is 2796 kcal/Nm3, more important than the „airy gas”.

If coal is gasified for energy, combining the two types of processes described above so that the energy released to the air gas production is consumed in the endothermic reaction of water gas production, obtaining a gas mixture called synthesis gas, that contain CO, CO_2, H_2, N_2 and O_2 and whose calorific power is 1730 kcal/Nm^3.

Depending on the quality of coal, calorific power of synthesis gas can vary between 900 ÷ 1700 kcal/Nm^3, and if the oxygen is inserted in gasificator instead of air, calorific power can increase up to 2000 ÷ 3000 kcal/Nm^3. Calorific power can grow to a value close to that of natural gas (7000 ÷ 9000 kcal/Nm^3) if the gas of gasificator is treated additional to synthesize the methane. This process is performed at relatively low temperatures (200 ÷ 300 °C), but at high pressure and the presence of catalysts. Classical gasification efficiency, calculated as the ratio between related chemical energy of synthetic gas and coal, can vary between 40% and 60%.

A modern technique for producing electricity from related chemical energy of coal, clean and of high thermal efficiency, is the integrated gasification with combined cycle steam-gas use. Very low level of emissions is the result of coal gasification, while can be separated potentially polluting substances, such as sulfur, a part of nitrogen of organic origin, heavy metals and sterile, simultaneously with reduction of total CO_2 emissions by up to 20%. High thermal efficiency is a consequence of the use of steam-gas combined cycle, characterized by high efficiency and low consumption of water, because in the gas turbines cycle is not necessary to use cooling water.

Modular realisation of installations where synthesis gas burned makes them very flexible in changing the type of fuel, so these can operate with natural gas, synthetic gas and liquid fuel. In this way, the power plant can operate at nominal parameters before commissioning the gasificator as well as during periods when it is switched off for maintenance.

Modern gasificator works on the classical principle of obtaining synthesis gas by simultaneously blowing of oxygen and water over incandescent coal. Thus, in gasificator column, reactions take place simultaneously in the form (2.7) and (2.10). The amount of energy resulting from the exothermic reaction is significantly higher than that consumed in the endothermic reaction. The extra energy produced and some of the energy released by combustion of a quantity of coal synthesis gas temperature increases up to 1350 °C ÷ 1400 °C.

Industrial gasificators may be several types, two examples that provide high efficiency conversion of carbon over 95% of existing coal are those made by Texaco Industries and Global Energy Inc. (E-GAS ™), whose schematic representations are shown in Figure 2.4.

Whatever type of gasificator, in the gasification column is inserted a mixture of coal powder and water, solid phase of suspension being in proportion of 60 ÷ 70% and 95% oxygen purity. Coal is processed by crushing and grinding of the classic systems, and then washed with water without having to follow the elimination of inorganic sulfur combinations. Oxygen is obtained by separation of atmospheric air.

If the sulfur content of coal is up to 3.5%, the approximate composition of synthesis gas in volume percent is as follows: CO - 42 ÷ 45% CO_2 - 14 ÷ 16% H_2 - 34 ÷ 38% CH_4 - 0.1 ÷ 1.9%, N_2 - 1.9 ÷ 3.3%, Ar - 0.6 ÷ 0.8%, water vapor - 0.3 ÷ 0.5%, H_2S - 60 ÷ 200 ppmv, carbonyl sulfide (COS) - 10 ÷ 40 ppmv. Relatively large amount of sulfur compounds requires a high degree of his recovery for the installation to be able to fit within the allowable SO_2 emission.

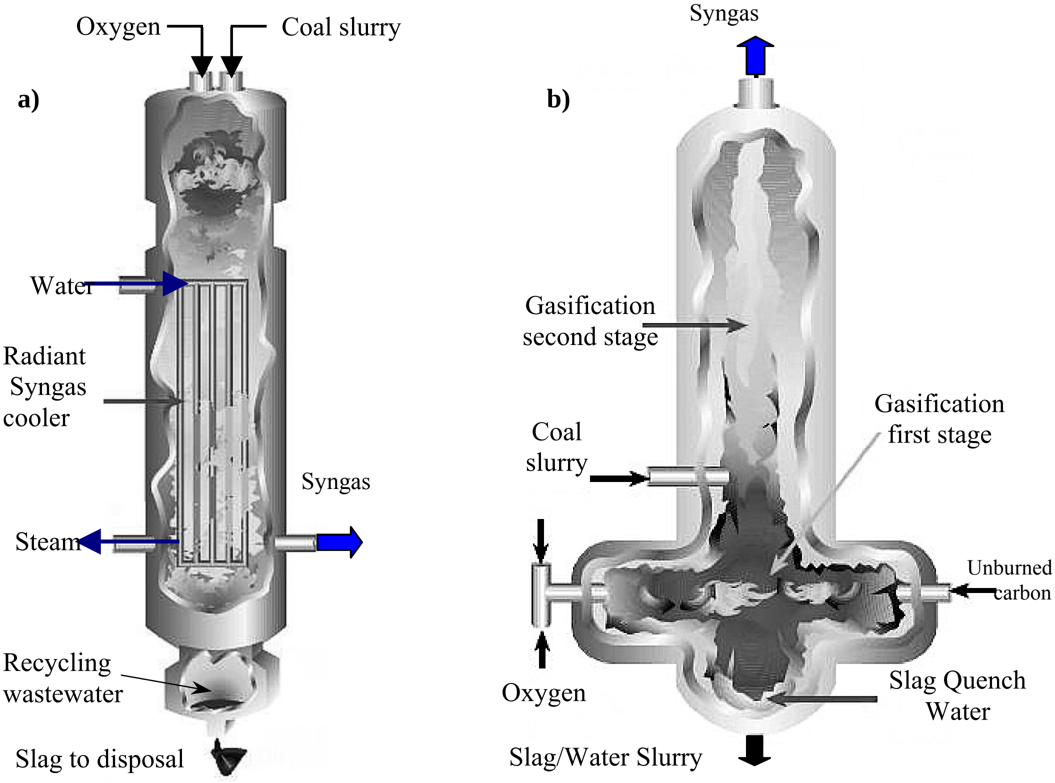


Fig. 2.4. Modern gasificators, used in integrated systems for gasification and utilization of combined steam-gas cycle: a) gasificator with synthesis gas cooling (Texaco Industries); b) gasificator with gasification in two stages (E-GAS™, Global Energy Inc.).

For installations with single stage gasification, synthesis gas is passed through a radiant heat exchanger; a portion of heat generated is used to obtain steam from the boiler water-steam circuit.

At the bottom of the column, gas flow changes its direction of flow so that the ash particles are deposited in the slag quench water and are cooled forming a compact mass, which is extracted from the same area regularly and then deposited. Water from slag quench water is purified, neutralized and then recirculated to the preparation installation of the coal suspension. Fine particles, however, are driven by the flow of synthesis gas, requiring a subsequent washing of the gas outside the column, washing for cooling the raw gas and retaining of solids and hydrochloric acid.

In case of gasificators two stages (Figure 2.4.b), the suspension of coal in water and oxygen are introduced to the bottom of gasificator. The heat released by partial combustion of coal, make the gasification reactions evolve very quickly, and ash to melt, leaking in the slag quench water, located at the base of the tire where it solidifies. At this stage, the synthesis gas temperature is about 1370 °C and pressure of 28 atm. The second stage of the process is conducted in a vertical column of gasificator, which introduces an additional quantity of coal suspension in water, reacts with synthesis gas from the first stage. High temperature of gas causes coal devolatilization and its pyrolysis. Through reaction with water vapor, occurs partial gasification of the coal introduced in the second stage.

In the second stage of the process increases the calorific power of synthesis gas and its temperature drops to 1040 °C, a portion of synthesis gas thermal energy is consumed for water vaporization and endothermic reaction of carbon with water vapor (2.10). In this way, the existence of the second stage eliminates the need to use the radiation heat exchanger, which is big and expensive.

Because in the column of this gasificator type is not changing direction of gases flow, a relatively large amount of coal particles are driven by synthesis gas flow. The quantity of coal that leaves the gasificator is relatively high because, in the second stage, gasification is not complete. In these circumstances, is indispensable the gas treatment in a particulate filter system, the coal separated being conducted to the first stage of gasification. The filter system operates in an area where the gas is hot and should retain very fine particles. The only filters that can meet these conditions are ceramic filters. Whatever gasificator type, first raw synthesis gas purification is carried out after cooling it to about 400 ÷ 430 °C, the heat being used to produce saturated steam.

Retention of pollutants in the raw synthesis gas can be achieved in several types of technological schemes, all aimed at separating solid particles, HCl and NH_3 removal and more importantly, retention of sulfur compounds. The installations used for conversion of sulfur compounds in marketable substances (sulfur or sulfuric acid) can be relatively complex, more so as one of the sulfur compounds is carbonyl sulfide, which can not be eliminated by simple absorption as hydrogen sulfide. If no carbonyl sulfide from synthesis gas is extracted, it becomes SO_2, the amount of pollutant is greater as the concentration of sulfur in coal is higher.

A schematic diagram of the raw synthesis gas purification, resulting in several analysis techniques in industrial operation, is shown in Figure 2.5.

Whatever gasificator type (1), the first stage of treating raw synthesis gas is cooled to about 400 °C in steam generator (2), saturated steam obtained having temperature and pressure large enough to be directly usable in power plant turbine (100

÷ 110 atm pressure and temperatures between 309 ÷ 316 °C). Fine particles of fly ash and unburned carbon are retained, either by washing with water in a column for washing (scrubber 3) or dry filtration in installations with ceramic filter elements. If separation is the wet type, hydrochloric acid simultaneously detained. Water containing pollutants is driven by the installation of the leachate treatment and neutralization (sludge process) and then recirculated to the installation for preparation of coal suspension, which supplies the gasificator. If the filter is dry type, specific for gasificators with two stages (Figure 2.4.b), the solid phase is reintroduced into the gasificator, in the area where the first stage of gasification occurs.

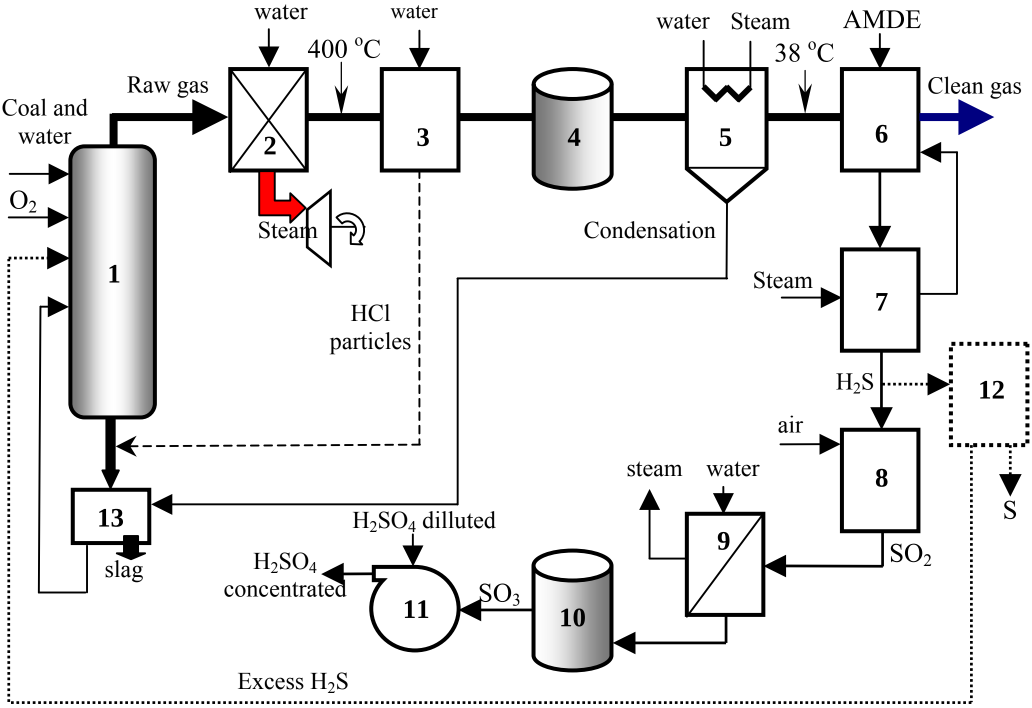


Fig. 2.5. The schematic diagram of a installation for synthesis gas purification: 1- gasificator; 2 – steam generator; 3 – scrubber; 4 – catalytic reactor for the COS hydrolysis; 5 – cooler; 6 – absorbtion column; 7 – separator; 8 – H_2S combustion chamber; 9 –SO_2 cooler; 10 - reactor catalytic reactor for the SO_2 conversion; 11 – installation for concentrated (98 %)H_2SO_4 production; 12 – Claus installation for elemental sulfur productionc (purity 99,99 %); 13 – process water treatment and recycling.

In the next stage of treatment it aims to flue gas desulfurization and sulfur recovery. Because carbonyl sulfide (COS) can not be retained by simple absorption, as can be extracted H_2S, first stage of desulfurisation is hydrolysis (4), where COS reacts with water in the presence of a catalyst, according to the reaction

$$COS + H_2O \xrightarrow{catalizator} H_2S + CO_2\,. \tag{2.11}$$

In these conditions, the only sulfur compound remains H_2S, while the catalyst degradation is insignificant. Hydrogen sulfide can be removed by absorption with amines (amine metildietanol - FMEA) in an absorption column (6).

Before this process, synthesis gas must be cooled to 38 °C water in a battery of heat exchangers (4). The cooling condenses water vapor from the gas. The condensed water contains a series of solutes, such as NH_3, H_2S and CO_2, so must be directed to the treatment-neutralization installation of process water (13).

The steam resulting after cooling of gas has not corresponding parameters for the relaxation in turbine, but may be used for:

- ✓ preheat the synthesis gas before its combustion;
- ✓ amine separation;
- ✓ steam turbine circuit, but only after additional heating.

After absorption of hydrogen sulphide (6), clean synthesis gas is directed to gas turbine of power plant. Absorber with high H_2S content and a dissolved CO_2 is directed to a separator (7), where, by reducing pressure, gas pollutants are taken by steam and directed to the sulfur recovery stage. Absorber so recovered is recycled into the absorption column (6).

Sulfur recovery phase is chosen depending on the final product configuration that is intended to achieve. Thus, if the purpose of obtaining H_2SO_4, sulfur recovery stages are as follows:

- ✓ the combustion of H_2S;
- ✓ the conversion of the SO_2 into SO_3;
- ✓ obtaining concentrated H_2SO_4 (98%) by reaction between SO_3 and H_2SO_4 diluted.

Through combustion of H_2S in the presence of air, SO_2 is obtained (8). SO_2 gas thermal energy, due to combustion, is transferred to water in a surface heat exchanger (9), resulting steam with medium pressure.

The following is a step oxidation of SO_2 to SO_3 in the catalytic reactor (10), catalytic layers are made of vanadium pentoxide (V_2O_5). In the reactor (11), SO_3 reacts with dilute H_2SO_4.

If it aims at obtaining elemental sulfur, H_2S is processed in a Claus unit type. A part of the H_2S is burned to produce SO_2, elemental sulfur being obtained by the reaction of H_2S remained with SO_2:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O\,. \qquad (2.12)$$

Unreacted hydrogen sulfide is compressed and returned to the gasificator.

In the treatment-neutralization installation of process water, solid residue cooled and retained, and dissolved gases (H_2S and CO_2) are retained and directed to the sulfur recovery stage.

In a second stage of treatment, NH_3 is removed and the water is used in the preparation of a suspension of coal. Excess water is treated with activated carbon and discharged.

Synthesis gas and steam get into combined cycle of power plant, as is shown in Figure 2.6.

The synthesis gas is introduced simultaneously with the air in the combustion chamber of gas turbine. To reduce the amount of NO_x formed during combustion of synthesis gas, it is necessary to introduce a flow of steam. It is preferable that the amount of steam to be small, reason for that synthesis gas is humidified before introduction into the combustion chamber.

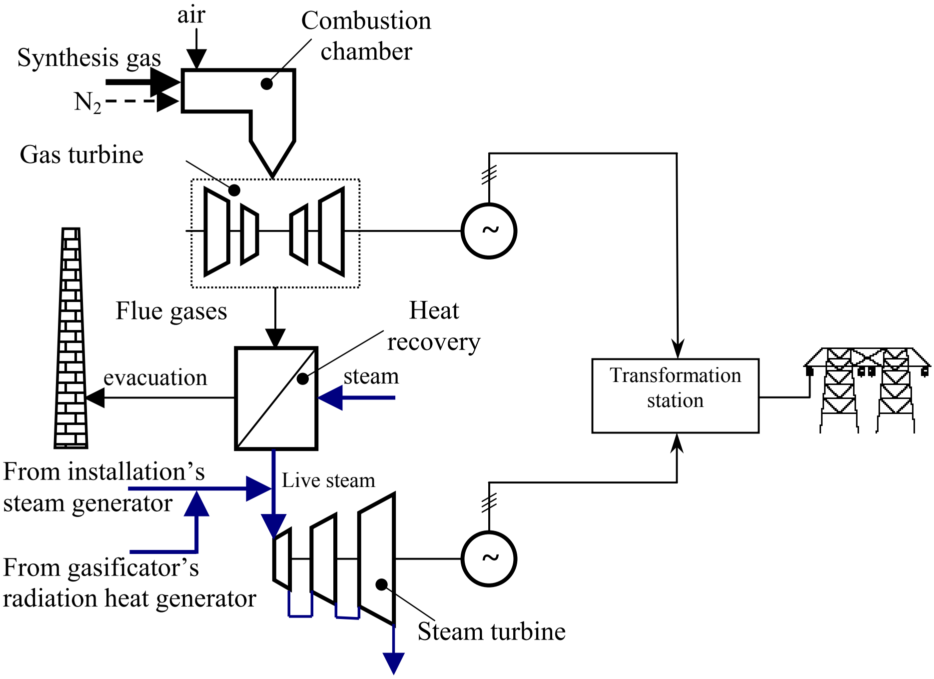
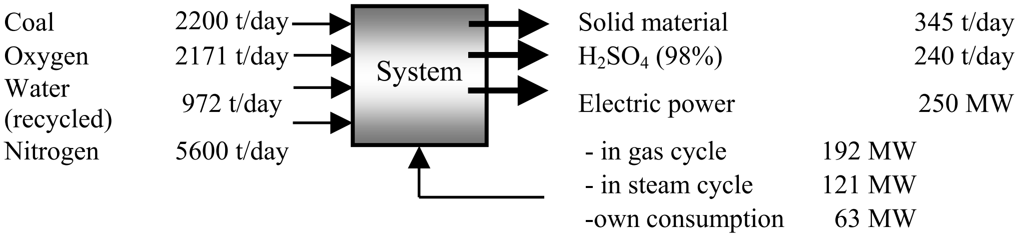


Fig. 2.6. Diagram for synthesis gas utilisation in power station

A viable alternative for reducing the emission of NO_x is injected simultaneously with the synthesis gas, a flow of N_2, with purity of 98% that is however obtained by air separation installation (which supplies the necessary oxygen for coal gasification). In addition to reducing NO_x emissions from the combustion chamber, injection of N_2 leads to increasing the amount of energy produced by gas turbine, resulting from higher gas turbine mass flow and increase overall efficiency of the system.

Combustion gases in gas turbine relaxed, but still hot, are passed through a heat recovery, which produces steam at different pressures. The flow of steam along with live steam from the main steam generator of integrated system, possibly from radiation heat exchanger of gasificator, relaxes in the steam turbine.

For one type of installation in operation, the balance of the integrated system is as follows:



Coal	2200 t/day
Oxygen	2171 t/day
Water (recycled)	972 t/day
Nitrogen	5600 t/day

Solid material		345 t/day
H_2SO_4 (98%)		240 t/day
Electric power		250 MW
- in gas cycle	192 MW	
- in steam cycle	121 MW	
-own consumption	63 MW	

Such complex installations in operation, handled in a single gasification unit, large amounts of coal (2200 ÷ 2600 t/day), while reducing emissions far below their corresponding direct combustion of pulverized coal (see Table 2.4) and recovery of appreciable quantities of sulfur, either as concentrated H_2SO_4 (240 t/day) or as high-purity sulfur (48 t/day or 8 kg/MWh). The values given in parentheses correspond to consumption of 375 kg coal having a sulfur content of 5.9% for each MWh of electricity produced.

Table 2.4. Pollutant emissions issued in atmosphere

Power station type	**Emission** (kg/MWh)				
	SO_2	NO_x	CO	Particles	Volatile Organic Compounds
Unique cycle with steam and pulverized coal combustion	17,3	4,2	0,29	0,38	0,013
Gasification integrated system and gas – steam combined cycles	0,6	0,5	0,17	undetect able	0,009
Depollution degree (%)	**96,5**	**88,1**	**41,4**	**99,9**	**30,8**

If the conventional gasification of coal to reduce sulfur content, to the extent that would ensure compliance with the emission of SO_2, generally lead to price increase than economically acceptable limits, requiring combination with other types of gasification desulfurization techniques, integrated techniques gasification - use of combined cycles and sulfur recovery involving the cost of the same order of magnitude to that side of desulfurization secondary technologies, while the first category of techniques provides a significant reduction in the emission of nitrogen oxides, being preferable control integrated techniques.

2.2.2. Intra-combustion desulfurization techniques

Primary desulfurization techniques consist of injecting a sorbent directly into the boiler furnace, in an area where the temperature is favorable evolution of the absorption and neutralization reactions of SO_2 and SO_3. This type of desulfurization is applicable to boilers that burn coal; some older applications were also realised to the boilers that burn sulfur heavy liquid fuel.

Absorber can be a calcium compound or a sodium compound. Even if the affinity of sodium compounds in relation to sulfur oxides is higher than of calcium compounds, in thermo applications calcium compounds are used exclusively because of their lower cost and availability. This is justified by the fact that efficiency of intra-combustion techniques is not very high, a certain amount of neutralizing substance remaining unreacted.

Primary methods of desulfurization have some peculiarities, depending on the adopted combustion technique, as follows:

- ✓ pulverized coal combustion;
- ✓ fluidized bed combustion.

2.2.2.1. Intra-combustion desulfurization of pulverized coal combustion

Absorber is injected as a fine powder in the furnace area where the temperature is 1200 ÷ 1250 °C so as to achieve neutralization of big quantities of SO_2, until the combustion gases reaches in those areas of the furnace where the temperature drops to about 870 °C.

Absorber used is a calcium compound such as calcium carbonate ($CaCO_3$), dolomite limestone ($CaCO_3$ $MgCO_3$), slaked lime ($Ca(OH)_2$) or hydrated dolomite ($Ca(OH)_2 \cdot Mg(OH)_2$). Since calcium compounds are used exclusively, this technique called the Limestone Additive Process, schematic diagram of the process is reproduced in Figure 2.7.

Neutralizing substance is injected into the furnace through burners with the secondary or tertiary air, or blowing air through the openings of the upper side, above the flame. Also, for this purpose may be used special injection holes or injection lances, which penetrate the injection and the walls of the boiler furnace, up to a certain well-defined depth. Airflow, which is circulated through the absorbent powder, is in amount of 1 ÷ 5% from the air necessary to complete coal combustion.

Whatever type calcium compound, in the oxidizing atmosphere from furnace occurs its calcination, a process that runs until the furnace in those areas where the temperature is higher than 980 °C. The new calcium compound reacts mainly with sulfur oxides.

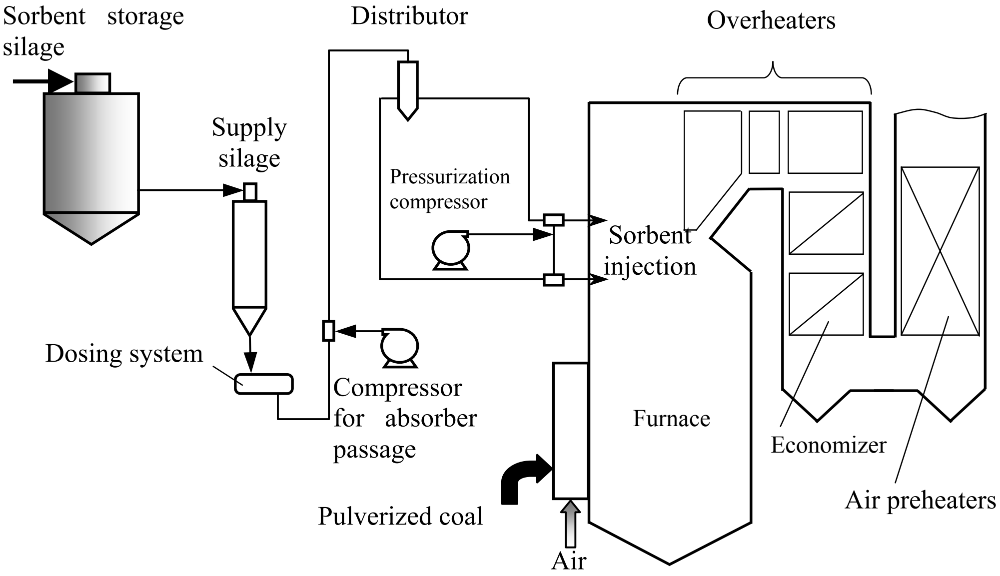


Fig. 2.7. The main diagram of *Limestone Additive Process* technique

Thus, if the additive is the $CaCO_3$, then SO_x neutralization reaction sequence is as follows:

$$CaCO_3 \rightarrow CaO + CO_2, \qquad (2.13)$$

$$CaO + SO_2 + \tfrac{1}{2} \cdot O_2 \rightarrow CaSO_4, \qquad (2.14)$$

$$CaO + SO_3 \rightarrow CaSO_4, \qquad (2.15)$$

relation (2.13) describing the endothermic reaction of limestone calcination, the other two corresponding to neutralize reactions of sulfur oxides, from which the calcium sulfate is obtain. Reaction (2.14) can be conducted in two stages, first the formation of calcium sulfite and the second of its oxidation to calcium sulfate:

$$CaO + SO_2 \rightarrow CaSO_3, \qquad (2.16)$$

$$CaSO_3 + \tfrac{1}{2} \cdot O_2 \rightarrow CaSO_4. \qquad (2.17)$$

Sulfur oxides can be neutralized and through their direct reactions with $CaCO_3$ powder by reactions of the form:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2, \qquad (2.18)$$

$$2 \cdot CaSO_3 + SO_2 \rightarrow 2 \cdot CaSO_4 + \tfrac{1}{2} \cdot SO_2, \qquad (2.19)$$

$$CaCO_3 + SO_3 \rightarrow CaSO_4 + CO_2. \tag{2.20}$$

In the specific temperature range (1200 ÷ 870 °C), CaO is more active than $CaCO_3$, so reactions (2.13) ÷ (2.15) have a higher weight than direct reactions of sulfur oxides with limestone powder. However, reactions of type (2.18) ÷ (2.20) can deploy in colder areas of the boiler at temperatures between 550 °C and 850 °C.

If for controlling NO_x emissions is used combustion technology in steps or post-combustion technology, then in furnace are created combustion areas characterized by a strongly reducing environment. In such an environment, the desulfurization reaction sequence is as follows:

$$4 \cdot CaSO_3 + 2 \cdot SO_2 \rightarrow 4 \cdot CaSO_4 + S_2, \tag{2.21}$$

$$SO \ + C \rightarrow CO_2 + \tfrac{1}{2} \cdot S_2, \tag{2.22}$$

$$2 \cdot CaO + S_2 + C \rightarrow 2 \cdot CaS + CO_2, \tag{2.23}$$

$$CaS + 2 \cdot SO_2 \rightarrow CaSO_4 + S_2. \tag{2.24}$$

If the additive is of dolomite provenience, dry, SO_2 neutralization involves the following reactions:

$$(CaCO_3 \cdot MgCO_3) \rightarrow (CaO + MgO) + 2CO_2, \tag{2.25}$$

$$(CaO + MgO) + SO_2 + \tfrac{1}{2} \cdot O_2 \rightarrow (CaSO_4 + MgO), \tag{2.26}$$

the first being that of dolomite calcination, and the second sulfation.

If the additive is hydrated during calcination will release water vapor:

- ✓ in case of additivation with hydrated lime

$$Ca(OH)_2 \rightarrow CaO + H_2O, \tag{2.27}$$
$$CaO + SO_2 + \tfrac{1}{2} \cdot O_2 \rightarrow CaSO_4;$$

- ✓ in case of additivation with hydrated dolomitic lime

$$Ca(OH)_2 \cdot Mg(OH)_2 \rightarrow (CaO + MgO) + 2H_2O, \tag{2.28}$$

$$(CaO + MgO) + SO_2 + \tfrac{1}{2} \cdot O_2 \rightarrow (CaSO_4 + MgO).$$

When it uses additive of dolomitic nature, dry or hydrated, it observes that magnesium does not react with sulfur, which involves injecting into the boiler of a neutralizing substance in larger quantities at a molar ratio Ca/S.

In stoichiometric conditions, for the binding of 1 kg of sulfur, there are necessary 56/32 = 1.75 kg of calcium oxide. For a ratio Ca/S = 1, under ideal conditions, 3.125 kg of limestone are needed for each kilogram of sulfur content by the coal.

Retention of reaction by-products like $CaSO_4$ powder, MgO and unreacted additive, is performed simultaneously with fly ash separation, in hot electrostatic precipitators operating at temperatures of 300 ÷ 350 °C or in bag filter devices.

If the retention of particles in the flue gas is achieved in electrostatic precipitators must be taken into account that the absorbents injection changes some physical properties of particles.

In terms of electrostatic separation, intra-combustion desulfurization increases the particle's resistivity higher than 10^{11} Ω·cm due to the reduction of sulfur oxides concentration. Highly resistive particles are difficult to retain in electrostatic precipitators, requiring the injection of additional additives.

The desulfurization degree of this technique can achieve a value of 50%, being dependent on a number of parameters, such as:

- ✓ type and size of the furnace,
- ✓ fuel composition,
- ✓ absorbent composition and grain size,
- ✓ combustion conditions.

The parameters with the greatest influence on the degree of desulfurization, which depend to some extent by the parameters listed above, are:

- ✓ reaction area temperature,
- ✓ residence time of gases and additive in the reaction area,
- ✓ the distribution of absorber in the furnace,
- ✓ quantity and composition of absorbing substance,
- ✓ specific surface area.

For calcination and neutralization reactions of SO_2 to be fast enough at a certain period of residence of particles in the furnace, it is necessary that the temperature from the evolution area of reactions to be between 870 ºC and 1080 ºC.

At temperatures below 850 ºC, calcium sulfate deposited on the support of insufficient limestone calcined, reducing area which pollutant has access.

If the temperature is less than 1080 ºC, frit CaO particles, lose their porosity and hence reduce its contact area. This phenomenon is called the *dead burning*. When choosing the injection area should consider that it is desirable that as much of $CaCO_3$ to calcine before reacting with sulfur oxides. For this reason, the injection can be done at temperatures above 1080 °C to 1200 °C. Due to the high speed of flue gases, particles of $CaCO_3$ and CaO are moved quickly into areas where the sintering phenomenon can not occur. Higher temperatures of 1200 °C causes thermal decomposition of calcium sulfate formed only, with the release of SO_2. Thermal decomposition of $CaSO_4$ and the danger of sintering of CaO particles are the main causes that limit the efficiency of this technique, making it less suitable for boilers works with sulfur heavy fuel or coal dust.

It is essential to achieve an intimate mixture between particles of absorbent flows and combustion gases. Because the absorbent is injected into the area above the burners, where the cross section of gas is high, it is difficult to achieve a good mix between the two phases. Good results are obtained when the absorbent powder is injected through the injection lances holder.

The degree of desulfurization increases with the amount of neutralizing agent to a molar ratio Ca/S = 4. Over this value, retention efficiency of SO_2 not increases significantly. In addition, increasing the amount of absorber results in higher charge particles, and thus increased energy consumption for flue gas dedusting.

Grit particles of absorber are a major influence on the desulfurization degree, making a fine mist providing a large contact surface. The degree of desulfurization increases when the diameter of absorber particles is reduced. This trend is also up to the order of 2 μm diameter, further increasing finesse having not significant effects on the degree of desulfurization. Particle fineness, energy consumption growth implies additional absorber preparation, being necessary to establish an optimal technical and economic between the two trends. The system is effective when the average diameter of particles is of the order of 15 mm, but do not exceed a maximum diameter of 60 mm.

Contact surface area can be increased through the addition of absorber, not only by its fine grinding. Increasing the active area is known as the addition of additive. It recommends the addition of limestone with baking soda. This is uniformly deposited on the limestone particles, forming an eutectic which has a lower melting temperature. SO_2 diffusion through the liquid mass towards the core particle of calcium oxide is easier and therefore it can react the entire mass of the absorbent. Thus, it remains only a small amount of unreacted core, blocked by $CaSO_4$ particles that are deposited on the surface of the absorber. Also, the presence of magnesium in absorber can effectively improve the efficiency of using limestone. MgO limits the trend to agglomerate of CaO particles resulted from calcination of limestone, pollutants thereby having access to a larger reaction surface.

The degree of desulfurization of this technique decreases with the increase in power generated by combustion installation to its nominal power. If the degree of desulfurization at rated load shall not exceed 50%, at half rated load of the boiler, desulfurization degree can reach 70%. In operation of this type of desulfurization systems, special attention should be paid to the fact that calcium oxide reacts exothermically with water, must therefore avoid ash contact with water or with water vapor, in both waste-gas flue and over the entire route of transport and storage of ashes.

Injection of calcium absorbers in the furnace has some advantages, such as:

- ✓ the investment costs are relatively low;
- ✓ does not involve major changes in existing facilities;

- ✓ the space is limited to the new installations;
- ✓ the installation-time is quite small;
- ✓ the reliability, availability and the maximum power of the boiler are not affected;
- ✓ the absorber’s price is inexpensive, available and economically exploitable in large amounts;
- ✓ the main by-product of the reaction ($CaSO_4$), dry extract, can be used to manufacture gypsum;
- ✓ the technique may be associated with the use of low NO_x emission burners or burning in the global stage, and thus reducing NO_x emissions.

All these advantages recommend use of the process for upgrading old power plants, average power, with relatively short remaining life and are perfectly applicable in countries that are difficult to make major investments. Also, due to its simplicity, the process may be used in any circumstances, as a first step to reduce the content of SO_x from flue gases.

Disadvantages of this technique arise from the relatively low degree of desulfurization, the need for more frequent cleaning of heat exchange surfaces and adverse impact on the operation of electrostatic precipitators. Thus, due to low level of desulfurization is not sufficient to use only this technique, being necessary to combine them with more expensive techniques.

To avoid clogging of convective heat exchangers of the second and third combustion gas channel (Figure 2.7), the installation of additional systems cleaning by blowing hot air is necessary. Negative effects of $CaCO_3$ injection on the operation of electrostatic precipitators is manifested by:

- ✓ significant increase in the amount of particles in the flue gas; it can occur even doubling the concentration of dust, which implies a corresponding increase in energy consumption for the separation, removal, transportation and storage of particles retained;
- ✓ the particles sizes that result in desulfurization process are smaller than those of fly ash and, consequently, they are more difficult to retain;
- ✓ because of very high chemical affinity for SO_3 absorber, it is integral retained, determining in lower acid dew point temperature corresponding, so that the resistivity of particles increases, making them more difficult to separate from the combustion gases.

In addition to negative effects on the operation of electrostatic precipitators, $CaCO_3$ injected into the furnace is not economic because should be used excessive absorber, some of which remains unreacted, while the energy was consumed for operation, transport and its preparation as and for heating and roasting it.

These disadvantages of the Limestone Additive Process technique can be partially removed by further treatment of flue gas on exit from the air heaters. This treatment involves the reactivation of the absorber was in excess, by injecting a water flow. Fine water spray is injected into the flue gas, at particular premises for this purpose.

The combination of this treatment in two stages, using low emission of NO_x burners (LNB), makes this technique in a hybrid technique, performed by Babcock&Wilcox Company, as the *Limestone Injection Multistage Burner*.

As can be seen from Figure 2.8, unlike the classical technique of injection of $CaCO_3$ in the furnace, the boiler is provided, along the gas pipe downstream of the heaters, with a humidification chamber (12). Obviously, the humidification system must be formed of water pumps, grids with nozzles for water (11) and compressors, compressed air being necessary for uniform distribution of water droplets in the flue gas.

Humidification chamber is dimensioned so that the residence time of combustion is the order of 2 seconds when the boiler is operating at rated load.

Because the temperature of combustion gases from their entry into the humidification chamber is too high (about 150 °C) for an efficient desulfurization by soaking and blowing air are cooled to the optimum.

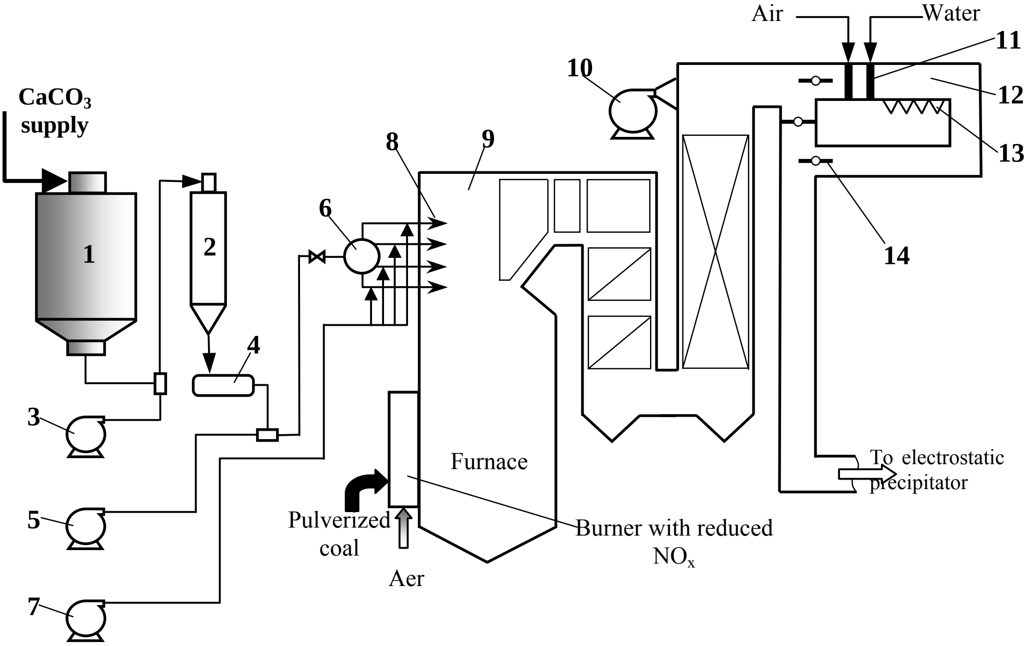


Fig. 2.8. Schematic diagram of *Limestone Injection Multistage Burners* procedure:
1 – sorbent storage silage; 2 – supply silage; 3 – compressor for sorbent transfer;
4 – system for sorbent dosing; 5 – compressor for sorbent passage;
6 – distributor; 7 – compressor for sorbent injection; 8 – system for sorbent injection;
9 – upper combustion chamber; 10 – exhauster; 11 – water injection nozzeles;
12 – humidification chamber; 13 – humidification chamber's bunkers;
14 –bypass damper system.

The presence of water droplets in a gas channel area in which the concentration of dust is high, the tendency is to emphasize the deposition of solids, with the risk of blocking the flue gas duct. To minimize this risk, the humidification chamber is equipped with bunkers (13), upon which the suspension is decanted and the particles can be evacuated. On the other hand, open bunkers operation creates a danger of penetration of large amounts of cold air from outside, which leads to increased speed of agglomeration of particles and their adhesion to the walls of the humidification chamber. To avoid this disadvantage, particle removal is not carried out continuously, and the bunkers are equipped with deflectors and shutter caps, which prevent entry of additional quantities of cold air. SO_2 retention efficiency is highest at a temperature close to adiabatic saturation temperature. On the other hand, at this temperature, the particles tend to deposit on the walls of the flue gas duct reaches a maximum.

Operating temperature, resulting in the humidification chamber as an optimal two contrary trends, is greater than 5 to 10 °C adiabatic saturation temperature. In this way it avoided reaching of the acid dew point in electrostatic precipitator, but not on the entire path of exhaust gases. Usually, before their removal from electrostatic precipitator the flue gases are easily reheated. Humidification chamber can be removed from service via the bypass pipes and valves (14). This system can be used as a control element, modifying the gas flow moving directly to electrostatic precipitator and overpassing the second stage of treatment.

This technical solution has all the advantages of basic variant, additional benefits resulting from the technical and economic optimization of electrostatic precipitator operation and more efficient use of the absorber, so that the overall degree of desulfurization can reach 55 ÷ 70%.

2.2.2.2. Fluidized bed combustion scrubbing

Fluidized bed coal combustion technique began to be used in the 1970s, causing permanent advantages of this technique to develop industrial scale, so it came to the realization of large units, with powers up to 250 ÷ 300 MW, is expected to achieve 600 MWe units, installations under increased performance, flexibility and reliability in their operation, the relative costs are becoming lower.

Latest developments and improvements of these installations aim to collect particle systems, cooling the ash and temperature control. The last industrial installations realized by companies like Babcock & Wilcox, Foster Wheeler Power Group Inc., Lurgi, Von Roll fits into those tend.

Fluidized bed combustion technique consists in blowing air into the furnace, in those parameters to maintain solid the fuel in a constant swirl motion. Thus, incomplete mixing crushed coal and air mixture behaves as a fuel mixture consisting of a liquid fuel and air, air jets providing a good exposure of the granules of coal in combustion air and a sufficient period of residence.

Blowing air speed causes two types of fluidized bed combustion:

- ✓ stationary fluidized bed combustion,
- ✓ circulating fluidized bed combustion.

One schematic representation of the main components of the fluidized bed combustion boilers is that given in in Figure 2.9, for both types of boilers.

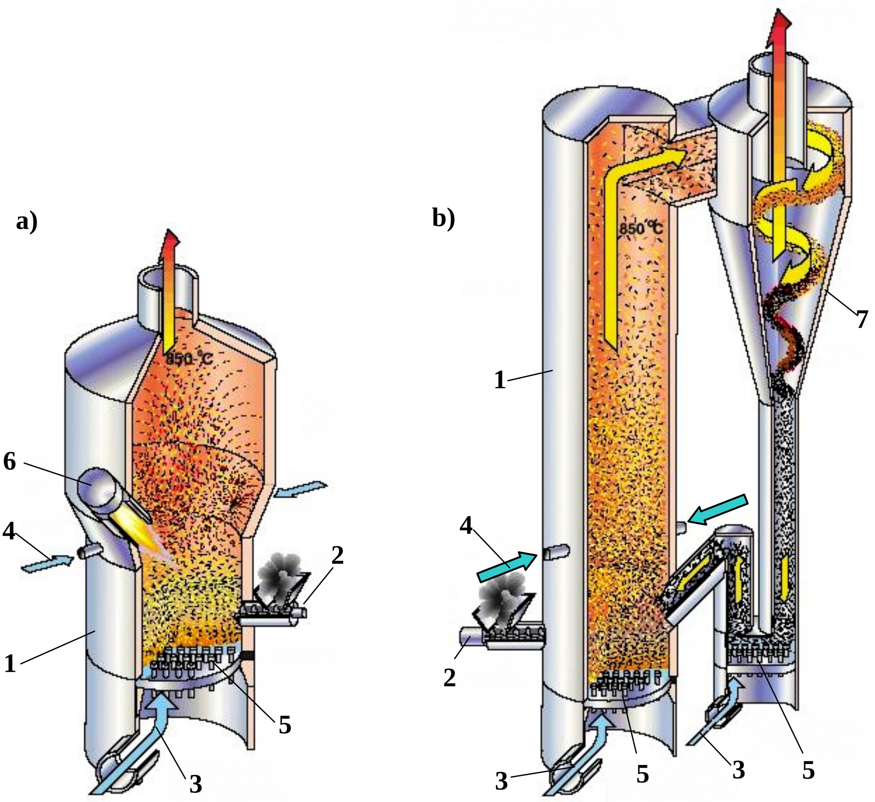


Fig. 2.9. Furnaces with fluidized bed combustion: a) – stationary; b) – circulating; 1 – boiler’s furnace; 2 – fuel supply system; 3 – primary air; 4 – secondary air; 5 – primary air injection nozzles; 6 – burner with liquid fuel, that works at boiler’s startup; 7 – cyclone.

Regardless of the type of construction of the furnace, coal is introduced at the bottom of it’s, fluidized by primary air was maintained and supported by metal grills. Originally, these were the type grates with bars, but next-generation installations are equipped with grills membrane, cooled with water.

Primary air is introduced through the grate bars or special nozzles provided in the membrane racks. Secondary air is introduced into the combustion zone completion. In the case of installations with circulating fluidized bed, a secondary air flow can be introduced on top of the main combustion zone.

In the case of circulating fluidized bed combustion (Figure 2.9.b), fuel particles have a size of up to 15 ÷ 20 mm. The primary air is blown through the nozzles at high speed or, more rarely, through the grill bars. In a first step, at the bottom of the furnace, in dense area, primary air is mixed with fresh fuel and emissions by recycling particles from the cyclone system. Cross section of the primary area, surrounded by the walls of the membrane from the bottom of furnace and first level of blast secondary air is lower than that of the upper chamber of the column to ensure the formation of a homogeneous mixture as fuel.

A big part of the mass of solids, with an ash content of about 95%, is continuously trained to the outside, separated in cyclone and reintroduced into the furnace, either directly in the hot state (Figure 2.9.b) or cooled in an external heat exchanger (Figure 2.10). Because of this recirculation, the possibility of partial or total ash cooling and because of the potential change in the ratio between primary and secondary air flow can be controlled permanent both temperature furnace and oxygen concentration in different areas of it.

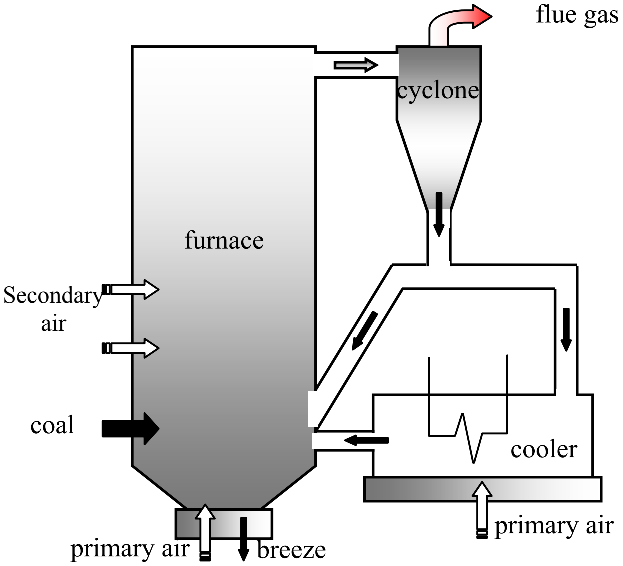


Fig. 2.10. Schematic representation of a furnace with circulating fluidized bed combustion, with additional cooling of fluidized layer.

SO_2 emission control of such furnaces is done by injecting a quantity of coal simultaneously with $CaCO_3$, possibly contaminated with $MgCO_3$, iron and aluminum oxides. Grain scale is up to 1 mm, significantly higher than for pulverized coal combustion. Furnace temperature (850 ÷ 900 °C) is suitable for desulfurization reactions evolve in the same sequence as desulfurization of gases results from burning pulverized coal: the exothermic reaction of limestone calcination (2.13), followed by an endothermic reaction sulfation and oxidation calcium oxide (2.14). Calcium sulfate, thus obtained, is in solid and can be drained from the fluidized layer.

Unlike pulverized coal boilers, when it used coal with low sulfur content, it is necessary to introduce an additional quantity of sterile, fluid layer, to maintain the solids concentration in the whole boiler.

The introduction of additional quantities of limestone is not economic, the necessary quantity of limestone being higher than where it is used as absorbent and not as a sterile medium. In addition, the lime resulted by calcining limestone is very porous, which causes the formation of very fine particles, which have not the desired effect on the balance of gas - solid, because they are handled quickly by the end of the furnace. Also, fine particles are difficult to collect in the flue gas. Therefore it is preferable to use sand, possibly quartz, as additional sterile, both for energy coal burning and domestic waste.

The degree of desulfurization of this technique can reach 85 ÷ 90%, significantly higher than for pulverized coal combustion, both due to the temperature of the furnace, and because of intimate contact between flue gas and absorbent, great period of residence in reaction area and continuous recirculation of the unreacted absorber.

Desulfurization efficiency depends on several parameters, such as:

- ✓ the concentration of sulfur in fuel,
- ✓ the amount of absorber (expressed in molar ratio Ca/S),
- ✓ limestone's reactivity,
- ✓ the temperature into the furnace,
- ✓ the residence time of the two phases,
- ✓ the absorber's particle size.

Regarding the amount of absorbent, the maximum efficiency of the method is obtained at a molar ratio Ca/S ratio of only 1.5 ÷ 2 for layers assets, compared to 2.5 ÷ 3.5, the dense layers of coal.

Even if the emission of SO_2 in fluidized bed combustion boilers is reduced, the main advantage of this technique is that of low NO_x emissions. Low level of NO_x pollution effects can be explained by a combination of burning in global stage with those of low temperature and low coefficient of excess air into the main combustion zone. Further reducing NO_x emissions by up to 40 to 60% can be achieved by injecting a quantity of NH_3 in the final area of furnace. Thus, fluidized bed combustion combined with selective non-catalytic reduction (SNCR).

Factors influencing the further reduction of NO_x emissions are:

- ✓ the amount of reducing agent,

✓ the initial concentration of NO_x,
✓ the level and the temperature distribution in the furnace,
✓ the uniform distribution of the NH_3 droplets into the flue gas,
✓ the residence time.

CO emission in furnace with fluidized bed combustion is generally very low. Formation of CO, the effect of incomplete combustion, depends on several factors, such as the following:

✓ the fluidized bad’s temperature,
✓ the excess air,
✓ the fuel’s type,
✓ the fuel’s distribution in the air flow and flue gas flow,
✓ upper secondary air mixing uniformity,
✓ the residence time of the fuel mixture into the furnace.

Solids are retained in the mechanical separation, changing direction of gas flow and solid phase continuous recirculation with a favorable effect on the degree of separation. However, most conventional installations must be equipped with electrostatic precipitators or bag filters installed at the exit gases from the boiler.

A very efficient solution for retaining particles, with favorable effects on the efficiency of combustion and desulfurization, is made by Babcock & Wilcox Company, which consists of beam profiles "U" installing (Figure 2.11) on top of the furnace and out the furnace.

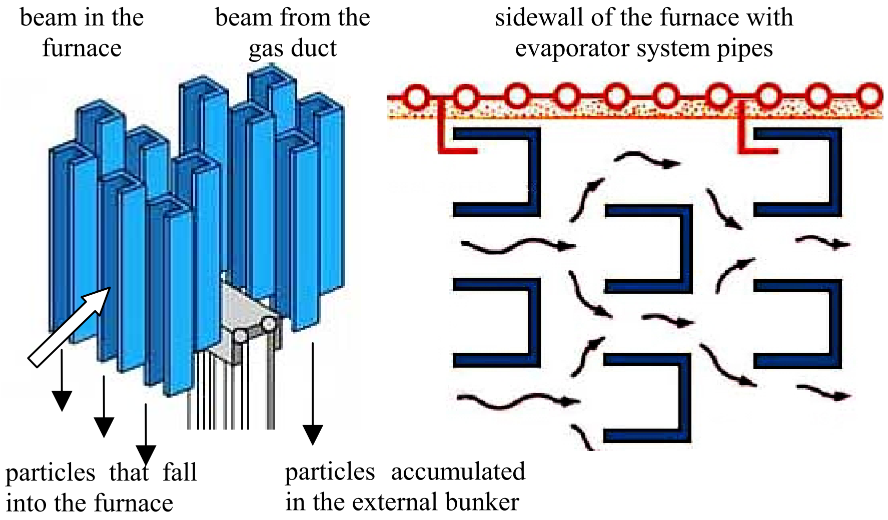


Fig. 2.11. Beam profile **U** of Babcock & Wilcox boiler construction

At the conclusion of the above, result that the circulating fluidized bed combustion has some advantages, from technical, economic and environmental impact points of wiev, compared with pulverized coal combustion:

- ✓ the facilities are characterized by high reliability and availability (> 95 %);
- ✓ they operate at variable load in very large limits (5:1), without requiring an auxiliary fuel support;
- ✓ the combustion efficiency is higher than for other types of furnaces can reach 98 ÷ 99%, an effect of achieving an intimate mixture of coal particles and gas, as well as an increased residence time of particles in the furnace;
- ✓ it can be burned qualitatively different colas, from the lower to the upper quality, mixed coal, coal wastes and household waste;
- ✓ the combustion's stability is high, even if there are short interruptions in coal supply;
- ✓ the combustion is self maintained type, even for coal having lower calorific power and even in the case of the partial loads of the installation; hydrocarbons are consumed only for ignition;
- ✓ the preparing process of the coal and of the absorber is brief, which causes significant reduction in electricity consumption and reduce the depreciation speed of preparation and delivery installations;
- ✓ compact construction of the furnace and gauges much lower than those of conventional boilers make heat losses to be much smaller; if the particles are separated into an internal phase, furnace size by 30% decrease in plant size with cyclones separation;
- ✓ the flying ash is effectively retained by circulating in the furnace, where a proportion of only 15% of fuel mass is necessary, the remaining 85% can be sterile;
- ✓ the degree of flue gas desulfurization can reach 85 ÷ 90%, in terms of an absorber manufactured cheaply and summary;
- ✓ NO_x emissions may be reduced to 100 ppm (mean, 100 mg/Nm^3, compared to 400 ÷ 800 mg/Nm^3 that is in furnace with pulverized lignite) due to low temperature and excess air coefficient and due to the strongly reducing atmosphere created into the dense fluidized area.

Even with the existence of these multiple benefits that cannot be neglected in the fluidized combustion of significant increases emissions of nitrous oxide (N_2O), gas that destroys the stratospheric ozone layer and contributes to increased greenhouse effect. In the case of burning pulverized coal, the emission of N_2O is less than 10 ppm, whereas for the emission in fluidized bed combustion is the order of 50 ÷ 100 ppm. N_2O emission can be reduced by increasing the temperature into the furnace and by increasing the molar ratio Ca/S.

2.2.3. Post-combustion desulfurization

Post-combustion desulfurization involves flue gas treatment on their route of escape to the stack. The classification system of treatment in the combustion plant is different, depending on the type of treatment. Thus, desulfurization system can be placed after the economizer, after the air heaters or after solids collection installation.

Treatment of SO_2 by action post-combustion takes place, in most situations, the processes based on the neutralization reaction with calcium compounds ($CaCO_3$, $Ca(OH)_2$, CaO), magnesium compounds ($MgCO_3$), sodium compounds (Na_2SO_3, Na_2CO_3) or NH_3. Latest techniques call for more efficient reactions of oxidation and reduction using Cu and Br_2 or physical adsorption. Depending on the type of reactions involved in the process, how their management and state of aggregation of products results, secondary desulfurization techniques can be classified into the following categories:

- ✓ dry processes,
- ✓ semi-dry processes (quasi-dry) or semi-humid processes,
- ✓ humid processes.

Dry processes provide a natural binding of SO_2.

Quasi-dry processes involve both absorption and adsorption. Thus, in a evaporation reactor spray an alkaline solution or a suspension for connecting pollutant, mainly by absorbtion. After evaporation of the liquid phase, excess reagent adsorbs a quantity of pollutant and reaction by-products resulting always in the form of fine crystals, as for dry-type techniques.

In wet type secondary techniques, reaction by-products are in liquid, requiring further treatment to avoid pollution of other media.

Some comparative data on three categories of secondary desulfurization techniques are given in Table 2.5.

Table 2.5. Comparative data on secondary desulfurization techniques

Type control technique	**Relative cost of investment**	**Operating costs**		**Desulfurization degree**
		Relative cost	Ca/S consumption	
Humid	***	***	1 ÷ 1,5	95 %
Quasi-dry	**	**	1,5	80 ÷ 90 %
Dry	*	***	2 ÷ 3	40 ÷ 60 %

Simultaneously with the reduction of SOx emissions from flue gases, post-combustion desulfurization installations retain a proportion of particulate matter, other acid gases, heavy metals and volatile organic compounds. Relative efficiency is shown in Table 2.6.

Table 2.6. Relative efficiency of secondary techniques for treatment pollutants from flue gases

Pollutant / **Technology**			**Dust**	**Heavy metals**		**Acid gas**		**Dioxin Furans**	**Volatile organic compounds**
				Particles	Vapours (Hg)	HCl, HF, HBr,HI	SO_x		
Secondary neutralizing of classic processes	Dry methods	reactiv calcic	• • •	• • •	•	• •	•	•	
		reactiv sodic	• • •	• • •	•	• • •	• •	•	
	Quasi-dry methods		• • •	• • •	•	• •	•	•	
	Humid methods		• • •	• • •	• •	• • •	• • •	•	•
	Combined methods		• • •	• • •	• •	• • •	• • •	•	•
	Condensation		• • •	• • •	• • •	• • •			•
Complementary processes	Adsorption on activated carbon or lignite				• • •	•	•	• • •	• •

Note: • Technologies used only for partial purification,
• • Efficient technologies,
• • • Advanced technologies that yield high levels of purification.

Whatever type of technology or absorber, methods of SO_x emission control, not simultaneously reduce NO_x and CO emissions.

2.2.3.1. Secondary quasi-dry process

The additive used is a solution or a suspension of $Ca(OH)_2$ or Na_2CO_3, in water, finely sprayed into the flue gas, for a particular reactor for desulfurization and provided with atomization of the additive installations. Thus, washing the aqueous solution used in wet processes is replaced by very fine spray additive (spray drying) in the flue gas stream.

Schematic diagram of the quasi-dry process is shown in Figure 2.12.

After passing through air preheater, the flue gases are passed through the dust filter and routed to the reaction room, where the neutralizing agent is injected.

In a first step, a part of the water introduced as a solvent of the suspension or solvent is vaporized, cooling the combustion gases to the optimum temperature needed to absorb the pollutant into the neutralizing agent.

At the contact between fine particles of liquid and combustion gases, pollutants enter in absorption reactions, which continue in the sequence: SO_3/HCl/HF/SO_2/CO_2.

Thus, if the additive is calcium hydroxide, reactions that occur are:

$$Ca(OH)_2 + SO_3 \rightarrow CaSO_4 + H_2O, \tag{2.29}$$

$$Ca(OH)_2 + 2 \cdot HCl \rightarrow CaCl_2 + 2 \cdot H_2O, \tag{2.30}$$

$$Ca(OH)_2 + 2 \cdot HF \rightarrow CaF_2 + 2 \cdot H_2O, \tag{2.31}$$

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O\,, \tag{2.32}$$

$$Ca(OH)_2 + SO_2 + 0{,}5 \cdot O_2 \rightarrow CaSO_4 + H_2O\,, \tag{2.33}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O\,, \tag{2.34}$$

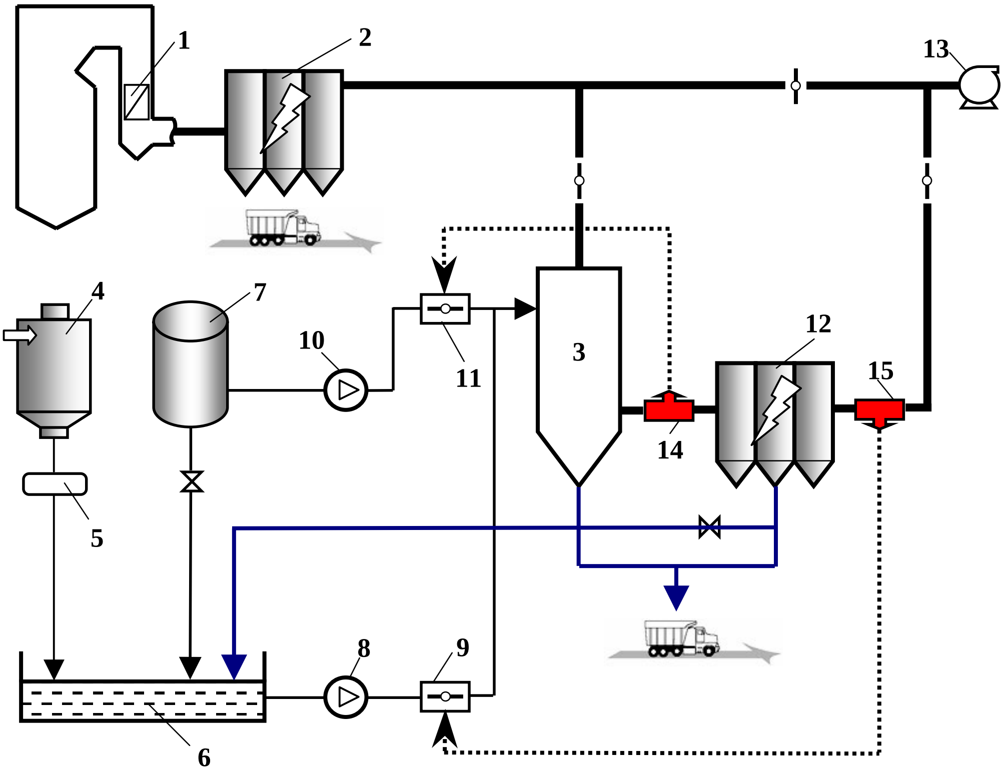


Fig. 2.12. Schematic diagram of the quasi-dry process of secondary desulfurization:
1 - air preheaters; 2 – electrostatic precipitator; 3 – reaction chamber; 4 – $Ca(OH)_2$ storage deposit; 5 – concentration assay system; 6 - pool absorbing suspension preparation; 7 – process water tank; 8 – absorber injection pump; 9 – dosage element of the amount of absorbent; 10 – water injection pomp; 11 – dosage element of the water amount; 12 – final electrostatic precipitator; 13 – flue gas discharge treated; 14 - temperature transducer; 15 – SO_2 concentration transducer.

Since the amount of SO_3 in the flue gas is very small, weight of the reaction (2.29) is less significant.

At this stage neutralization takes place between gas and liquid phase, thus with a high kinetics, which determines obtaining high degree of desulfurization, approximately 80 to 90%. In case of suspension of $Ca(OH)_2$, such a degree of desulfurization is achieved when the molar ratio Ca/S is close to 1.5 relative units.

Due to relatively high temperature of combustion gases, to the reaction chamber the water is vaporized, leading to a solid and dry suspension in gas. The solid phase consists of the final products of chemical reactions, unreacted absorbent and particles of flying ash that passed the filtering system.

At this stage, the additive excess enters in absorption reaction with sulfur dioxide, this stage becoming a dry type desulfurization stage, having much lower efficiency than that of the wet phase. Thus, overall, the neutralization of SO_2 is done both through absorption and adsorption.

Finally, it results dry particles that are removed from the system depending on their size. Thus, large particles are collected in the reaction chamber, where they are released periodically, and small particles are collected in an electrostatic precipitator or a bag filter.

If the treatment sequence of the type described above, the by-products of reactions can be marketed in the form of gypsum.

If desulfurization precedes fly ash collection, raw residue is difficult to capitalize because it contains a significant amount of ash. Heat and mass exchange between flue gas and additive is especially good as the additive is finer and more evenly dispersed in the flue gas flow.

To achieve atomization of neutralizing agent, use swirl atomizer with large dispersion angle of drops jet or axial atomizer, whose angle of dispersion is smaller, but can achieve a higher density of sprinkler.

The degree of desulfurization of quasi-dry technique can reach 90% and is influenced mainly by the amount of absorber, the pollutant concentration and the temperature at which absorption occurs.

Average consumption of the absorber is in a molar ratio Ca/S = 1.5, achieving maximum efficiency when the combustion gas temperature is very close to adiabatic saturation temperature.

In these circumstances, adjusting the process' parameters involves the control of two factors:

- ✓ the SO_2 concentration in the clean gas (measured by the transducer 15 of Figure 2.12), depending on which it is settled the concentration of absorber solution;
- ✓ the gases' temperature at their exit from the reactor (measured by the transducer 14, Figure 2.12), temperature can be altered by the flow of water introduced into the reactor.

With a proper dosing of the absorber, can be noticed that:

- ✓ quasi-dry process selectivity and efficiency are much higher than the dry process, because of the wet phase in treatment technology;
- ✓ process's efficiency is maximum near the saturation temperature, a phenomenon explained by the low reactivity of SO_2 in the dry state, which is compensated by using water as the intermediate absorber;
- ✓ Na_2CO_3 solution is more efficient than suspension of $Ca(OH)_2$, but the use of sodium compound involves costs significantly higher;

- ✓ because the temperature of the flue gases after the wet desulfurization stage is small, dry desulfurization efficiency, from the last stage, is much smaller than that of the wet phase; however, the last stage is necessary to retain, in dry state, the final products of the reaction and the excess absorber.

2.3.3.2. Advanced Quasi-dry process

Advanced quasi-dry process involves the use of unreacted absorber recirculation, according to the scheme given in Figure 2.13.

If this technique of desulfurization, the largest amount of SO_2 is retained by absorption, in a process similar to conventional quasi-dry desulfurization, according to the following chemical reactions:

$$\begin{cases} Ca(OH)_2 + SO_2 \rightarrow CaSO_3 \cdot \frac{1}{2} H_2O + \frac{1}{2} H_2O \\ CaSO_3 + \frac{1}{2} O_2 \rightarrow CaSO_4 \end{cases} . \qquad (2.35)$$

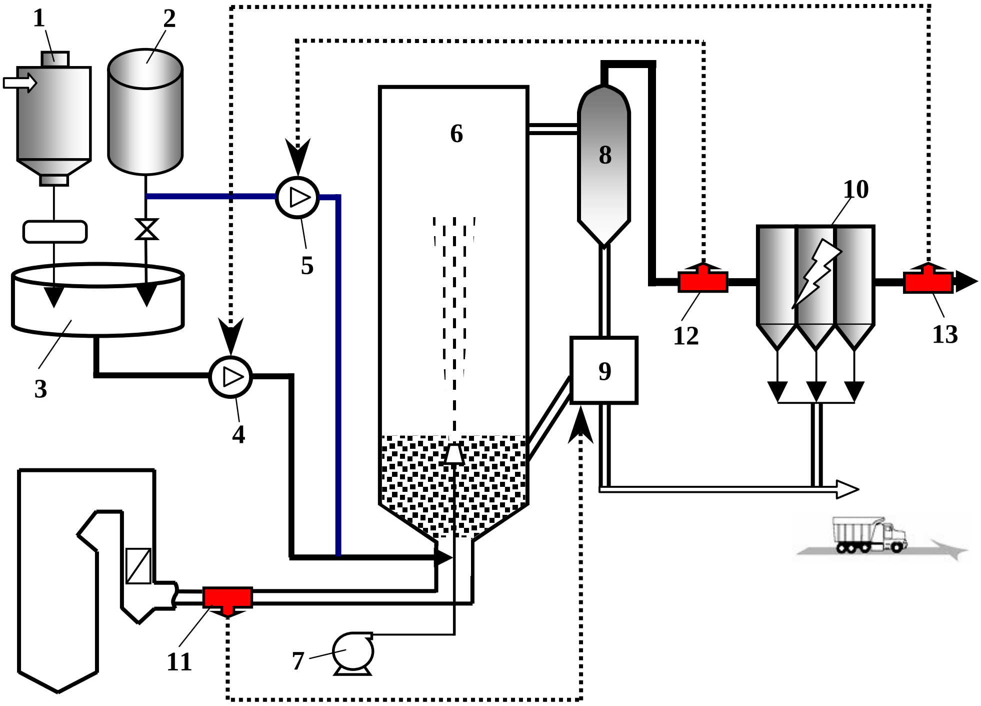


Fig. 2.13. Schematic diagram of the advanced quasi-dry process:
1 – slaked lime storage silo - $Ca(OH)_2$; 2 – process water tank; 3 – reservoir for absorbing suspension preparation; 4 – absorber injection pump; 5 – water injection pump; 6 – reaction chamber; 7 – atomizing air compressor absorber; 8 – cyclone; 9 – recirculated material dosing element; 10 – electrostatic precipitator; 11- flue gas flow rate sensor; 12 – temperature transducer 13 –SO_2 concentration transducer

At the reactor is introduced fresh absorber, in the form of a suspension of $Ca(OH)_2$ in water, finely powdered through a stream of compressed air. In this second phase of treatment takes place all stages specific to the quasi-dry desulfurization (cooling gas, SO_2 absorption and water vaporization).

Since the flow of absorber carried forward a large quantity of solid particles situated at the core, keeping them suspended, on their surface is formed a film of absorber. In this way, increases the contact surface between pollutant and absorber, and thus increases the desulfurization efficiency.

After water vaporization, in the area at the outlet of the reaction tower, in the flue gases are found, in the solid phase, particles of flying ash, covered with a film of $Ca(OH)_2$, and neutralization reaction products ($CaSO_3$ and $CaSO_4$).

The degree of desulfurization is more than 90%, approaching that of wet-type secondary techniques, thanks to gas treatment in two stages, increased contact surface of the mixture of absorber and strong eddy flows, which ensure an intimate contact and sufficient long between SO_2 and absorber.

At the reactor outlet, the stream of the flue gases having a high concentration of suspended solids is directed to installation's cyclone. Although the mechanical separation is not effective enough in retaining flying ash, the use of cyclones in quasi-dry desulfurization installations provide advanced degrees of separation, of approximately 99%. The higher efficiency of particle collection is due to the surface depositing of the increased particle size and mass of $Ca(OH)_2$, $CaSO_4$ and $CaSO_3$. In these circumstances, the suspension separations in cyclone installations achieve high levels of efficiency.

Desulfurized flue gases, having a low concentration of fine particles (of about 1% from theirs initial concentration), are directed to an electrostatic precipitator or a bag filter system, where very fine particles are retained. Obviously the final amount of energy required to collect solid suspension is much lower than if the installation is sized for the separation of the total quantity of solid substance.

Particles collected in the cyclone are directed to a silage distributor, where one part of a solid mass is directed towards the area at the reactor, the remainder being discharged outside the plant. In this way, unreacted absorber is returned and reactivated in the reactor, the global consumption of absorber being lower.

Automatic control of the process is carried out through three control loops (figure 2.13):

- ✓ the loop for dosing the amount of recycled solid, consisting of sensor 11 and the actuator of the dispenser of recycled solid; a dynamic pressure sensor measures the flow of flue gases, converting it into flow rate and hence into the debit. Depending on the amount of flue gas flow, change the speed of the screw that feeds the reactor with recycled material, thus existing direct proportional relationship between the flue gas flow and the amount of the recycled material;
- ✓ the loop of the control depending of the gas temperature, consisting of sensor 12 and the actuator cooling water pump; temperature sensor, placed between the

cyclone and the electrostatic precipitator, controls the speed of the cooling water pump;

✓ the control loop according to the final concentration of SO_2 in the flue gas, consisting of sensor 13 and actuator of the feed pump with fresh absorber; SO_2 sensor, installed near the mouth of the flue gas exhaust, feed pump speed control of the reactor with fresh absorber.

Precise control of the quantity of cooling water, the fresh absorber and recirculated solid mass, such that the temperature of the reactor at a value very close to the saturation temperature, resulting in the increase of desulfurization degree. Desulfurization degree dependence of the amount of fresh absorber and temperature, as difference from the adiabatic saturation temperature, is that shown in Figure 2.14.

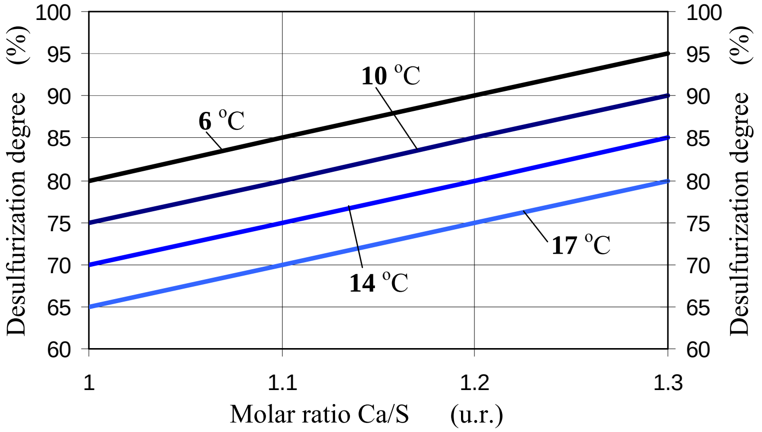


Fig. 2.14. The dependence of the desulfurization degree of advanced quasi-dry processes by molar ratio Ca/S and near the operating temperature of adiabatic saturation temperature.

Under these conditions, plant reactors can operate at higher temperatures with only 4 °C over the saturation temperature, while the quasi-dry conventional systems do not work properly if the temperature drops to less than 10 ÷ 11 °C over the saturation temperature. If the temperature of conventional reactors would fall below the threshold limit would increase the amount of particles deposited on the walls of the installation, resulting from higher tendency of agglomeration of wet particles.

In advanced plants reactors, particle deposition rate is reduced, both because of their movement and impact of intense turbulence of absorber particles to the reactor wall surface, and due to good mass transfer and pronounced drying of the solid phase in final area of the reactor.

Besides the advantages mentioned above, an important advantage of this type of technology is that of low maintenance requirement, which derives from the installation simplicity and lack of moving components in contact with the flue gas. The only items apt to pronounced corrosion and the risk of blocking are fresh absorber injection nozzles. Their mechanical systems are designed so that nozzles can be cleaned or changed in a very short time, without requiring the decommissioning of the installation and even its nominal load. Under these conditions, the availability of these installations is very close to 100%.

All components of such installation can be made from carbon steel without special coatings, corrosion rate of installation elements being reduced. Investment and operating costs are lower than other types of desulfurization installations. Thus, for a 300 MW power plant, which burns sulfur coal (2.6% S), the investment cost is about 150 $/kW, compared to 215 $/kW - necessary to effectuate one of the secondary wet desulfurization installation. Also, the investment cost is lower than the cost of achieving quasi-dry conventional systems. Operating and maintenance costs are also reduced due to the followings:

- ✓ the system's simplicity;
- ✓ the smaller amount of the reagent;
- ✓ low deposition rate of particles;
- ✓ rapid change and cleaning nozzles;
- ✓ lack of staff specifically for carrying out maintenance;
- ✓ scarceness of water in the reaction by-products, which allows a relatively easy storage, and use them to manufacture lightweight cement;
- ✓ the reduced tendency of corrosion and erosion of the boiler's components.

2.2.3.3. Wet desulfurization

For flue gas desulfurization generated by burning coal in power plants greater than 200 MWe, wet type secondary processes currently used.

The main advantage of wet desulfurization derived from high kinetics of the neutralization between a gas and a liquid phase, so the degree of desulfurization is very high, exceeding 95%, in terms of cheap absorbers.

Wet neutralization of SO_2 takes place after the flue gas dust filtration and leads to the formation of sludge sulfites, and if oxidation is sufficient, the formation of sulfate sludge. To avoid pollutant transfer to another medium, the levigate must be supplementary treated and neutralized, there can even use it to manufacture gypsum.

Since the absorber is a liquid, to avoid solution boiling is required prior cooling of flue gases leaving the heaters at the appropriate temperature (above 200 °C) to a temperature of about 60 ÷ 70 °C. Such a sharp cooling of the flue gas may require reheating them before discharge to avoid reaching the acid dew point and corrosion of the final elements of the combustion installation. Additionally, by heating is obtained a better dispersion of flue gases at the stack level.

Flue gases can lead particles during treatment and residual fly ash particles, so that in some cases, their necessary passage through a collection of particles before discharge.

Situating a wet desulfurization installation in combustion technology flow is shown schematically in Figure 2.15.

Most secondary wet desulfurization installations are equipped with special reaction chambers, called washing towers, washing columns or scrubbers. There are, however, technologies whose installations are not equipped with special reaction chambers, the absorber is introduced directly in gas pipes.

SO_2 absorption is the basic physico-chemical process of wet secondary techniques. By absorption, both SO_2 and other gaseous components of flue gas flow are dissolved in a liquid wash.

Because absorption have appropriate kinetics, absorber is necessary to choose suitable, to achieve the largest possible contact area between absorber and polluting gases and ensure a sufficient residence time of the two phases in the reaction area.

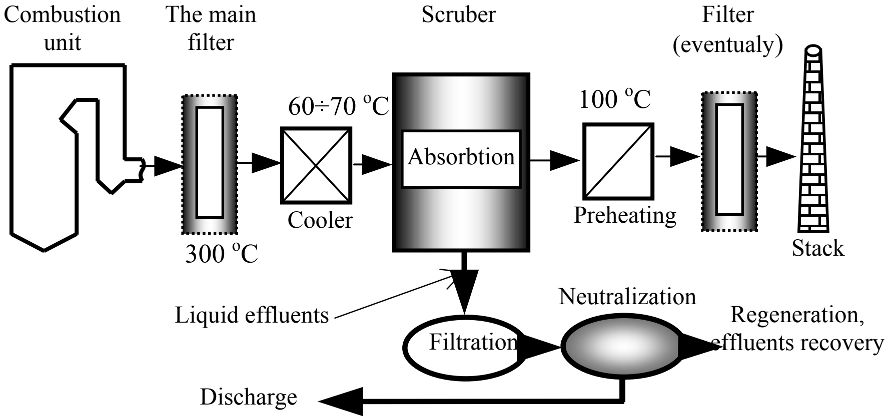


Fig. 2.15. Framing a secondary wet desulfurization installation in the technological process of coal combustion.

To satisfy the last two conditions, desulfurization installations are equipped with special reactor, called scrubbers. The main types of scrubbers are represented schematically in Figure 2.16.

In the scrubbing, SO_2 combines with absorbance, forming a solid sulfate. After droplets separation, the clean gas is discharged to the stack, and the solid and liquid phases, forming levigate (leachate) are discharged at the bottom of the scrubbing. Sulfate can be recovered, but that should not be neglected in the scrubber, is obtained a certain amount of sulfuric acid.

Some manufacturing companies are following their performance scrubbers: Babcock & Wilcox, Croll-Reynolds, Lurgi, Svedala Industries, Procedair, Sulzer ABB, Von Roll and Servithen.

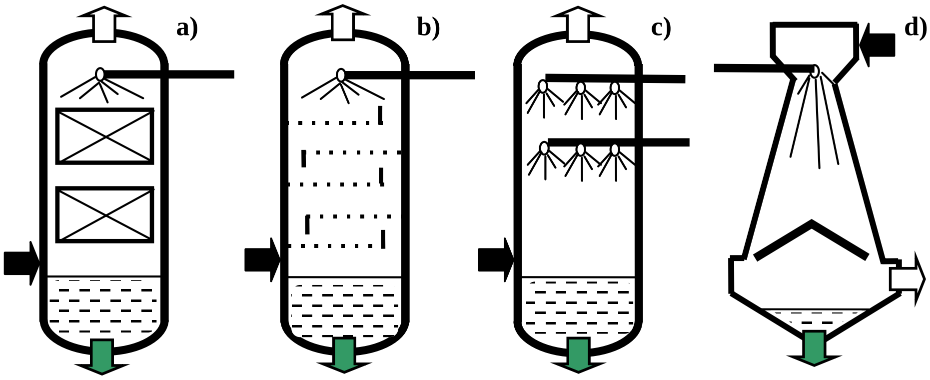


Fig. 2.16. Scrubber types:
a) – with fill; b) – with sieves-tray; c) – with spray nozzles; d) – with Venturi system.

Depending on the physico-chemical properties of the absorbers, wet desulfurization processes can be classified into the following categories:

➊ Procedures using an alkaline absorber (sodium compounds);
➋ Procedures using ammonia as absorber;
➌ Procedures using an absorber alkaline earth compounds (calcium and magnesium compounds).

Besides these categories, there are regenerative techniques, so named because the substance is formed in process and is regenerated in the same technological process. These techniques involve difficult to drive chemical reactions, higher energy consumption, consumption of catalysts, but provides that the final reaction products, SO_2 - in liquid, concentrated H_2SO_4, and almost pure sulfur.

➊ Procedures using an alkaline absorber

These processes serve as absorbers of sodium and potassium compounds. These compounds are characterized by very good solubility in water so that the neutralizing solution is clear and does not lead to sedimentation, conditions where erosion of pumps and fans is much diminished.

The main disadvantage of the use of alkaline compounds lies in the high solubility of salts formed from the desulfurization reactions, so that their storage involves special precautions in order not to transfer the pollutant to the soil or groundwater.

If the absorber is NaOH, the sequence of reactions involve the formation of compounds such as sodium sulphite (Na_2SO_3), sodium bisulphite ($NaHSO_3$) and sodium sulphate (Na_2SO_4), according to the reactions of the form (2.36), which can be globally written by form (2.37).

$$\begin{cases} 2 \cdot NaOH + SO_2 \leftrightarrow Na_2SO_3 + H_2O \\ Na_2SO_3 + SO_2 + H_2O \leftrightarrow 2 \cdot NaHSO_3 \\ NaHSO_3 + NaOH \leftrightarrow Na_2SO_3 + H_2O \\ 2 \cdot Na_2SO_3 + O_2 \rightarrow 2 \cdot Na_2SO_4 \end{cases} . \qquad (2.36)$$

$$4 \cdot NaOH + 2 \cdot SO_2 + O_2 \rightarrow 2 \cdot Na_2SO_4 + 2 \cdot H_2O . \qquad (2.37)$$

Due to the high cost of alkaline absorbers, desulfurization processes are completed, in most situations, by the principle of regeneration of the absorber, being less important to obtain a quantity of Na_2SO_4.

Regenerative processes flue gas desulfurization operates after a schema like in Figure 2.17, the absorber being a salt obtained in the technological process (Na_2SO_3), supplementary absorber from outside is only required for starting and loading installation and to compensate for technological losses of active substance in the form of Na_2SO_4.

Before introducing in the absorption tower (2), flue gases, which were separated from flying ash, are cooled in a prewash tower (1), achieving a treated gas preconditioning. Through prewash is simultaneous obtained removal of sulfuric anhydride (SO_3), hydrochloric acid (HCl), hydrofluoric (HF) and waste flying ash.

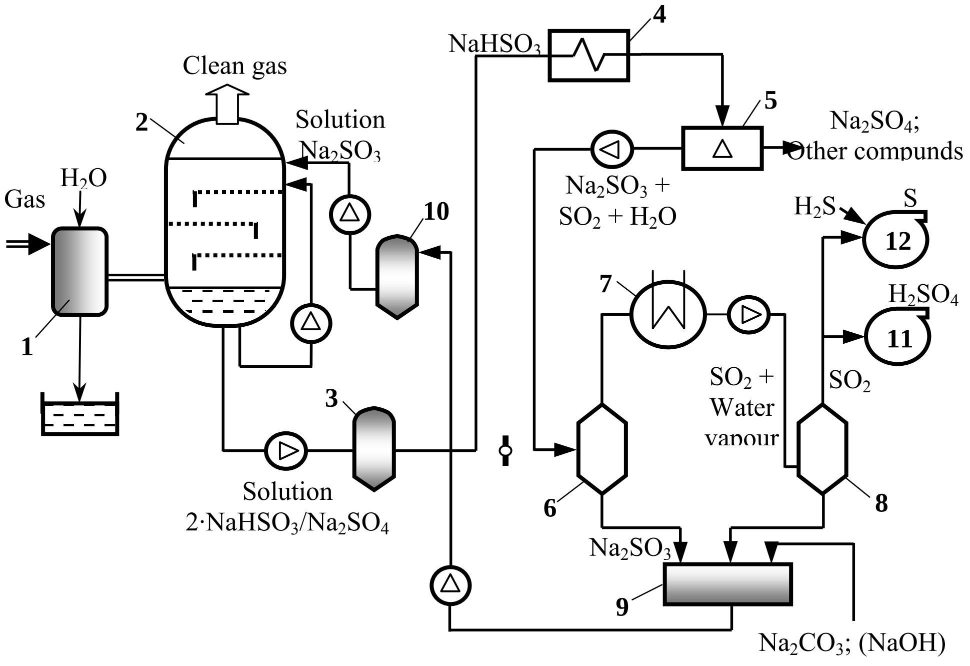


Fig. 2.17. Schematic diagram of the regenerative process, the sodium absorption: 1 – prewash tower; 2 – pan scrubber; 3 and 10 – decanters; 4 – heat exchanger, heating the $NaHSO_3$ solution; 5 – crystallized; 6 and 8 – drop separators; 7 – condenser; 9 – absorber preparation installation; 11 –H_2SO_4 preparation installation; 12 – elemental sulfur preparation installation.

After this treatment, the gas is directed to an absorbent system, where sulfurous anhydride (SO_2) is offset by absorption by a solution of Na_2SO_3 formed in the desulfurization process and is dispersed on the reaction scales tower. By absorption of SO_2 into Na_2SO_3 solution is formed a solution of sodium bisulphite ($NaHSO_3$) where there may be a certain amount of sodium sulphate (Na_2SO_4), according to the reactions of the form (2.36). $NaHSO_3$ is easily soluble in water, avoiding almost entirely the formation of deposits.

The resulting solution from the scrubber is treated for absorber regeneration, the following steps:

- ✓ $NaHSO_3$ warming solution in a heat exchanger (4) by its decomposition, according to chemical reaction, endothermic,

$$2 \cdot NaHSO_3 \xrightarrow{caldura} Na_2SO_3 + SO_2 + H_2O\,; \tag{2.38}$$

- ✓ treatment of phases mixture in a crystallized (5), where it separates as a solid Na_2SO_4;
- ✓ separation gas phase (SO_2 and water vapor), in the droplet separator (6);
- ✓ cooling the mixture of water vapor and SO_2, into the condenser (7);
- ✓ the condensate's separation (8) and its guiding to the absorber preparation installation (9);
- ✓ SO_2 rich gas processing (about 85% parts by volume) to obtain H_2SO_4 (11) or elemental sulfur by treatment with H_2S, following *Claus process*.

$$2 \cdot H_2S + SO_2 \rightarrow 3 \cdot S + 2 \cdot H_2O\,. \tag{2.39}$$

In absorber preparation installation (9), is introduced continuously, a certain amount of Na_2CO_3 or NaOH, that compensate the loss of active substance in the form of Na_2SO_4.

❷ The process of SO_2 absorption by ammonia

When the ammonia (NH_3) is used as an absorber agent, sulfur oxides are retained in the form of ammonium salts: ammonium sulfite (NH_4HSO_3), ammonium sulphite ($(NH_4)_2SO_3$) and ammonium sulphate ($(NH_4)_2SO_4$), according to:

$$\begin{cases} SO_2 + NH_3 + H_2O \rightarrow NH_4HSO_3 \\ SO_2 + 2 \cdot NH_3 + H_2O \rightarrow (NH_4)_2SO_3\,. \\ SO_3 + 2 \cdot NH_3 + H_2O \rightarrow (NH_4)_2SO_4 \end{cases} \tag{2.40}$$

Because the amount of SO_3 is reduced compared to the amount of SO_2, the amount of the resulted $(NH_4)_2SO_4$ is also reduced. Since it is preferable to obtain the $(NH_4)_2SO_4$, especially when the reaction by-products are used to manufacture chemical fertilizers, the $(NH_4)_2SO_3$ must be oxidized, according to the following reaction:

$$(NH_4)_2SO_3 + 0{,}5 \cdot O_2 \rightarrow (NH_4)_2SO_4 \,. \qquad (2.41)$$

The use of the NH_3 for gas desulfurization is mainly found in the pulp and paper industry, the method "Air Industry" recovering large amounts of SO_2 in the form of ammonium sulphite (NH_4HSO_3). “STACKPOL S” and “STACKPOL SO_2” processes are regenerative type industrial processes, the sequence of reactions, particularly with H_2S, leading to recycling of ammonia and sulphur production (process STACKPOL S) or SO_2 concentrated liquid (process STACKPOL SO_2).

❸ Methods with use of an alkaline earth absorbers

In these processes, the absorbent environment is a combination of calcium or magnesium, in the form of oxides or carbonates. Even if the basic substance is more expensive, the process based of magnesium compounds is, overall, more economically than that with calcium, because the absorber can be regenerated. The schematic diagram of the desulfurization process based on magnesium is given in Figure 2.18.

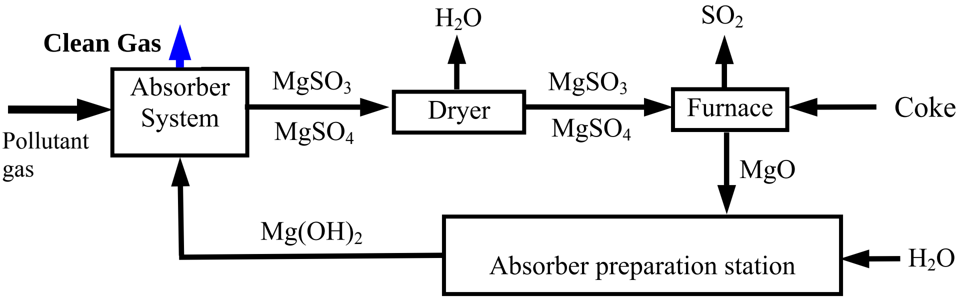


Fig. 2.18. Schematic diagram of the technological process of flue gas wet desulfurization through an absorber based on magnesium.

Flue gas desulfurization occurs in the absorber system, where the following chemical reaction takes place, with the main weight of a reaction (2.42):

$$Mg(OH)_2 + SO_2 \rightarrow MgSO_3 + H_2O \,, \qquad (2.42)$$

$$Mg(OH)_2 + SO_3 \rightarrow MgSO_4 + H_2O \,. \qquad (2.43)$$

Sulphite solution and magnesium sulphate is passed, first through a dryer, where most of the water is evaporated. The crystals obtained are heat treated in a furnace, which, by thermal decomposition, regenerates the absorber, according to reactions:

$$MgSO_3 \rightarrow MgO + SO_2 \,, \qquad (2.44)$$

$$MgSO_4 \rightarrow MgO + SO_3 \,. \qquad (2.45)$$

Magnesium oxide is reintroduced into the circuit for treatment of flue gas while the waste gas, rich in SO_2 and SO_3, is used to manufacture sulfuric acid.

Secondary wet desulfurization installations which use compounds of calcium, utilize suspension of $Ca(OH)_2$, but operational experience has shown, however, that it is cheaper to use a solution or a suspension of $CaCO_3$. In this case, the sequence of chemical reactions is as follows:

- ✓ SO_2 absorption and formation of sulfurous acid

$$SO_2 + H_2O \rightarrow H_2SO_3\,; \tag{2.46}$$

- ✓ oxidation of sulfurous acid in sulfuric acid

$$H_2SO_3 + 0{,}5 \cdot O_2 \rightarrow H_2SO_4\,; \tag{2.47}$$

- ✓ neutralization of sulfuric acid and gypsum crystal formation

$$H_2SO_4 + CaCO_3 + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2\,. \tag{2.48}$$

After absorption of SO_2 and H_2SO_3 formation, chemical reactions can evolve according to the following sequence of reactions, the final result being the same:

- ✓ neutralization of sulfuric acid and the formation of calcium sulfite

$$CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + CO_2 + H_2O\,; \tag{2.49}$$

- ✓ calcium sulfite oxidation and formation of gypsum crystals

$$CaSO_3 + \tfrac{1}{2} O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O\,. \tag{2.50}$$

Schematic diagram of the technological process of flue gas desulfurization, with absorber based on $CaCO_3$ is shown in Figure 2.19.

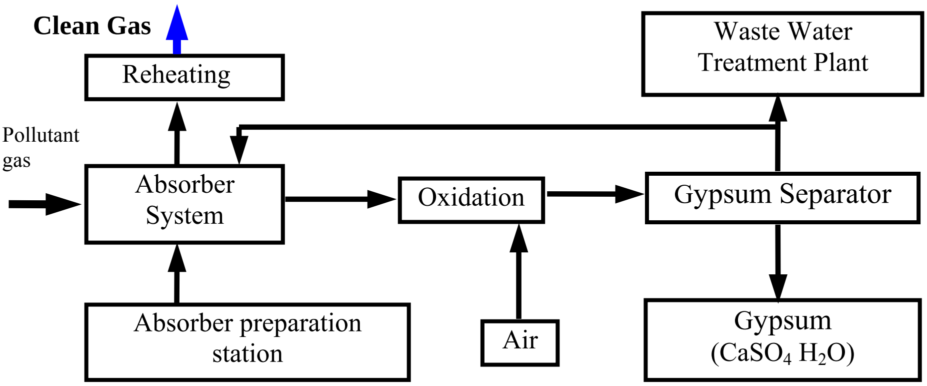


Fig. 2.19. Schematic diagram of the technological process of wet deulfurization of flue gas through a composite based on calcium absorber.

Before the entrance into the scruber, the flue gases are cleaned from flying ash.

At the entry into the scruber, there is a cooling zone, where the gases are cooled from high temperature they have when they leave the regenerative pre-heater to the saturation temperature. This cooling is achieved through a water flow process, which has a fine spray injection system.

Further, the gas passes in the main wash zone, where is sprayed the absorbent solution. Thick separators retain large droplets and fine aerosols are retained in the final fine separators.

After reheating, the flue gas is discharged to the stack.

Oxidation of $CaSO_3$ to $CaSO_4$ occurs in the oxidation zone, usually integrated in the absorption tower. This area brings a stream of air. Gypsum suspension is circulated to a hydro-cyclone, where there is a physical process of concentration, until it is obtained a solid content of 40 to 60%. Simultaneously, it is obtained a splitting of the solid phase, depending on particle size. The aim of filters installed after hydro-cyclone is to separate wastewater in order to achieve a maximum concentration of 10%. In these filters, the gypsum is washed with water to reduce chlorine content.

2.2.3.4. Advanced wet techniques

Wet type advanced technologies use as the suspension of $CaCO_3$ as absorbent medium, keeping the advantages of using a cheap and available absorber. Sequence of chemical reactions of desulfurization are identical to those occurring in the treatment schemes of conventional wet processes, (2.46) ÷ (2.48) or (2.46) and (2.49) (2.50).

Classical wet techniques as the main element vertical reaction chamber, flue gases moving countercurrent absorber suspension. Thus, the flow of treated gas to a required degree of desulfurization is limited by mass transfer characteristics of the system, leading to a significant increase in cross-section of scrubbing.

The potential for clogging and fouling of conventional scrubbers and piping is high, effect of the presence of the recirculated absorber composition of two calcium salts: $CaSO_3$ and $CaSO_4$. Last disadvantage of conventional installations causes other disadvantages related to need frequent removal from service, to perform maintenance. In many industrial applications, it is necessary to install a back scrubber, sized to temporarily take over the entire gas flow treated by a basic wash unit.

Advanced techniques, wet type, involves the use of a single installation, very effective, in which takes place all stages of wet treatment:

- ✓ cooling and preconditioning, of flue gases;
- ✓ pollutant absorption,
- ✓ oxidation of the main product of reaction until it became sulfate.

In addition, these installations are equipped with gypsum separators that provide a marketable product and wastewater evaporation systems, without additional energy consumption, they recovering waste heat from flue gases.

Schematic diagram of advanced wet technology is shown in Figure 2.20.

The first phase of the gas treatment is performed at the evaporator (1), where combustion gases are cooled, and the residues from wastewater are retained.

Solid suspension in the flue gas comprising flying ash and solid residues resulted from the evaporation of waste water, is collected in plant's electrostatic precipitator (2), then the dedusted gases are introduced into the treatment installation (3).

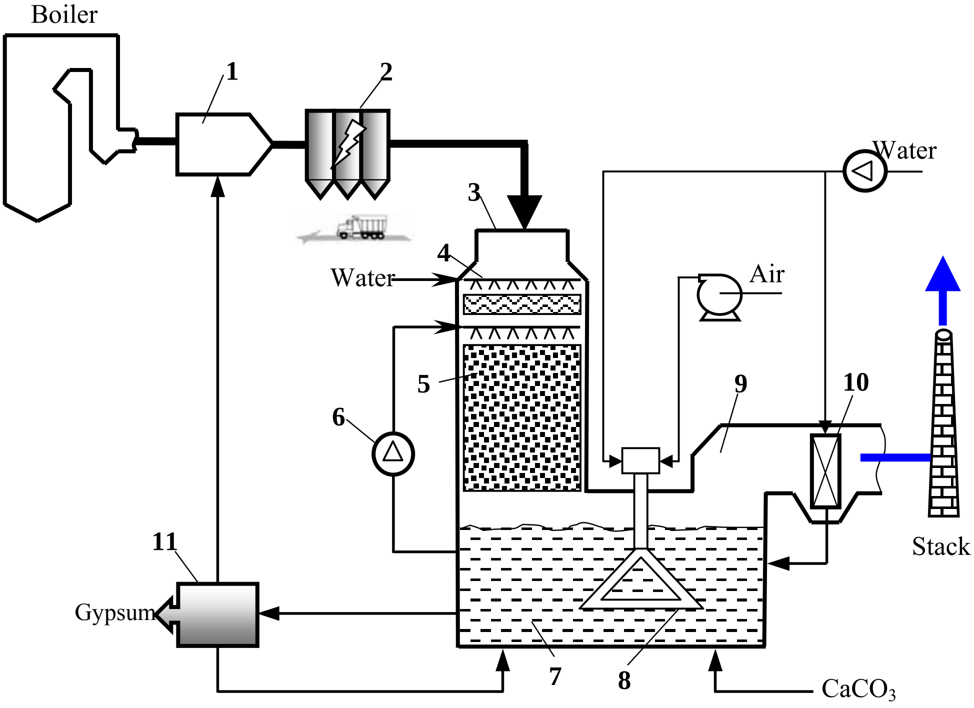


Fig. 2.20. Schematic diagram of advanced wet technology:
1 – wastewater evaporation system; 2 – electrostatic precipitator; 3 – advanced system's scrubber; 4 – cooling and flue gases humidification area; 5 – filling area; 6 –absorber recirculation pump; 7 – absorber reservoir and main reaction final area; 8 – mixing and oxidation air injection devices; 9 – calming gas area; 10 – final wash and drops separation area;
11 – gypsum's centrifugation system.

At the top of the reaction tower's column, combustion gases are cooled and moistened by water injection (4), then fall in the filling area (5), in which takes place the first stage of SO_2 absorption by $CaCO_3$ suspension.

After completing the filling area, the gas enters a calm area (9), relatively large, located above the liquid in the absorber reservoir (7). In the basic reservoir, residual acids react with fresh absorber, being almost completely neutralized. Purified gases enter in the final area of reaction chamber, are washed in a stream of clean water, passed through a droplet separator (10) and finally are discharged.

In the reservoir where is prepared the absorber is inserted, without pretreatment, $CaCO_3$ powder. Homogeneity of absorbent suspension is ensured by a continuous mixing system (8), through which is introduced the flow of water needed to prepare the suspension and an airflow, which keeps the solution in an increased turbulence. In addition, the airflow ensures $CaSO_3$ oxidation into $CaSO_4$, at the level of preparation basin of the suspension absorbing.

Continuously a certain amount of mixture of phases existing in the reactor is extracted, in order to be processed in the gypsum's centrifugation system (11). At the level of that installation, levigate is in the beginning, partly dry. Follows a new wash with fresh water to remove chlorine compounds and finally processed in a centrifugal separator. Water clarity, resulting in the centrifuge is returned to the absorber preparation reservoir, and wastewater is directed towards the evaporation system (1).

This technology has some advantages compared with traditional secondary technologies, wet type, such as:

- ✓ uniflow movement of the two phases allows the use of higher rates of gas flow up to 6 m/s, so that at the same flow of treated gas the passing section of reactor's vertical column can be reduced, leading thus, to more compact installations;
- ✓ unpressurized distribution of absorbent suspension over reactor's filling, result of uniflow movement, has the effect of reducing up to 30% the electricity consumption of absorber's recirculation pumps (6);
- ✓ by the fact that the absorber is not finely pulverized, the concentration of fine particles of liquid, driven by treated gases, is reduced by up to 95%, which allows reducing the sizes and loading the drops separator;
- ✓ absorber preparation technique directly in the reactor’s reservoir leads to a reduction of the required equipment at pre-treatment (storage silos, mixing reservoirs, pumps, circulation and distribution piping);
- ✓ mixing and oxidation combined system leads to increases reactor’s performances;
- ✓ by wastewater evaporation is realized a very good control of chlorine compounds emission;
- ✓ investment costs and the area occupied by the systems in this category are approximately 50% lower than those corresponding to conventional wet systems.

All these benefits increase the degree of desulfurization, even up to 94 ÷ 98%, and the overall effectiveness of treatment, while the availability of the installation is of the order of 99.5% (calculated at 26,300 hours of operation). At this level of availability, are not necessary backup reactors, as in conventional technologies.

2.2.3.5. Dry-type hybrid techniques

Desulfurization hybrid techniques are, in the majority of cases, the result of the combination between a intra-combustion process with a secondary one. Virtually, in all industrial applications, the secondary process is one of quasi-dry type.

The typical example of hybrid technology is **LIFAC** (*Limestone Injected into the Furnace with Activation of Untreated Calcium Oxide*), which is developed by

Tampella Oy Power Corporation from Finland. Subsequently, this technology has been applied on a large scale for power plants in the U.S., Canada, China and Russia.

In the intra-combustion stage, very fine powder $CaCO_3$ is pneumatic injected on the top of the furnace, in the area where flue gases' temperature is between 1000°C ÷ 1100°C. The desulfurization process stages are similar with the intra-combustion process, which is specific to the pulverized coal combustion:

- ✓ the calcinations of $CaCO_3$ powder, obtaining CaO;
- ✓ the neutralization of SO_2 and SO_3, obtaining $CaSO_3$;
- ✓ oxidation of $CaSO_3$ at $CaSO_4$, according to (2.13) ÷ (2.17).

Unlike the classic method, the reactions are such conducted in order that the degree of desulfurization of this stage should not exceed 25%, compared to 50% as might be obtained when the intra-combustion stage is the only treatment step. In this way, the result is a large amount of unreacted CaO, available in post-combustion stage. The control of the reactions evolution is done by injecting the neutralizing powder in a furnace's area where the flue gas temperature's is lower than that corresponding to the primary classical method.

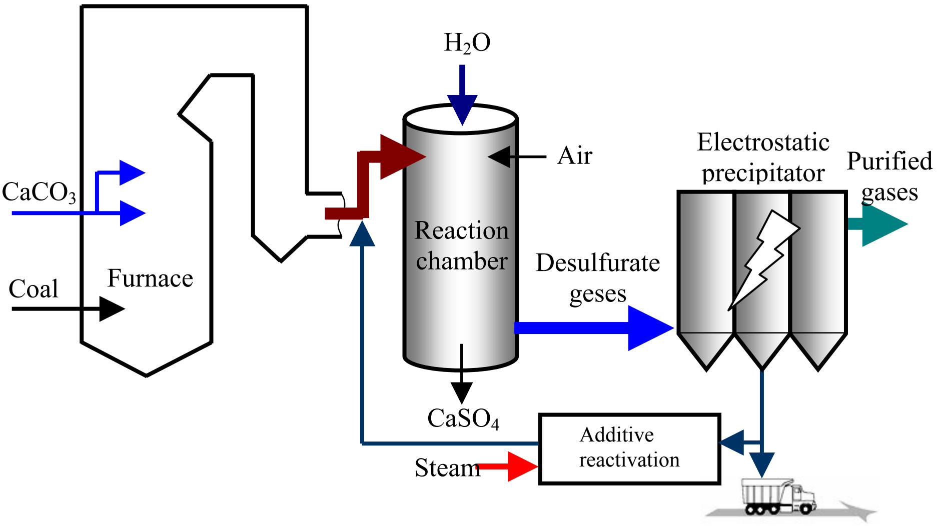


Fig. 2.21. Schematic diagram of the **LIFAC** method

In the second stage of the treatment, water is injected at the level of a vertical reaction chamber, located between the air heaters and the electrostatic precipitator of the combustion plant. In this way, CaO is activated, being transformed into $Ca(OH)_2$, according to the reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2 . \qquad (2.51)$$

In addition, water injection causes the cooling of the gases to a temperature level that is optimal for the absorption of SO_2, like in the quasi-dry process.

The reaction of the second stage is:

$$SO_2 + Ca(OH)_2 \rightarrow CaSO_3 + H_2O\,. \tag{2.52}$$

Determination of water flow is controlled in such a matter that the droplets are to be evaporated at the base of the reaction chamber, the necessary energy for this process being contained by the flue gas.

The oxidation of $CaSO_3$ powder at $CaSO_4$ is achieved by injecting a stream of air to make sure that is realized the excess of oxygen required for a proper kinetics of the oxidation reaction.

From the both phases of the hybrid process it results a certain amount of $CaSO_4$ and CaO in solid fine forms, which are simultaneously retained with the fly ash in an electrostatic separation installation.

As long as all these suspensions are solid, their collection is made without problems. In addition, the presence of water vapor makes the resistivity of particles optimal for electrostatic separation.

Even if the degree of desulfurization in the second stage is 80 ÷ 85%, a large amount of neutralizing substance, like CaO and $Ca(OH)_2$, is collected in addition with fly ash by the filtration system. To increase the efficiency of desulfurization and thus the overall economic efficiency of the system, the material collected is directed to an activation reactor, where by steam injection, the unreacted additive is separated and recycled into the system before the second stage of treatment. Thus it is created a cyclical process of activation and recycling of the ash. Under these conditions, the overall degree of desulfurization can reach 75 ÷ 85%, with a relatively low consumption of the additive (in a molar ratio Ca/S, it can reach at 2 relative units).

The parameters that have the greatest influence on the degree of desulfurization of this technique are:

- ✓ the granulation degree of the $CaCO_3$ particles,
- ✓ the quantity of the additive,
- ✓ the temperature from the second stage of treatment
- ✓ the recycle rate of the ash.

By increasing the fineness of the additive particles and the Ca/S molar ratio, it is obtained the increase of the desulfurization degree, as is shown in Figure 2.22.

Recycling the unreacted absorbent may lead to a significant growth of the desulfurization rate, up to 20 %, while reducing the determined costs with the absorber preparation and wastes' depositing.

The investment costs of the LIFAC systems are smaller than those of quasi-dry or wet techniques. These costs depend on the boiler's installed power, as follows:

- ✓ 100 \$/kW – for installed powers of 65 MW_e;
- ✓ 75 \$/kW – for installed powers of 150 MW_e;
- ✓ 65 \$/kW – for installed powers of 300 MW_e.

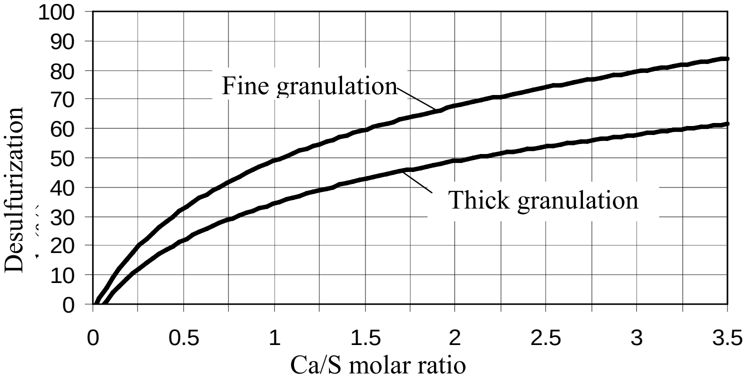


Fig. 2.22. The dependence of the desulfurization degree with the additive fineness and level.

Almost 50 % of all operating costs are related to limestone's acquisition and preparation, as for a 95 % $CaCO_3$ concentration, 4.3 tons of limestones are requested for one ton of SO_2 sequestration, at a desulfurization rate of 75% and a molar ration Ca/S of 2 relative units. In these condition the operating cost are about 65 \$/ton of SO_2 sequestrated.

Considering the aspects presented above the system's advantages are:

- ✓ a cheaper and highly available additive usage;
- ✓ the final products are in dry condition, with no major pollution risk when storing;
- ✓ a relatively small number of equipments requested in the technological flow of treating;
- ✓ smaller investment and operating costs, at 70 ÷ 85 % desulfurization rate;
- ✓ a greater flexibility in exploitation;
- ✓ a good applicability for in use boilers' reconditioning due to small investment's costs and small area usage.

The use of **LIFAC** systems present the following disadvantages:

- ✓ an existing penalty of up to 3 % of the boiler's load;
- ✓ the need to reduce the time interval between two successive cleaning operations of the vaporizing system's pipes and over-heaters, due to limestone's fine powder usage;
- ✓ this technology does not retain the arsenic from coal;
- ✓ a certain quantity of methylene chloride is present in colected ash.

Even so, these disadvantages are not so significant to restrict the utilization of the procedure both for the coal burning installations and also for sulfurous heavy fuel burning.

The thermal power plant from St.Andrä, Austria, is an example of independent utilization of those two desulfurization techniques. The principle's diagram of the desulfurization system is that given in figure.2.23, where both stages of the desulfurization process can be observed, as follows:

- ✓ the intra-combustion stage, which consist in $CaCO_3$ powder injection into the furnace, similar as for classical technique, with an independent operation, reaching so almost a 50 % desulfurization rate;
- ✓ the post-combustion stage, achieved through a quasi-dry procedure, with a sodium absorber instead of a calcium one. From the main gas channel, before the air pre-heater, some of the flue gases are taken and a $NaHCO_3$ solution is injected in it.

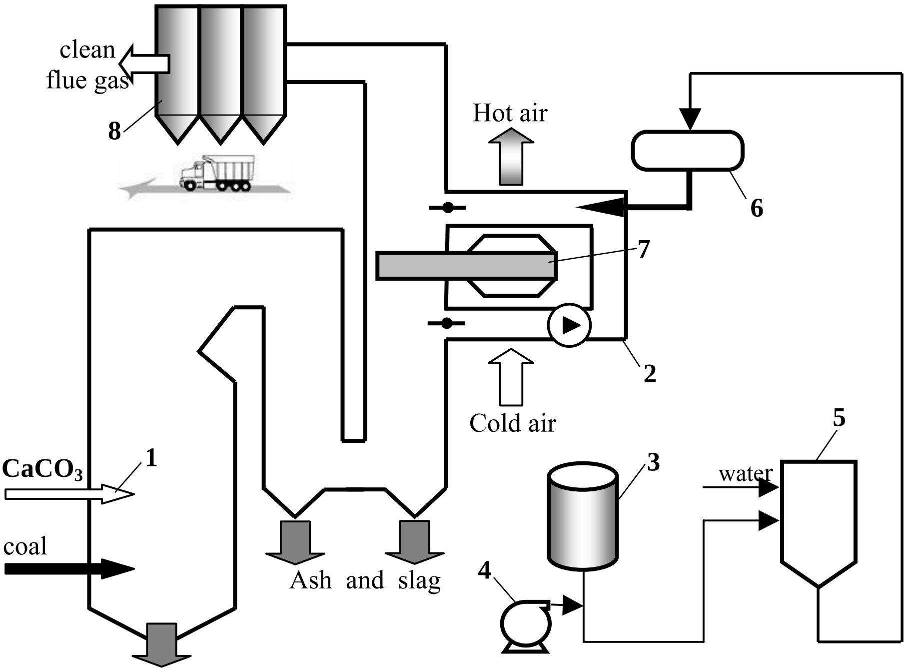


Fig. 2.23. The principle diagram of a combined desulfurization installation: 1 - $CaCO_3$ powder injectors; 2 – the secondary procedure treating cycle; 3 - $NaHCO_3$ storage tank; 4 - $NaHCO_3$ powder transmission compressor; 5 – the preparing installation of the absorbent solution; 6 – absorber dosage system; 7 – air pre-heater; 8 – filter with bags.

In the second stage of the process, in contact with hot combustion gases, reactions of the following form occur:

$$2 \cdot NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O\,, \tag{2.53}$$

$$Na_2CO_3 + SO_2 + 0{,}5 \cdot O_2 \rightarrow Na_2SO_4 + CO_2\,. \tag{2.54}$$

Finally, sodium sulfate and fly ash are collected in bag filters.

Such type of installation provides a desulfurization degree of about 80%, while the total amount of additive is 2.5 relative units of Ca/S and 1.2 relative units of Na/S, in molar ratio.

Not all the hybrid methods involve the use of an intra-combustion technique in combination with a post-combustion one. The best example showing the use of other techniques is that of the process so-called ElectroDynamic Venturi (**EDV**).

This method combines the desulfurization techniques with the collecting of secondary suspensions of gas in more complex installations, but much more effective than methods of dry desulfurization, integrated in the bag filter systems.

EDV process was imagined by Japanese company Hitachi Zosen, equipping, since 1964, municipal waste incinerators. Subsequent developments, in collaboration with LAB SA of France, lead to the development of industrial installations for treating combustion gases from the combustion of coal, installations that have multiple applications in Japan, France, Switzerland and Austria.

EDV systems retain both acid gases (HCl, HF, SO_3) and alkaline dust (flying ash). Simultaneous retain of the two categories of pollutants permits to use the natural alkalinity of the flying ash, leading to a significant economy of alkaline reagents and in a lower production of waste.

At the output the EDV treatment installation, the concentration amount of pollutants in the flue gas is of:

- ✓ 50 mg/Nm^3 – dust and
- ✓ 300 mg/Nm^3 – SO_2,

under complete retain of heavy metals and large quantities of organic and inorganic compounds of chlorine.

Installations can be designed for operation at lower loads of solids, in this case they being located downstream of the electrostatic precipitators. In such an industrial application, there are no longer required very strict terms of the separation degree for the electrostatic precipitators, especially for very fine particles.

Basically, in the same technological process are taking place the following physico-chemical processes:

- ✓ wet gas washing, with or without neutralizing,
- ✓ adiabatic relaxation,
- ✓ particles ionization,
- ✓ electrostatic separation of phases.

These processes occur in the main modules of the system EDV (Fig 2.24): absorption and dedusting column (1), the Venturi particle collector (2), absorption column (5) and electrostatic separator (7, 8).

Combustion gases, which may be partly dedusted, are introduced into the column where they are absorbed, dedusted and rapidly cooled by the $Ca(OH)_2$ solution. The concentration of this solution is between 5 ÷ 10 %.

Larger particles are driven, by the absorbent solution drops, to the tank located at the base of the column. Dusting takes place simultaneously with a rapid process of neutralizing acid gases, very active, as HCl, HF and SO_3 and partial retaining of SO_2.

Neutralizing solution is recirculated, fresh lime milk being inserted into the absorbent circuit in such an amount in order to maintain the pH within 1.5 ÷ 2.5.

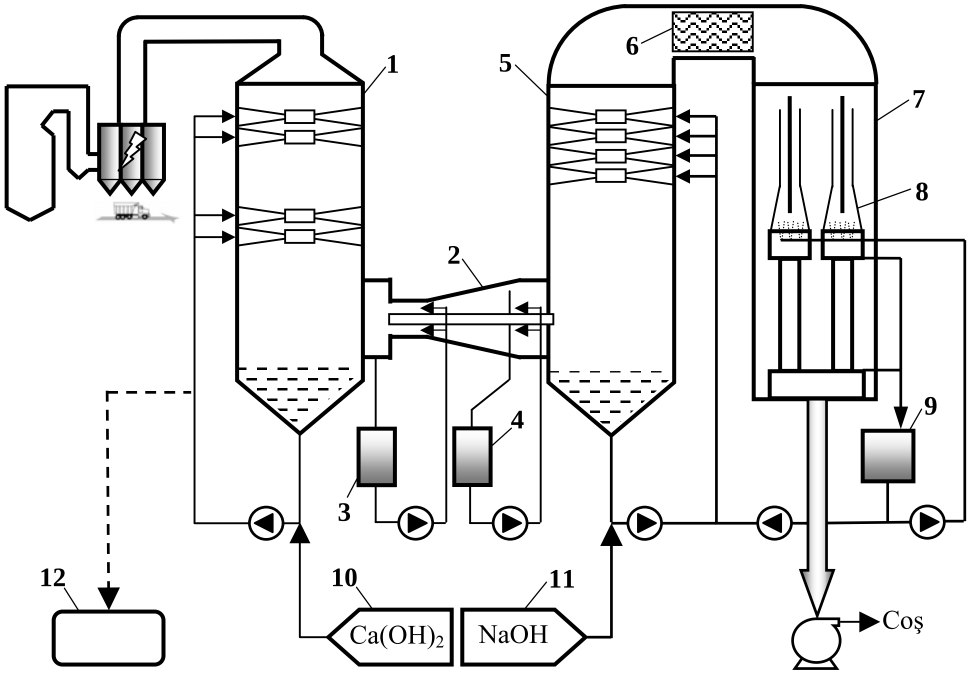


Fig. 2.24. Schematic diagram of the hybrid treatment method **EDV**:
1 – Absorption and dedusting column; 2 – The Venturi particle collector; 3, 4 – collectors and settling recipients; 5 – absorption column; 6 – drop separator; 7 – electrostatic separator chamber; 8 – electrostatic precipitator modules; 9 – water tank; - 10, 11 - absorber preparation stations for the first and second stage treatment 12 – waste water treatment station.

A certain amount of the solution is continually directed towards wastewater treatment installation, treatment involves the following processes:

- ✓ additional homogenization and neutralization;
- ✓ clotting by the addition of ferric chloride and polyelectrolyte;
- ✓ decanting, after which is obtained the levigate and a quantity of clean water;
- ✓ levigate dewatering, through filtration and pressing, until it is obtained a solid cake, chemically stable and which can be stored without the risk of major impact on the environment.

After the processing into the absorption and dedusting column (1), gases are directed to the Venturi type fine particles collector (2). In it are retained and evacuated fine particles of flying ash and absorbent, which could not be collected in the electrostatic precipitator and, even less, in the previous column. Through adiabatic relaxation, particles are covered with condensation and collected by water jets, disposed at the entrance and exit of the Venturi collector. Water necessary to collect particles is recirculated through pumps and collection-sedimentation recipients (3, 4).

After leaving the Venturi collector, the content of suspension in gas is very low, but the concentration of SO_2 is inadmissible high for its exhaust into the atmosphere. In order to reduce the emission of SO_2, flue gases are treated in an absorption column, the high efficiency of desulfurization at this level being determined by the use of highly active absorber, 10 % NaOH solution in water, and by the absorber's fine pulverization into the gas flow.

Because of wet treatment in the absorption column, the flue gases trains absorber drops, requiring passage of gas through a droplet separator (6) before the final separation of the phases, at the level of electrostatic precipitator.

Electrostatic separator consists of several modules, where is processed the gas and water mixture, until saturation. By electrostatic separation, fine particles of water are retained, as well as organic and inorganic chlorine compounds and fine particles of heavy metals.

High concentration of sodium compounds (NaCl and NaOH), dissolved in the washing solution, makes increase the particles conductivity to an area where the dry electrostatic separation can become difficult, due to rapid loss of electric charge accumulated by the particles.

However, it can obtain a high fine particle separation by making electrostatic modules in the wet type Venturi system. Even under these conditions, special attention should be given absorber injection nozzle sizing and its injection pressure, which leads, finally, the dominant size of the particles in suspension in the flue gases. It is also important to be properly sized separation modules and to adopt an adequate supply voltage for the module designed for electrostatic precipitation.

Advantages like compact construction, simultaneous treatment of several pollutants and heavy metals removal from flue gases, EDV systems recommended for use on a large scale in power generation.

2.3. Calculation example

Applying the methodology for the assessing emissions of SO_2 and suspended dust in case of installing a treatment system to an existing combustion plant, involves the steps given in the following calculation example.

At its nominal load, the boiler CR 12 (50 t/h, 40 bar and 45 MW), installed in an urban area, consumes B = 3528 kg/h heavy fuel, with inferior calorific power H_i = 39500 kJ/kg and a sulfur content in fuel of S_c = 3,35 %. It has to be determined the preliminary consumption of active substance that is necessary to reduce the SO_2 content from the flue gas, under the limit of 1700 mg/Nm^3, the intermediate phase calculation algorithm consisting of SO_2 determination of the combustion plant. Dry gas volume reported at the amount of fuel burned is V_{gu} = 10,23 Nm^3/kg, at a concentration in the fuel gases of oxygen $O_{2\,ref}$ = 3 %.

A possible way to resolve such a problem is presented in the box 2.1.

Box 2.1. Example of SO2 emission evaluation and requirements of neutralizing substance

Boiler's thermal power is:

$$P_t = B \cdot H_i = \frac{3528}{3600} \cdot 39500 = 38{,}71\ MW.$$

Since the unburned fuel is liquid and the power is smaller than 300 MW, according to GD no. 541/2003 concerning the pollutants emissions limitation in combustion installations, results that the admissible SO_x emission is 1700 mg/Nm^3, expressed in SO_2 equivalent.

SO_2 debit is calculated with the following relation:

$$m_{SO_2} = 20 \cdot S_c \cdot B \cdot (1-\eta') \cdot (1-\eta'') = 20 \cdot 3{,}35 \cdot \frac{3528}{3600} \cdot 1 \cdot 1 = 65{,}66\ g/s = 236{,}37\ kg/h.$$

SO_2 concentration in wet combustion gases is:

$$C_{SO_2} = \frac{m_{SO_2}}{B \cdot V_{gu}} = \frac{65660}{\frac{3528}{3600} \cdot 10{,}23} = 6549\ mg/Nm^3 .$$

It can be observed that the value resulted from calculation, for SO_2 concentration in wet gases, is bigger than the recommended limit value.

If is adopted the LIFAC desulfurization technology, injecting the calcium carbonate powder, through the existing hole in the output window of flue gases from furnace, where the temperature is t_{g0} = 1030 ^{o}C, the calcium carbonate calcinates and the resulting calcium oxide enters in reaction with SO_2.

Quantitatively, the $CaCO_3$ decomposition reaction into CaO and CO_2 can be written such as:

$$1\ kmol\ CaCO_3 \rightarrow 1\ kmol\ CaO + 1\ kmol\ CO_2$$

or

$$100\, kg\, CaCO_3 \rightarrow 56\, kg\, CaO + 44\, kg\, CO_2 .$$

Similarly, anhydrous $CaSO_4$ forming chemical reaction is:

$$1\ kmol\ SO_2 + 1\ kmol\ CaO + 0{,}5\ kmol\ O_2 \rightarrow 1\ kmol\ CaSO_4$$

or

$$64\ kg\ SO_2 + 56\ kg\ CaO + 16\ kg\ O_2 \rightarrow 136\ kg\ CaSO_4 .$$

Thus results that in order to bind 64 kilos of SO_2 are necessary 100 kilos of $CaCO_3$, respectively for binding 236.37 kg/h of SO_2 will be needed:

$M_{CaCO_3} = \frac{236{,}37}{64} \cdot 100 = 369{,}32\ kg/h$ calcium carbonate, which will result

$M_{CaSO_4} = \frac{236{,}37 \cdot 136}{64} = 502{,}28\ kg/h$ anhydrous calcium sulphate.

If it is accepted that, at a molar ratio of Ca/S = 1.75, in first stage, the wet desulfurization's efficiency is $\eta_1 = 0.40$, and in the second stage, when is water or steam is injected into the reactor, the efficiency is $\eta_2 = 0.7$, so that the SO_2 mass balance will be:

- SO_2 debit retained in the furnace

$$\left(m_{SO_2}\right)_F = \eta_1 m_{SO_2} = 0{,}40 \cdot 236{,}37 = 94{,}548\ kg/h;$$

- SO_2 retained in reactor

$$\left(m_{SO_2}\right) = \eta_2\left[m_{SO_2} - \left(m_{SO_2}\right)_F\right] = 0{,}7 \cdot [236{,}37 - 94{,}548] = 99{,}2754\ kg/h.$$

Following, SO_2 concentration in wet combustion gases, leaving the stack, when the oxygen content is O_{2ref} = 3 %, will be:

$$\left(C_{SO_2}\right)_{CF} = \frac{\left(m_{SO_2}\right)_{CF} \cdot 10^6}{BV_{gu}} = \frac{42{,}5466}{3528 \cdot 10{,}23} = 1178{,}85\ mg/Nm^3.$$

For a molar ratio Ca/S = 1.75, in the furnace is inserted the following debit of calcium carbonate

$$\left(M_{CaCO_3}\right)_F = 1{,}75 \cdot M_{CaCO_3} = 1{,}75 \cdot 369{,}32 = 646{,}3\ kg/h.$$

Appropriate, is calculated the calcium oxide debit

$$M_{CaO} = 0{,}56 \cdot \left(M_{CaCO_3}\right)_F = 361{,}9336\ kg/h,$$

And the carbon dioxide debit:

$$M_{CO_2} = 0{,}44 \cdot \left(M_{CaCO_3}\right)_F = 284{,}3764\ kg/h.$$

From CaO debit, obtained through calcination in furnace, one part is combined, in furnace, with SO_2, i.e.

$$\left(M_{CaO}\right)_F = \frac{\left(m_{SO_2}\right)_F \cdot 56}{64} = \frac{94{,}548 \cdot 56}{64} = 82{,}7295\ kg/h,$$

And in reactor

$$\left(M_{CaO}\right)_R = \frac{\left(m_{SO_2}\right)_R \cdot 56}{64} = \frac{99{,}2754 \cdot 56}{64} = 86{,}8660\ kg/h.$$

Remains unreacted and is eliminated over the electrostatic precipitator, as powder, the following CaO debit

$$\left(M_{CaO}\right)_{EF} = M_{CaO} - \left(M_{CaO}\right)_F - \left(M_{CaO}\right)_R = 192{,}3381\ kg/h.$$

After the chemical reactions, are formed the following $CaSO_4$ debits:

- in furnace

$$\left(M_{CaSO_4}\right)_F = \frac{\left(m_{SO_2}\right)_F \cdot 136}{64} = \frac{94{,}548 \cdot 136}{64} = 200{,}9145\ kg/h,$$

- in reactor

$$\left(M_{CaSO_4}\right)_R = \frac{\left(m_{SO_2}\right)_R \cdot 136}{64} = \frac{99{,}2754 \cdot 136}{64} = 210{,}9602\ kg/h$$

So, the dust debit that enters in electrostatic precipitator is:

$$\left(M_{praf}\right)_{EF} = \left(M_{CaO}\right)_{EF} + \left(M_{CaSO_4}\right)_F + \left(M_{CaSO_4}\right)_R = 604{,}2128\ kg/h\,.$$

Dust concentration in combustion gases is:

$$\left(C_{praf}\right)_{EF} = \frac{\left(M_{praf}\right)_{EF}}{B \cdot V_{gu}} = \frac{604{,}2128 \cdot 10^6}{3528 \cdot 10{,}23} = 16741{,}17\ mg/Nm^3\,.$$

If electrostatic precipitator's efficiency is 99.5 %, then the dust concentration in flue gases evacuated through the stock is

$$C_{praf} = (1 - 0{,}995) \cdot \left(C_{praf}\right)_{EF} = 83{,}70\ mg/Nm^3\,,$$

bigger than the 50 mg/Nm^3 maximum admissible concentration, appropriate to liquid fuel combustion. In the same time, this concentration is smaller then the maximum admissible for coal combustion, even in new installations (140 mg/Nm^3).

CHAPTER 3

NITROGEN OXIDES' EMISSION CONTROL

3.1. Nitrogen oxides forming into combustion processes

The atmospheric air is polluted with nitrogen oxides, from their category making part: monoxide (NO), dioxide (NO_2), trioxide (N_2O_3), pent oxide (N_2O_5) and nitrous oxide (N_2O). Of all these oxides, the most important role in air pollution have it NO and NO_2. Generally, these two categories of oxides are called NO_x. Nitrous oxide, initially considered as harmless, has a negative impact on the ozone layer.

Emission standards, imposed on fossil fuel burning installations for energy purposes, refer to the total emissions of nitrogen oxides, without being specified their share in the total emission. In the stack of the steam generators, the largest share in total emission of nitrogen oxides holds NO_2. Emission standards refer only to NO_2, because the amount, however small, of NO is rapidly converted, in the free atmosphere, to NO_2.

Nitrogen oxides formation approach based exclusively on these observations lead to the wrong conclusion of mainly training of NO_2. In reality, in the combustion chambers of steam generators are formed mainly NO, nitrogen dioxide accounting 5-10 % of the total nitrogen oxides. Subsequently, in the gas ducts and in the free atmosphere, NO is oxidized to NO_2.

In the process combustion, nitrogen monoxide is formed by three distinct mechanisms, namely:

- ✓ *thermal* mechanism;
- ✓ *nitrogen oxide formation* mechanism *prompt* or *early*;
- ✓ *NO formation* mechanism *of the existing nitrogen in the fuel*.

By the thermal mechanism and the early one, NO results from oxidation of molecular nitrogen found in the air needed for combustion, at high temperature from flame and under the conditions of excess oxygen. If in mechanism thermal the reactions are, mainly, oxidation reactions, in the case of prompt mechanism oxidation reactions take place only in the end of the process. Thus, in the early stages of combustion, free radicals are formed, type cyanide (HCN) and oxi-cyanide (HNCO), that participate at complex reduction reactions. This leads to various species of ammonium (NH_i, i=0,1,2,3), which are finally oxidized.

Schematic representation of forming arrangements and, at the same time, the reduction of nitrogen oxides, to molecular nitrogen, is given in Figure 3.1.

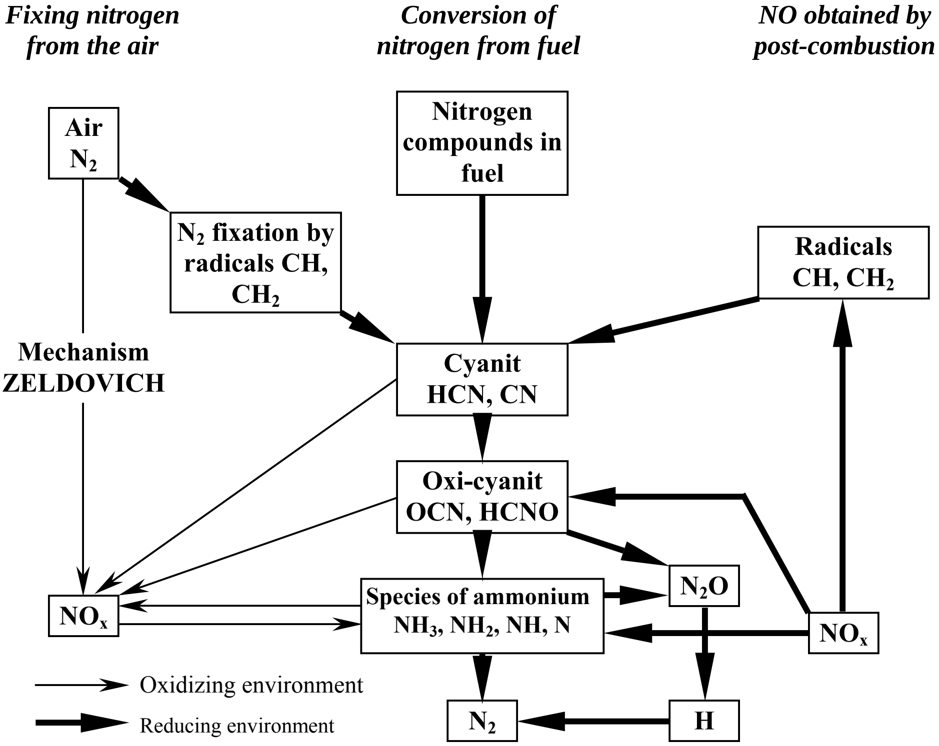


Fig. 3.1. Formation and reduction of nitrogen oxides in the combustion of fossil fuels

The diagram in Figure 3.1, is an additional way to the three mechanisms of formation of NO_x. This corresponds to reduce NO_x by post-combustion method, in which case, an amount of fuel is introduced downstream of the main combustion zone.

A summary of reactions that leads to the nitrogen oxides production from fossil fuels', installation area in which they operate, and the parameters that influence the reaction kinetics, are those given in Table 3.1.

Prompt NO formation mechanism is characterized by high speed of development, the formation of NO from the existing nitrogen in the fuel is slower, and the slowest NO formation mechanism is the thermal one.

Table 3.1. Formation of nitrogen oxides

Nitrogen oxides		**Production zone**	**Reaction mechanism**	**Factors influencing**
NO	thermal	- flame, - area after reaction.	*after Zeldovici*: a) excess air: $O + N_2 = NO + N$ $N + O_2 = NO + O$ b) excess fuel: $N + OH = NO + H$	- atomic oxygen concentration; - reaction time; - temperature (over 1300 °C).
	prompt	- flame	*after Fenimore*: $CN + H_2 = HCN^* + H$ $CN + H_2O = HCN^* + OH$ $CN + H_2 = HCN^* + N^*$	- atomic oxygen concentration; - coefficient of excess air.
	the existing nitrogen in the fuel	- flame	(CN and CH) + (H_2, H_2O and N_2) ↓ Cyanit (HCN) ↓ radicals NH_i+(O or OH) → NO	- nitrogen concentration in the fuel; - oxygen concentration; - coefficient of excess air; - flame temperature.
NO_2		- flame	*after Fenimore*: $NO + H_2O = NO_2 + H_2$	- sudden slowing combustion reaction.
		- gas channels, - chimney.	*after Bodenstein*: $2 NO + O_2 = 2 NO_2$	- temperature (at temperatures below 650 °C); - oxygen concentration; - reaction time.
		- free atmosphere	$NO_2 + ruv = NO + O$ $O + O_2 + M = O_3 + M$ $NO + O_3 = NO_2 + O_2$	- oxygen concentration; - sunlight; - reaction time; - rank of opacity of the atmosphere.
Obs. $^{*)}$ products that may be considered will be transformed into NO_x *Notations*: ruv –ultraviolet radiation; M – the collision partner.				

Nitrogen conversion into NO is dependent on combustion temperature. This observation is evidenced by the curves in Figure 3.2 that gives the dependence of flame temperature and the amount of the NO produced by the three mechanisms.

Thus, at low temperatures, the degree of conversion of fuel nitrogen is strongly temperature dependent, while the degree of conversion at high temperatures is stabilized, almost, at a certain level, thus becoming less dependent on the flame's temperature.

When using chemical methods to reduce nitrogen oxides, it is important to know the weight of the two types of oxides (NO and NO_2), in the section where NO_x reduction system is installed. As previously noted, the share of NO_2 in the furnace's outlet is of approximately 5 to 10%. However, under certain operating conditions, the amount of NO_2 can exceed much 10% of total NO_x emission.

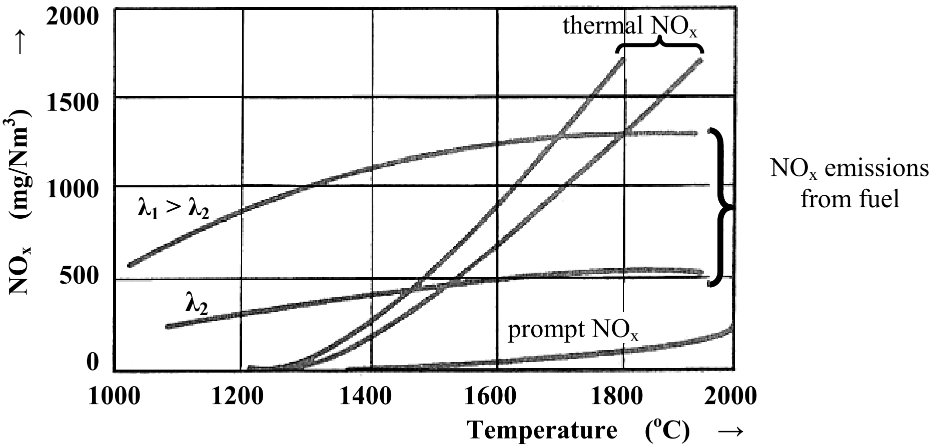


Fig. 3.2. Dependence on the amount of NO_x formed in the flame temperature, for the three mechanisms and different coefficients of excess air (λ).

According to Fenimore theory, NO_2 is obtained from NO reaction with water vapors, in the outbreak areas in which the flame is cooled rapidly (Table 3.1.). According to Hori's theory, the reactions of formation and decomposition of NO_2 in the furnace are of the form:

$$NO + HO_2 = NO_2 + OH \quad \text{- } NO_2 \text{ formation} \tag{3.1}$$

$$\begin{cases} NO_2 + H = NO + OH \\ NO_2 + O = NO + O_2 \end{cases} \quad \text{- } NO_2 \text{ decomposition} \tag{3.2}$$

Typically, the ratio NO_2/NO_x is small, even at relatively low temperatures, because the decomposition reactions of NO_2 are fast. However, if combustion gases are rapidly cooled by an additional airflow, may be recorded significant concentrations of NO_2. High values of NO_2 concentration in combustion gas and air mixture, occurs for temperatures between 800 and 900 K. In case of air excess, high concentration of NO_2 is due to higher initial amount of NO.

In case of fuel excess, the large amount of unburned and free radicals make to increase the concentration of such radicals HO_2 and, implicitly the amount of NO_2. The dependence between the quantities of NO_2 and NO_x by the amount of additional air, introduced above the flame (the introduction of *higher amounts of air* as a method of reducing NO_x emissions), is that illustrated in Figure 3.3.

It may be noted that higher air blowing reduces the total quantity of nitrogen oxides, however, precisely those higher air flow rates at which NO_x reduction effect is maximum, the amount of NO_2 is, also, maximum. In the gas channels and in free atmosphere, NO_2 is formed by further oxidation of nitrogen monoxide, regardless of the mechanism by which the NO occurred.

NO_2 formation process takes place relatively slowly in the flame, more rapidly in the flue gas channels and very fast in free atmosphere. High speed in free air oxidation of NO is due, mainly, to the high concentration of oxygen in atmospheric air.

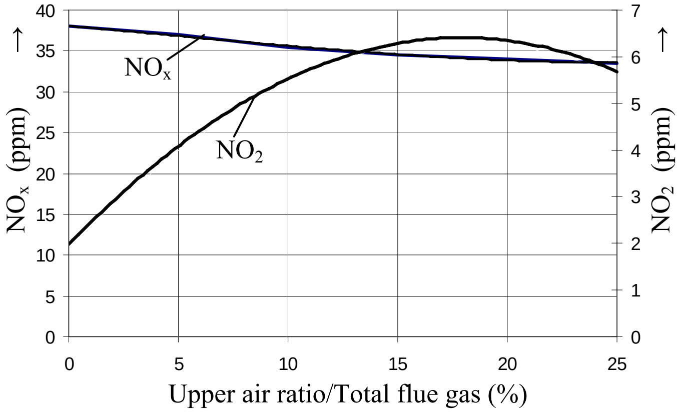


Fig. 3.3. Dependence quantities of NO_2 and NO_x by flow share higher air in total flue gas flow.

The share of three mechanisms in the total formation of NO_x is difficult to establish rigorously. The contribution of NO_x from existing fuel nitrogen can be determined by laboratory experiments, which introduces a mixture of oxygen and argon, instead of air. Obviously such experiments cannot be developed to scale power boilers being in operation.

Although it cannot rigorously specify which is the contribution of each mechanism in the formation of total nitrogen oxides, but it can be synthesized the following considerations:

- ✓ Participation of prompt mechanism in the formation of the total quantity of NO is low (5 to 10%), regardless of fuel type and combustion technology adopted;
- ✓ For pulverized coal combustion in the furnaces and ash disposal in solid form, where the combustion temperature is of approximately 1300÷1400 °C, thermal NO is less formed, than the highest amount of NO released from nitrogen along with volatile materials;
- ✓ In furnaces for brown coal combustion and in furnaces with fluidized bed combustion, NO is formed, almost entirely, by nitrogen existing in the fuel;
- ✓ In furnaces of pulverized coal and ash disposal in liquid form, thermal NO has the highest weight;
- ✓ Specific coal property to form NO depends on the nitrogen content, and volatile content and their rate of evolution;
- ✓ Reduce the amount of NO can be achieved by reducing the oxygen concentration, both in the burners, and the whole height of the furnace;
- ✓ Reduce excess air coefficient cause significant reduction of the concentration of NO_x, but, at the same time, leads to a significantly increased unburned coal.

3.2. Emissions control of NO_x from the flue gases

Treatment of nitrogen oxide emissions is more difficult and more complex than the control of the sulfur oxide emissions, the main difficulties arising from the indissolubility of the nitrogen monoxide in the aqueous solutions.

Techniques to control emissions of nitrogen oxides, regardless of the stage of combustion process which are applied, must be the result of analysis parameters that influence the amount of NO_x generated, in accordance with normal values of pollutant emission and immission.

The parameters that influence the amount of NO_x, produced in the steam generators, can be classified as follows:

- ✓ geometry of the boilers and theirs operating regimes:
    - temperature in the combustion;
    - coefficient of excess air,
    - type and the location of the burners,
    - boiler load;
- ✓ fuel quality:
    - nitrogen content;
    - calorific power;
- ✓ volatile matter content of the burned coal:
    - quantity,
    - temperature and rate evolution of the volatile materials.

Techniques to control emissions of NO_x can be applied at the furnace level or at the level of the secondary gas channels. Intra-combustion techniques are called primary methods of treatment, and the post-combustion is called secondary methods. In order of a higher reduce of NO_x emissions it can be simultaneously applied methods of primary and secondary treating, combinations of two secondary methods or secondary methods that simultaneously provides flue gases' desulfurization.

Unlike techniques for flue gases' desulfurization, in the case of NO_x control techniques does not exist emission reduction methods applicable since the stage of pre-combustion. In addition, a portion of NO_x emission comes from the transformation of existing nitrogen in the air needed for combustion, and the use of inert gases and oxygen mixtures is far from being economically applicable, on an industrial scale.

However, it can be considered as a method of control, pre-combustion type, choosing a fuel with low nitrogen content. Thus, natural gases do not have nitrogen in their composition, and liquid fuels have organic nitrogen less than the coal has. If the concentration of nitrogen in the fuel is less than 1.5%, virtually is not need to use any method of NO_x emission control.

Another possible solution to reduce NO_x emission, currently applied only in pilot power plants, is the simultaneous combustion of pulverized coal and biomass.

As can be seen in Figure 3.4, the relative cost index application on the primary methods is between 60 and 120, to a degree of reduction emissions between 20 and 62%.

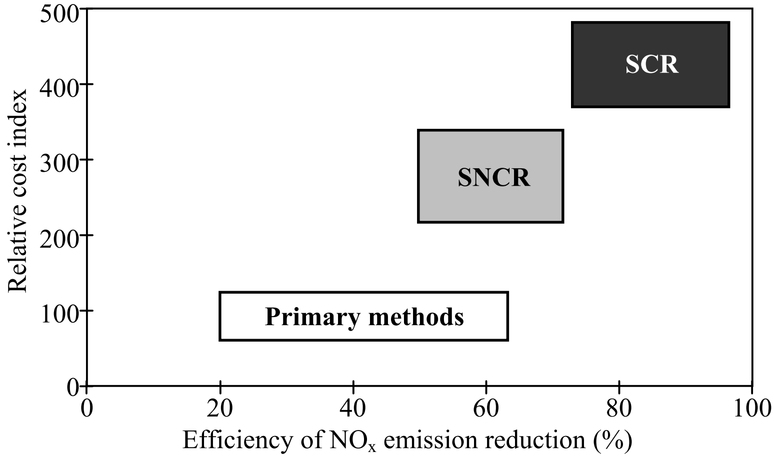


Fig. 3.4. The relative cost index of application denitriding techniques depending on their effectiveness (SNCR – selective non-catalytic reduction; SCR – selective catalytic reduction)

Post-combustion techniques are significantly more expensive than intra-combustion (relative cost indices between 250 % and 480 %, depending on the method), but these are only that ensure the reduction of emissions below normalized maximum allowable level (degrees of treatment between 50÷95%).

In the absolute costs, investments for application NO_x control primary techniques are of approximately 8÷17 EUR/kW in the case of the coal-based boilers and of 30÷40 EUR/kW at boilers that burn brown charcoal.

For remediation of flue gases and for attenuation of noise pollution generated from the power plants, the investment cost is about 27 % of the full cost of a new installation, while only the investing for the control of NO_x emissions may constitute approximately 7% of the total investment.

A possible classification of the techniques that control emissions of NOx from the flue gases is that given in Table 3.2.

Table 3.2. The classification of the techniques that control the emissions of NO_x

Intra-combustion Methods	Optimum sizing of the furnace
	Staged combustion (at the burners' level and/or at the entire furnace)
	Non-stoichiometric combustion (air flow control or fuel)
	Flue gas recirculation
	Modification of operative parameters
	Fluidized bed combustion

Post-combustion methods	**Dry Techniques**	Selective Non-Catalytic Reduction (**SNCR**)	
		Catalytic reduction	Selective (Selective Catalytic Reduction - **SCR**)
			Non-selective (Non-Selective Catalytic Reduction - **NSCR**)
		Adsorption on activated charcoal or copper oxide*)	
		Reduction through the accelerated electron beam*)	
	Wet *) Techniques	Oxidation – absorption - reduction	
		Oxidation – absorption	
		Absorption – reduction or Absorption – oxidation	
*) The procedures are used simultaneously to control the emission of SO_2.			

3.2.1. Intra-combustion techniques

Primary techniques, applicable in the furnace of the steam generators, acting on those parameters of combustion that significantly influence the amount of NO into flue gases, regardless of the mechanism by which it is generated in the outbreak, without input of additional reagents.

Since high temperature and high excess oxygen in the combustion zone lead to the formation of large quantities of nitrogen oxides, it is justified to seek intra-combustion methods that simultaneous decrease the temperature and the excess air coefficient. Factors critically influencing the formation of nitrogen oxides are closely related:

- ✓ the fuel's type ;
- ✓ the geometry of the boiler;
- ✓ the operational regime of the facility.

Besides these factors, strictly related to the formation of a certain quantity of nitrogen oxides, intra-combustion methods must take into account a number of secondary factors, which influence the efficiency of combustion technology and the lifetime of the combustion installation. Such factors are the following:

- ✓ flame stability;
- ✓ amount of unburned carbon in flying ash;
- ✓ amount of slag;
- ✓ speed of the evaporator's pipes corrosion.

The combination of several intra-combustion methods can provide an acceptable level of NO_x emission. But there are large steam generators, especially the kind that burn coal for energy production, for which the application of primary control measures is not enough, they failed to reduce NO_x emissions below the allowable limit. In these situations, the adoption of secondary measures of emission control is mandatory. Even in these circumstances, it is preferable to adopt primary control measures, partial reduction of pollutant having beneficial effects, both technically and economically, on installation operation of secondary NO_x control.

Thus, if the secondary system uses a catalyst and ammonia (**SCR**), to reduce the ammonia consumption and to increase the lifetime of the catalyst, the large steam generators based on coal combustion are equipped, in most industrial applications, with intra-combustion systems for NO_x emission control.

From evolution point of view, intra-combustion techniques can be classified as:

✓ *generation I :*

- **LEAC** (Low Excess Air Combustion) – reducing the excess air coefficient;
- **RAP** (Reduced Air Preheat) – reduce the temperature needed for combustion air preheating, which causes some reduction of temperature in the furnace;
- **BBF** (Biased Burner Firing) – injecting a larger quantity of fuel by some burning and reduction in others;

✓ *generation II :*

- **LNB** (Low NO_x Burners) – using burners, special construction, through which air, needed for combustion, is introduced in phases, creating, thus, an area of flame where reactions take place to reduce nitrogen oxides;
- **FGR** (Flue Gas Recirculation) – recirculation of the flue gases in furnace, so that utilizing a quantity of gas with a low concentration of nitrogen, the process is similar to case where would introduce a mixture of oxygen and inert gas;
- **OFA** (Over Fire Air) – placing a quantity of air needed for combustion, from the top of the furnace, to the completion of incomplete combustion, from its bottom;

✓ *generation III :*

- **LNB II** (Air/Fuel Staging and Burning) – using of special construction burners and their arrangement of greater height records, so that combustion is stable and distributed throughout the height of the combustion chamber.
- **IFNR** (In Furnace NO_x Reduction, Reburning in Furnace) – introduction of additional quantities of fuel, in the middle zone of the furnace, according to an under-stoichiometric combustion, creating, thereby, a strongly reducing area.

Primary methods of reducing NO_x emission are, actually, combinations of the above-mentioned methods. Recommended control techniques, without a ranking criterion of efficiency or economic criterion, are the following:

✓ optimal sizing of the furnace ;
✓ staged combustion:
  - individual, at the level of each burner – **LNB** (*Low NO_x Burners*),
  - overall, applied to the entire furnace:
    - **OFA (***Over Fire Air***)** – two stage combustion method,
    - **LNCFS** (*Low NO_x Concentric Firing System*),
    - **PM** (*Pollution Minimum System*);

✓ unstoichiometric combustion:

  - **OFA** method applied on several steps, higher specific energy units,
  - **INFR (***In Furnace* NO_x *Reduction***)** – post-combustion method or reburning;
- ✓ flue gases recirculation (**FGR**) ;
- ✓ changing the operative parameters of the combustion process ;
- ✓ use of the fluidized bed combustion technique.

3.2.1.1. Furnace's optimal design

One of the main causes of the formation of large amounts of NO_x in the furnaces of the power plants' boilers is their high specific thermal loading. By reducing the thermal loading of the furnace transversal area, it reduces the overall temperature and residence time of the fuel in those areas having higher temperature. In this way, it reduces the amount of thermal NO, at least. Changing the specific thermal load of the furnace section, between 60% and 140%, it changes the emission of NO_x between 85% and 155%, the variation being almost linear over the whole specified window.

The increase of the distance between the burners, on furnace's height, reduces by up to 20% the specific thermal load of the furnace's transversal section, compared with classical arrangement of burners and, accordingly, reduces with an approximately 10 % the NO_x amount generated into the furnace. In addition, lower thermal loading in the burners area tend to reduce slag deposition.

Classical arrangement and respectively a distant arrangement of the burners, in the furnace's burners belt, is schematically represented in Figure 5.

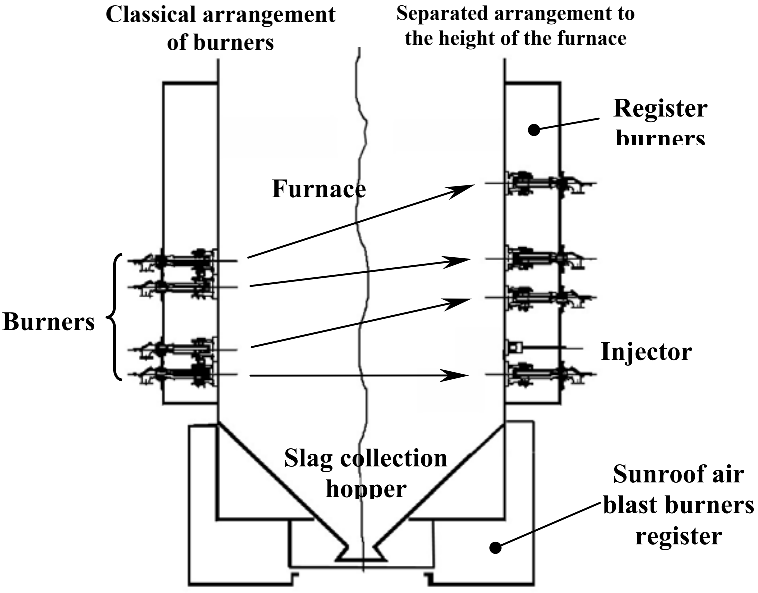


Fig. 3.5. Classical and separated arrangement of the burners

Additional air injectors are designed to decrease the corrosion rate of the reducing area, situated at the bottom of the furnace, without reducing the rate of ash deposition on the constructive elements of the upper evaporator.

3.2.1.2. Staged Combustion

Basically, staged combustion consists into the introduction of air into the furnace in such manner to obtain a low concentration of oxygen in the main combustion area. In this way, it is created a reducing environment, rich in fuel, simultaneously obtaining some decrease of the theoretical temperature of combustion (adiabatic). Staged combustion technique, in its some particular form of application, reduces up to 60÷65% the NO_x emissions of the steam generators.

Staged combustion's principle can be applied in two practical ways:

- ✓ individual staged combustion, applied on each burner;
- ✓ global staged combustion, applied on the whole furnace.

The application of the individual staged combustion technique involves the achievement of some special construction burners, through which they could be controlled fuel and air mixture, in order to reduce the flame's temperature and the concentration of oxygen, at certain stages of combustion. In this way, it reduces both the amount of thermal NO_x, and the amount of NO_x resulting from fuel nitrogen content. The furnace's area in which these effects are achieved is in the burners' belt zone. The remaining air, necessary for the complete combustion, is blown downstream of the main combustion zone, where the temperature is already relatively low that they no longer form a significant amount of thermal NO_x.

If in the furnaces with tangential firing, where the burners are arranged at the corners of the furnace (Figure 3.6.a), is not necessary to use some special burners, the effect of temperature reduction is achieved by vertically alternating the fuels' injectors and air. In the case of wall-mounted burners (Figure 3.6.b), the effective solution to reduce NO_x emission is that of the using of low NO_x emission burners (**LNB**). Use of these burners may reduce by up to 50÷65% the NO_x emission.

Low NO_x burners (**LNB**) began to be realized in years 1970, as swirl burner's form, and evolved to a very complex construction, where the air and fuel flows are separated into several components, very well controlled or that create fascicles swirling flame (multi-flames burners).

Companies producing low NO_x emission burners, by next generation, are Foster Wheeler Energy Corporation, The Babcock & Wilcox Company, Parker Boiler Company, Hamworthy Combustion Engineering, Combustion Associates Inc., etc.

For example, in Figure 3.7 is given a schematic representation of a burner type CF/SF (Controlled Flow/Split Flame), made by Foster Wheeler Energy Company. The use of these burners can reduce NO_x emission by up to approximately 60%, in the conditions of maintaining a short profile flame.

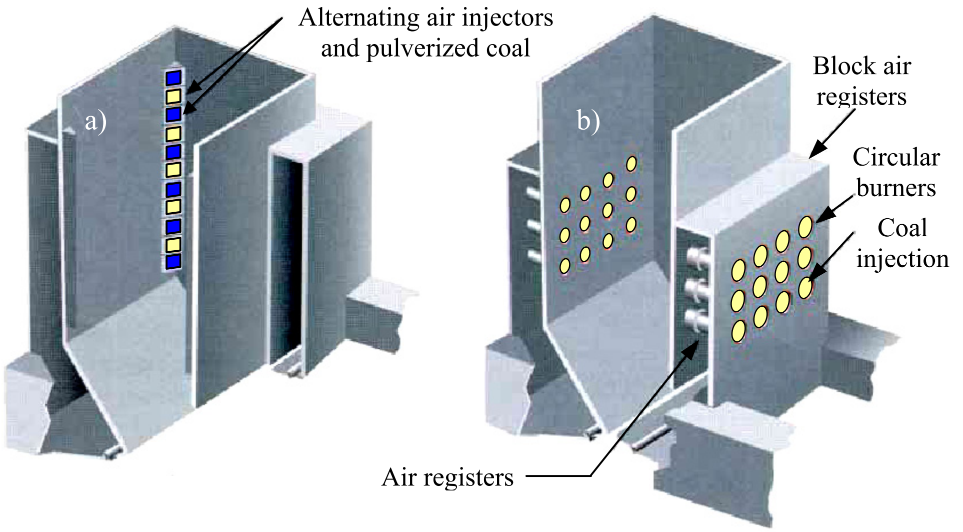


Fig. 3.6. Arrangement of burners in the corners (a) and furnace walls (b)

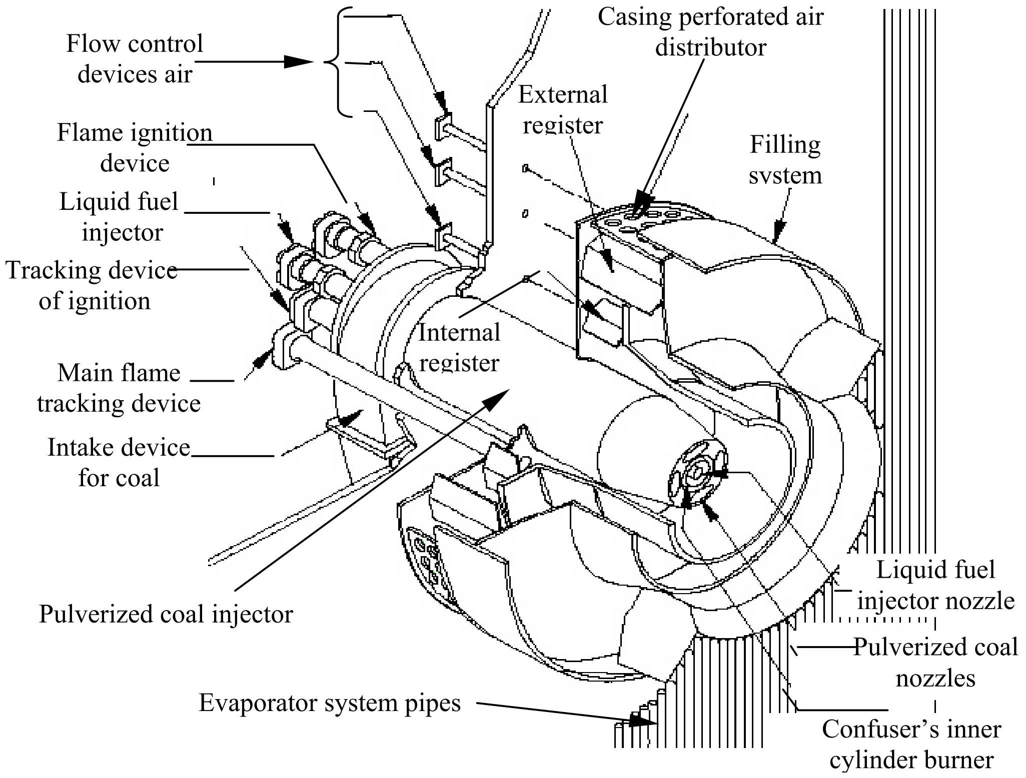


Fig. 3.7. Low NO_x emission burner, type CF/SF – Foster Wheeler Energy Company – general representation

NO_x emission reduction is achieved by controlling the secondary flow air and by introducing in steps, at the burners' level, the primary air and pulverized coal. Adjusting the position of flap air access, through the two registers, can modify the flame's shape and, implicitly, the emission of NO_x.

Perforated air distributor housing is designed to equalize the flow of secondary air, on the entire perimeter of the burner, while the casing perforated shutter system is designed to balance the secondary airflow between burners operating in a common housing distribution of hot air.

Interior registry regulates the amount of secondary air introduced locally, around the injection nozzle of primary air mixture and pulverized coal. By this airflow is achieved fine-tuning of the total quantity of air, which can be found in the vicinity of the burner front.

Basically, any constructive solution adopted for low NO_x emission burners, delayed formation of the mixture and the strict control of air and fuel quantities have the effect of creating a fuel rich flame core and with low temperature (Figure 3.8). In this area (A, B and C of Figure 3.8) occurs release of volatile materials, are formed free radicals carbohydrates and takes place the reduction reactions of NO_x. Combustion is completed in the oxidizing flame zone (zone D).

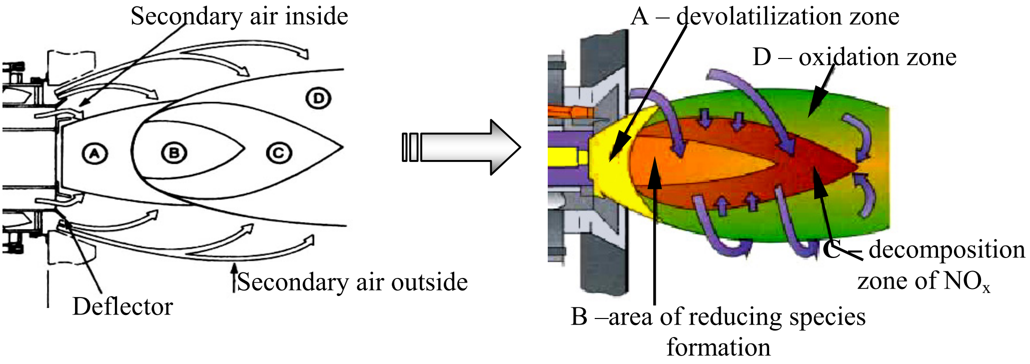


Fig. 3.8. Chart of combustion zones created in the flame of a burner with low emission of NO_x (detail of a burner flame conducted by The Babcock & Wilcox Company)

Reducing the amount of air from the primary combustion area, specific low NO_x emission burners may have a number of unwanted side effects. Thus, there may be increased the amount of unburned fuel, appears a greater tendency to deposit flying ash on to the equipment and increases the corrosion rate of the evaporator's pipes.

Global staged burning, applied to the entire furnace, consists in a differentiated control of the combustion in its different parts. Thus, at the bottom of the furnace the combustion takes place in the terms of oxygen deficit, the remaining air necessary for a complete combustion being introduced at the top of the furnace.

If the burners are arranged in the walls of the furnace, in the burners area is inserted only 80% of the air needed for the complete combustion, the remaining amount of air being blast above the burners' belt, in an amount that provide an overall value of the coefficient of excess air greater than 1,05. This technique, which controls the height of air needed for combustion furnace, is called *Over Fire Air* method (**OFA**) or upper secondary air method, and not necessarily associated with the use of low NO_x emission burners (**LNB**).

Simple classical rehabilitation of boilers, which burn pulverized coal, in the *Over Fire Air* system, can reduce the NO_x emissions, by up to 20 ÷ 40%. Higher degree of the emission reduction can be obtained for over fire airflow rates exceeding 20 % of the total quantity of air, resulting thus a larger reduction of temperature and, implicitly, the amount of thermal NO_x.

OFA classical systems take some of the hot secondary air, circulated through the housing block burners, and injects it over the burners' belt, as it can be seen in the schematic picture given in Figure 3.9.

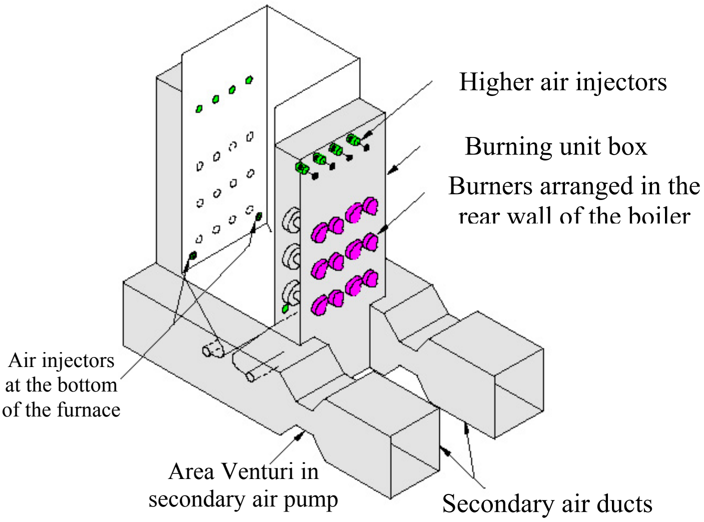


Fig. 3.9. Classic **OFA** System (*Over Fire Air*)

The correct sizing of the **OFA** system, both in terms of positioning the nozzle air and the higher airflow is essential to achieve a stable flame and to avoid incomplete combustion. Incorrect sizing leads to significant emissions of CO, unburned carbon, low combustion efficiency and accelerating the corrosion of the evaporator system.

OFA advanced systems (**AOFA**) combines classical principle of creating a fuel rich flames and a reducing environment, in the main combustion area, with a better control of upper air mixture and combustion gases, from above the flame (Figure 3.10), for achieve a complete combustion.

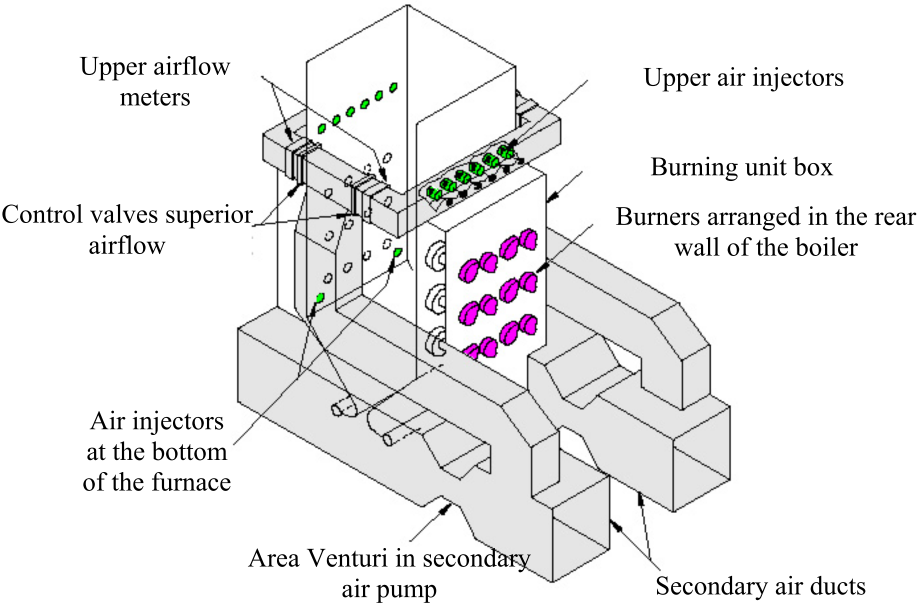


Fig. 3.10. Schematic representation of **A**dvanced **OFA** system (*Advanced Over Fire Air*)

In addition, in case of **AOFA s**ystems, superior air is introduced at o lower temperature than in conventional **OFA** system, which is taken directly from the secondary air duct and not from the common register of the burners (Figure 3.10).

In case of the tangential furnaces, with burners installed at the corners of combustion chamber (Figure 3.6.a), global staged combustion technique has two application forms, depending on the complexity of changes applicable to the columns of burners:

- ✓ **LNCFS** method (*Low NO$_x$ Concentric Firing System*), applicable to the rehabilitation of the installations being into operation,
- ✓ **PM** method (*Pollution Minimum System*), applicable only to new installations.

Classically tangential combustion chambers are equipped with slot burners, fuel and air injectors alternating vertical (Figure 3.12.a). Air and fuel flows are directed towards the center of the furnace, where the flame kernel is formed (Figure 3.11.a).

By the slight deviation of the nozzle axis, in relation to the diagonal cross-section of the furnace, is obtained the swirling combustion gases. Injectors' axis can be deflected easily by vertically, which allows control of temperature distribution along the height of the furnace. **LNCFS** method differs from the conventional method of tangential firing by directing secondary air so that it forms a circle outside the central kernel of the primary air and fuel (Figure 3.11.b).

The angle between the axes of the two jets may be constant, with a value of 22 deg, but may be also variable, ranging from 17 deg to 24,5 deg.

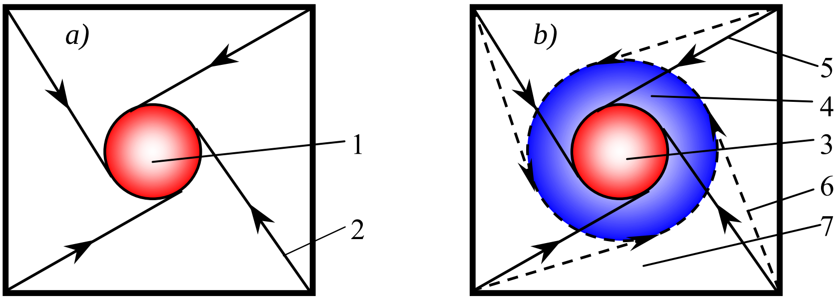


Fig. 3.11. Transversely section of furnace: a) – traditional tangential arrangement, b) – arrangement type **LNCFS**; 1 – central fire swirl; 2 – jet fuel and air; 3 – fuel-rich flame core; 4 – secondary air swirl; 5 – fuel jet and primary air; 6 – secondary air jet; 7 – area with low concentration of fuel.

Redirecting the secondary air flow towards the burner walls leads to an increased burning stability and to the development of a flame core rich in fuel. The oxygen deficit during the volatile gases emission from the burn process allows for the transformation of the organic nitrogen in molecular nitrogen thus reducing the total amount of NO_x. The **LNCFS** system, without any other auxiliary method, reduces the NO_x emissions by up to an approximately 25%. Furthermore if the axes of the two air jets are properly aligned, at a specific angle, the soot deposits are reduced alongside a decreased rate of the pipes' corrosion.

Due to its simplicity, the **LNCFS** method can be used to upgrade existing plants that are already in production, for a very wide range of installed powers (25 ÷ 950 MW_e) and a very wide range of coal types.

In tandem with the **LNCFS** system, the staged combustion technique can be used, by introducing a quantity of secondary air above the burners' belt.

If the superior secondary air injectors are installed very close to each other and positioned in the upper part of the burners, the system can be utilized in combustion furnaces already in use. A model of combined positioning is that depicted in Figure 3.12.b.

Combining the **LNCFS** system with step-by-step secondary air introduction in the upper part of the furnace leads to a 35% reduction of NO_x.

The **LNCFS** and **OFA** systems can be combined more effectively when additional secondary air injectors are installed at the upper section of the furnace. This method reduces de the NO_x emissions by up to an approximately 45 % but requires significant modifications of the combustion furnace. These modifications mean that the **LNCFS+OFA** method is similar to the **PM** method.

Like other intra-combustion methods, the PM technique requires a precise control over the air and fuel flows in such a manner that two components of the flame are to be obtained: one rich in fuel and the other one poor. By combining these two components an overall reduction of NO_x emission is achieved.

By comparison with a purely tangential system, the PM furnaces ensure a 60% reduction of NO_x. A comparative analysis between the previously described two systems is presented in Figure 3.12.e and 3.12.f.

In order to enhance the staged combustion, throughout the furnaces height additional secondary air injectors can be added, injectors with a blast angle horizontal adjustable (Figure 3.12.g and 3.12.h). Also in order to further enhance of the staged combustion's effects, the construction of the fuel and of the secondary air injectors needs to be modified.

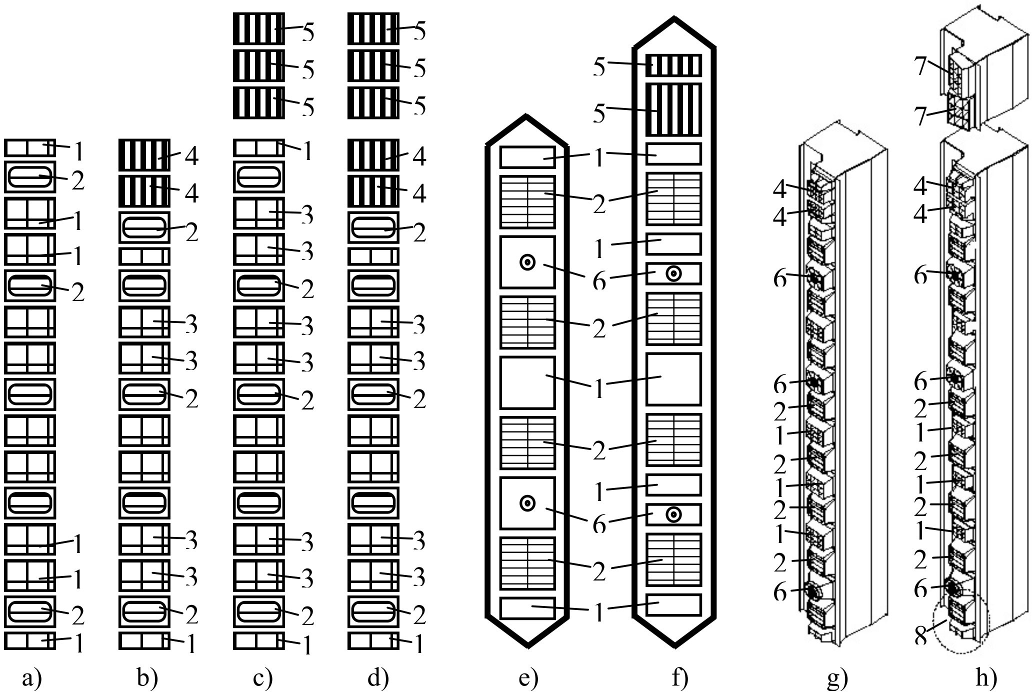


Fig. 3.12. Slot burner systems arranged in the classical system (a, e) and in **LNCFS** systems associated with **OFA** systems: 1 – secondary air; 2 – pulverized coal injection; 3 - secondary air injectors with deviated axis (**LNCFS**); 4 - superior air injectors in block burners; 5 – separated superior air injectors; 6 – heavy fuel injectors; 7 – higher air injectors with variable angle; 8 - injectors for control of combustion conditions in the furnace.

3.2.1.3. Unstoichiometric combustion

As a principle, the unstoichiometric combustion technique reduces the quantity of available oxygen and the flame temperature in similar manner with the staged combustion technique, but it depends on the different positioning of burners in large units.

The method can be implemented with good technical and economical results in existent installations, but, as in the case of staged combustion, extreme attention must be given to some side effects, as are the followings:

- ✓ an increase in unburned carbon,
- ✓ an increase in the wear rate of the evaporator,
- ✓ accelerated corrosion of the elements situated in the reduction environment.

Technically speaking, unstoichiometric combustion can be achieved in one of two ways: by controlling the airflow or by controlling the fuel flow.

If only the air is regulated, then at the base of the furnace the burn process is under-stoichiometric and the air needed for completing the combustion is injected in the upper part of the combustion furnace. In this aspect, the method is very similar with that one of *Over Fire Air*.

Most frequently, the unstoichiometric combustion technique implies the control over the quantity of the fuel introduced in the combustion chamber, the method earning the name of *post-combustion* method or *re-combustion method*. This technique is implemented in high power plants that burn coal, but uses can be found in installations that burn natural gases or heavy fuel, too.

The post-combustion technique implies the creation of three separate combustion areas in the furnace (Figure 3.13):

- ✓ the main area of combustion, at the base of the combustion chamber;
- ✓ the post-combustion area, also called the gas area or post-combustion area;
- ✓ the finalization area, at the top of the furnace, where the combustion is completed.

In the main combustion area, at the base of the furnace, granulated coal is introduces or pulverized, depending on the type of the fire. Usually, burning the coal in this area produces 70 to 80 % of the total amount of energy delivered by the plant.

Depending on the technique, the air to fuel ratio can be equal to the same needed for a complete combustion but can also have a value slightly inferior to the one required for a normal combustion. If the ratio is bigger then the unit ($\lambda = 1{,}13 \div 1{,}15$), in this area a great quantity of NO_x is produced. This important quantity of NO_x will be reduced in the latter stages of the combustion process. If the airflow is reduced, the temperature gradient is diminished and, implicitly, the produced NO_x quantity.

Because the energy produced in installation comes from burning coal only partially, it results that decreases the amount of NO_x formed from organic nitrogen per unit of energy generated, even if the share of energy supplied by burning coal should increase from 80% to 90%.

By reducing the amount of air from the main combustion area can get up to 10% reduction in the amount of NO_x, a further reduction being possible by using low NO_x emission burners (LNB).

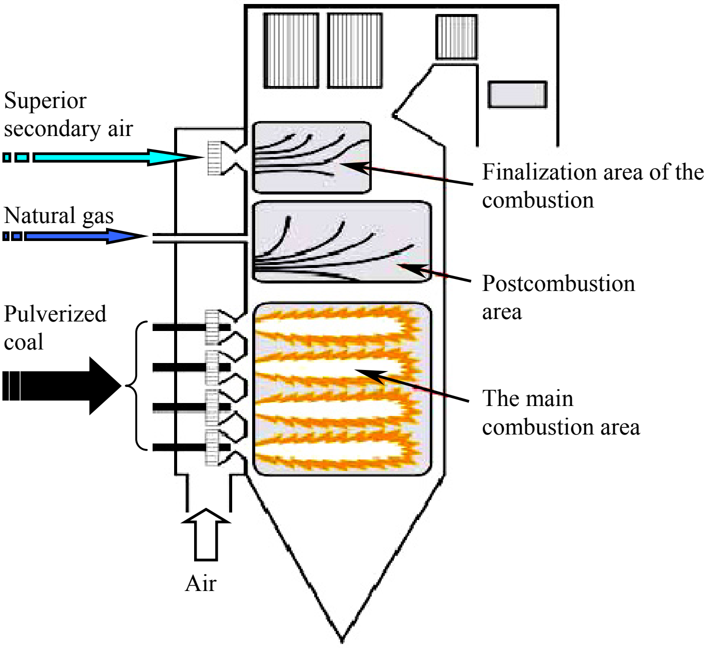


Fig. 3.13. Schematic representation of combustion zones corresponding post-combustion method.

The main reactions that take place in the area at the base of the combustion chamber are those of combustion and those that have NO_x as a result:

$$\begin{cases} Principal\ \ fuel + O_2 \rightarrow CO_2 + CO + H_2O + heat + other\ species \\ N\ organic + O_2 \rightarrow NO_x \\ N_2\ \ (from\ \ air) + O_2 \rightarrow NO_x \end{cases} \tag{3.3}$$

In the second area, natural gas burners are installed, or in some cases pulverized coal injectors. The amount of fuel in this area needs to generate the rest of the heat needed for the installation to achieve its target efficiency therefore it must generate 10 ÷ 30 of the total amount of heat, depending on the amount of excess air in the first combustion area. If it is smaller amount of excess air in the first combustion area, then a smaller the amount of fuel is needed in the post-combustion area.

The air coefficient in the reduction area is smaller than the unity ($\lambda = 0{,}85 \div 0{,}95$) which leads to the development of free radicals (NH_i, HCN), hydrocarbons fragments (CH, CH_2) and a large amount of CO. In this environment, complex chemical reactions take place involving the NO_x, transforming them into molecular nitrogen. In this way the polluting agent is highly reduced:

$$\begin{cases} \text{Re}\,combustion\;\; fuel \rightarrow CH_x + other\, species \\ CH_x + NO_x \rightarrow CN + NH_2 + H_2O \\ NO_x + NH_2 \rightarrow N_2 + H_2O \\ NO_x + CN \rightarrow N_2 + CO \\ NO_x + CO \rightarrow N_2 + CO_2 \end{cases} \tag{3.4}$$

In the post-combustion area, at the same time with the fuel, a recycled gas flow of unburned gases can be introduced. In this way the fuel flows depth of penetration is improved, increasing so the effectiveness of the air-fuel mixture.

In the third area, situated near the top of the combustion chamber, the goal is to complete the combustion, so that the CO emissions and the amount of unburned carbon to be minimum. In this area only superior secondary air is introduced, about 20% from the total amount introduced in the combustion chamber. To achieve a complete combustion, the air in the finalization area needs to be in excess ($\lambda = 1{,}15 \div 1{,}25$).

Even though the air amount in the finalization area is high, the quantity of NO_x is relatively small due to the low temperatures in this part of the combustion chamber.

The main chemical reactions that take place in the finalization area are:

$$\begin{cases} Air + CH_x + CO \rightarrow CO_2 + H_2O \\ CH + NH_2 + O_2 \rightarrow NO_x + CO_2 + H_2O \end{cases}. \tag{3.5}$$

The post-combustion technique allows for a 40-65% reduction in NO_x as compared to the classical tangential methods therefore we can say that this technique is very effective when applied to coal burning furnaces, either as a single method or as a part of a combined system.

The efficiency of the method depends on some parameters, as follows:

- ✓ the initial emissions level,
- ✓ the combustion chamber's properties,
- ✓ the amount of fuel in the reduction area (Fig. 3.14),
- ✓ the excess air coefficient in the reduction area.

The last parameter has the greatest influences in the reduction of the polluting agent, the optimum amount being comprised between 0,85 and 0,95. This is achieved when the fuel amount injected in the finalization area generates 10 to 30% of the total heat delivered by the boiler.

Applying this technique does not involve major changes in operating conditions. The most important side effect is the growth of corrosion rate of installation items that are located in reducing area. At the same time, a small decrease in the furnace efficiency can be noted, especially if the post-combustion fuel is the natural gas.

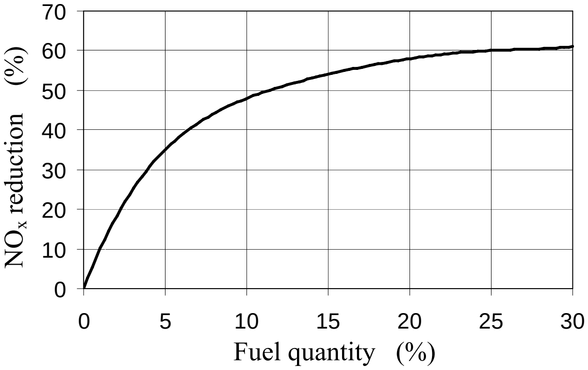


Fig. 3.14. Depending of NO$_x$ emission by the quantity of post-combustion fuel

Overall, investment spending are not major, upgrading the boilers in the post-combustion system involving capital expenditure of around \$ 66/kW - for the power plant of 110 MWe and 43 \$/kW - for 600 MWe units.

In addition, post-combustion technique is very flexible and can be applied to all types of furnaces (tangential combustion, cyclone, wall-mounted burners etc.). This technique may be associated not only with other techniques to reduce NO$_x$ emissions, but also with the primary techniques for reducing sulfur oxides emissions.

The flexibility of post-combustion technology is marked both by opportunity combined operation with another primary method of purification, and a secondary technique. Thus, advanced post-combustion technique combines classical post-combustion with that of injecting a reducing agent. Reducing agent is injected into areas where the gas temperature is high, similar to selective non-catalytic reduction method. Post-combustion associated with the use of low NO$_x$ burners (LNB) provides an emission reduction of more than 70 % and selective non-catalytic reduction of approximately 40 %. Combining the two techniques reduce overall NO$_x$ emissions by 95%, even more than the selective catalytic reduction method, the only commercially available method that can achieve such a level of NO$_x$ emissions' control.

Unlike the selective catalytic reduction method, advanced post-combustion not involves major changes of the flue gases channels and no significant expenditure required for periodic change of the catalyst and for storage of the spent catalyst.

3.2.2. Secondary methods for NO$_x$ emissions control

Secondary techniques of NO$_x$ emissions' control consist into flue gases treatment with some reagents. The purification degree of these control methods is much higher than the corresponding primary methods, but the costs of investment, operation and maintenance of related installations are significantly higher. A classification of the secondary techniques, which have been generically called **DENOX**, is given in the table below and the types of reactions that may be involved in the process are given in Table 3.3.

Table 3.3. Type of reactions - base of the secondary techniques for controlling NO_x emissions.

DENOX Technique	Type of reactions	Reagents, catalysts
Catalytic methods	*Decomposition*	metal oxides blends (Cu, Ni, Fe, Cr), at temperatures of over 1000 °C;
	Reduction	with H_2 and a Pt, Pd, Ni, Cr based catalyst
		with NH_3 and TiO_2 catalyst, combined with V_2O_5 or WO_3;
		with CO and CuO, CrO_2, $CuCrO_2$ based catalyst
		with hydrocarbons (CH_4), using platinum or non-platinum catalysts (copper chromites activated with Zn or Br);
		with reduction gases: NH_3 + ethanol on a Pd/Al_2O_3 catalyst; NH_3 + CO with a Ca/SiO_3 catalyst.
Non-catalytic methods	*Absorption*	in NaOH or NaOCl solution;
		in a 5-15 % H_2NSO_3H solution, in H_2SO_4;
		gas to solid reactions, with base elements CaC, Na_2CO_3, $CaCO_3$, CaO;
	Adsorption	active coal
		mordenit (aluminum-silicate crystalline);
		peat soaked with alkalis.
	Thermal reduction	with coke powder at 900 ÷ 1000 °C;
		with N_2H_4, at 750 ÷ 850 °C;
		with NH_3, at 950 ÷ 970 °C;
		with urea, at 900 ÷ 980 °C;
		with hydrocarbons $C_1 – C_4$, at 980 °C.

3.2.2.1. Selective catalytic reduction (SCR)

This secondary technique for NO_x reduction is currently the most used method (approximately 90% of installations use this method) and ensures an 80% to 90% reduction of NO_x from the flue gases. Increasing of purification degree, to levels close to 95%, involves the use of some hybrid systems of catalysts, both in terms of composition and design achievement. Also, the constructive elements of systems with high deNO_x degree operate at different temperature levels so that both catalytic reactor and its handling systems are more difficult to make.

❶ *Method's principle*

In general the selective catalytic method is based on the reduction of NO_x by combining it with NH_3 in the presence of a catalyst and at temperatures between 300÷ 400 °C. The base reactions release heat and enfold as they transform the NO_x into molecular nitrogen and water. Some constructors have managed to reduce the effective temperatures to 200÷ 300 °C.

The base reaction is highly efficient, and they enfold in near perfect parameters, limiting the ammonia slip (NH_3 atmospheric release) to 2÷5 ppm (parts per million).

Alongside the main reactions, in the catalytic reactor and in some equipment situated in its downstream, a series of reactions also take place, involving the sulphur dioxide already existing in the flue gases and limiting in this way the maximum working temperature.

Taking into account the temperature at which the reactions take place, for furnaces that burn fossil fuels the main reaction are:

$$4NO + 4NH_3 + O_2 \xrightarrow{Catalyst} 4N_2 + 6H_2O + heat \uparrow, \qquad (3.6)$$

$$2NO_2 + 4NH_3 + O_2 \xrightarrow{Catalyst} 3N_2 + 6H_2O + heat \uparrow. \qquad (3.7)$$

The secondary reactions are oxidizing reactions and reactions from which ammonium salts are obtained. The oxidizing reactions are:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O, \qquad (3.8)$$

$$2SO_2 + O_2 \xrightarrow{Catalyst} 2SO_3, \qquad (3.9)$$

and the ammonium salts reactions are:

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4, \qquad (3.10)$$

$$2NH_3 + 2SO_3 + H_2O + 0{,}5O_2 \rightarrow 2NH_4SO_4. \qquad (3.11)$$

Oxidation reaction of the reducing agent (3.8) takes place mainly at temperatures above 450 °C, limiting thus the temperature at which catalytic reactors operate. An even more strict limitation is imposed by oxidation of SO_2 to SO_3 in the presence of the catalyst. The SO_2 to SO_3 conversion accelerated when the temperature arises over 370 °C. For fossil fuels rich in sulfur, the catalytic reactors' temperatures need to be limited to 350-370 °C, operation at this temperature decreasing the oxidation rate of SO_2 to a lower level than 1%.

In the catalytic reactor, SO_3 reacts with ammonia forming ammonium bisulfate (3.10) or ammonium sulfate (3.11). Ammonium bisulfate (NH_4HSO_4) precipitates with decreasing temperature, blinding catalyst layers, air preheater, heat recuperators, and equipment and exhaust ducts of the boiler. The temperature at which precipitates the ammonium bisulfate depends on the concentration of NH^3 and SO_3 from flue gases, the curves giving the dependence being presented in Fig.3.15.

Both the ammonia sulfate and the ammonia bisulfate result as very fine particles that penetrate the micro-pores in the catalysts structure, diminishing its chemical activity. In order to avoid this side effect and to limit the corrosion speed, the pipes are cleaned with pressurized steam once a year, during annual maintenance.

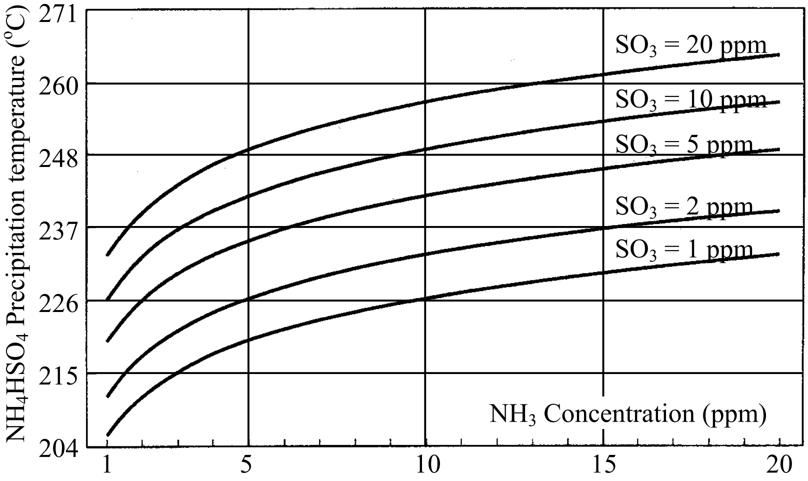


Fig. 3.15. The dependence of precipitation temperature of NH_4HSO_4 by NH_3 and SO_3 concentrations

The increased fouling risk for the equipments placed in the downstream of the catalytic reactor and the reduction into the catalyst's operation, by its fouling, limit the minimal operation temperature for the catalytic reactor. The minimal temperature is dependent on the sulfur content in the fuel, but the experience in operation has shown that there is no practical danger of fouling the catalyst with fine ammonium salts particles, especially when the temperature is higher than 300^0 C.

The principal reactions kinetics and the restrictions imposed by secondary reactions evolution determine a specific dependency for the reducing degree of NO_x, in relation with the temperature inside the catalytic reactor. The representation of this function is given in Figure 3.16.

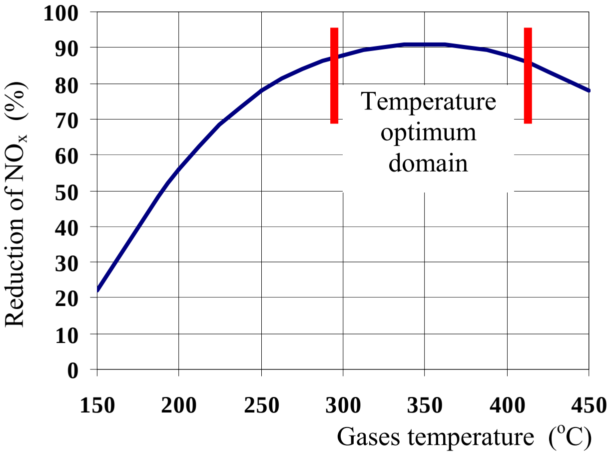


Fig. 3.16. NOx reduction rate dependence on temperature, in installations SCR type.

In order to lower the content of ammonium salts, also the excess of ammonium must to be controlled in such a way that the ammonia slip does not surpass the maximum level of 5 ppm. In the case of burning fuels with high content of sulfur, the ammonia slip generally should not exceed 2 ppm.

Another unfavorable effect of forming fine ammonium salts particles is that of increasing the emission of airborne substances of the power plants.

SO_2 to SO_3 oxidation can make necessary, also, the modification of minimal operation temperatures for the heat exchangers, to avoid their operation close to the acid dew point, the proper temperature for the acid dew point being directly dependent on the concentration of SO_3 in the flue gases.

When the burned fuel is the coal, a significant part in the ammonia slip (even down to 80 %) condenses on the flying ash. The ammonia, resulting this way, can have a negative impact on the technological process of treating and storing the wastes, because the ammonia is released in the atmosphere. Also, the ammonia content can affect the quality of the reactions' byproducts, facet not insignificant when they are used in the construction materials industry. Thus, the flying ash used as additive at making concrete can spontaneously release the ammonia, presenting a real danger for the operator's security. The spontaneous emission of ammonia can seriously affect the operation of the wet desulfurization installation for the flue gases, placed downstream of **DENOX** installation.

The main constructive elements of a **SCR** facility are the followings (Fig. 3.17):

- ✓ the catalytic reactor;
- ✓ the injection system for the reducing agent;
- ✓ the periodical cleaning system for the catalytic layers;
- ✓ the bypass pipe and valves for the reactor;
- ✓ the bypass pipe and valves for the economizer (heat saver);
- ✓ the air blowing system for dilution and the air cushion for insulating the catalytic reactor;
- ✓ the connecting pipes in the flue gases circuit of the boiler;
- ✓ the support metallic structure.

In the reactor there are installed the catalyst's elements, their emplacement depending on the technical solution chosen for the presenting form of the active substance of the catalyst.

The catalyst volume is chosen in terms of fuel type and its burning conditions, and also in terms of flue gases flow. The catalytic reactor's cross-section is designed for a certain flue gases' speeds, in the installation's regime of maximum load. Thus, in the case of solid fuels combustion, the gases speed has to be of approximately 5 ÷ 5,7 m/s. Knowing the necessary volume of active substance and the reactor cross-section, it results the catalytic layers thickness. This thickness (h_{cat}) can be calculated with a formula having the following form:

$$h_{cat} = k \cdot v_g \,, \tag{3.12}$$

where, v_g is the flue gases flow speed, and the residence duration correction coefficient (k) can take values between $0{,}55 \div 0{,}85$ s.

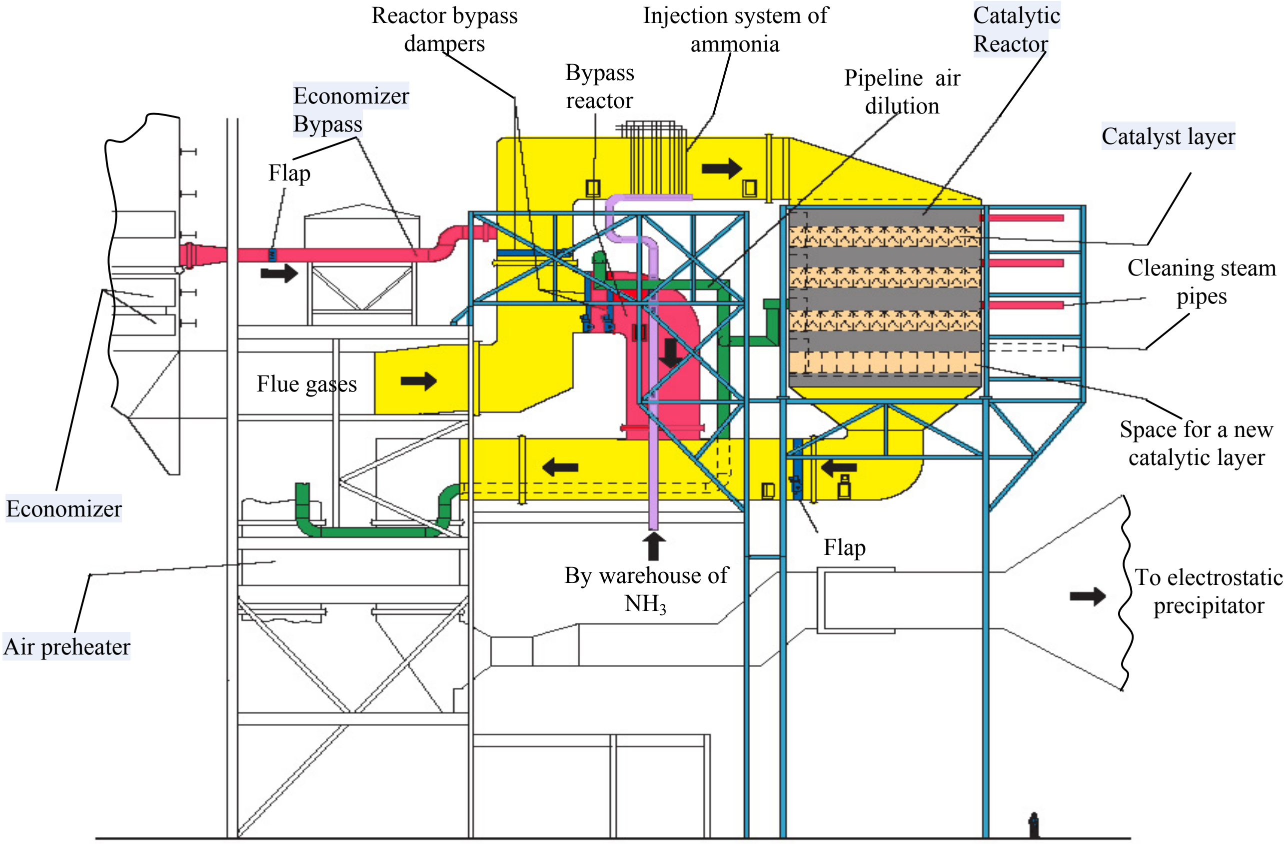


Fig. 3.17. Constructive elements of a SCR installation.

The catalytic substance is not disposed in a single layer but in a number of 2 ÷ 4 layers, thus creating the necessary spaces for periodical cleaning and maintenance. This way of constructive execution allows, also, the change of catalytic layers at different time intervals so that the installation can operate a longer period of time, until the change of the entire catalyst. For the same purpose, is provided, in the design stage, the possibility of installing a supplementary catalytic layer.

By adding all the dimensions in vertical plane of all of these elements, it results the catalytic reactor's height.

From the catalytic reactor sizing methodology, previously described, it follows the fact that modifying the installed power and, therefore, the flow of treated gases, determines, especially, the change of the reactors' cross-section and, to a lesser extent, of its total height.

Box 3.1. Dimensions for a catalyst found in operation

For example, in the case of a 675 MW installation, in the conditions that the concentration of NO_x, at the gases entry in the reactor, is of 0,85 g/kWh, and the NO_x control degree is of 90%, it follows a catalyst volume of 897 m^3, for treating a flow of approximately 4,000,000 m^3/h. The catalyst is installed in two identical reactors, following a cross-section of a reactor the order of 100 m^2 and the height of the catalytic layers of 2.5 m. In each reactor are installed three catalytic layers and is provided the option of installing, at a certain moment, of a fourth layer (Fig. 3.17), so that the total height of a reactor follows in a range of 10 ÷ 11 m.

The reducing agent is injected in the horizontal flue gas channel, placed upstream of the catalytic reactor, using a nozzle matrix. The schematic representation for this NH_3 injection system is that shown in Fig. 3.18, where can be observed the space emplacement for the nozzles in the flue gases channel.

The nozzle system allows the controlling of the ammonia amount, in strict accordance with the amount of NO_x from the flue gases and, so, in strict accordance with the boilers' capacity and load. As well, this task assures a good reducing agent distribution in the entire cross-section of the flue gases' channel.

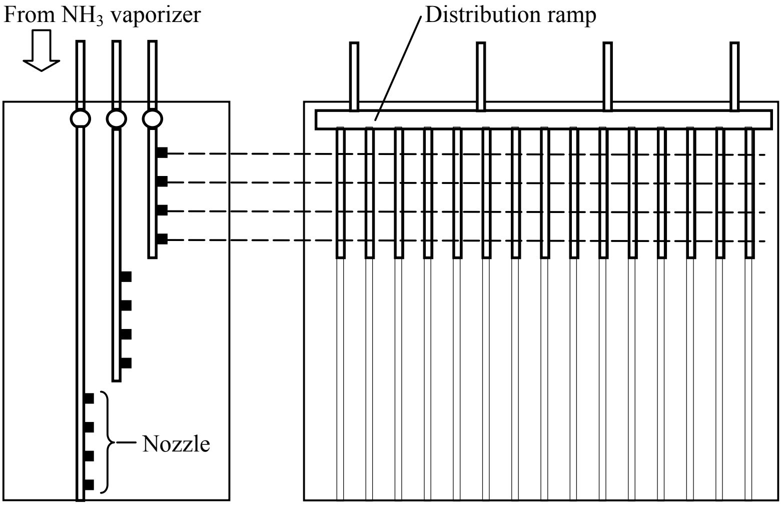


Fig. 3.18. Schematic representation of injection system of reducing agent

The uniform distribution of the reducing agent has to be also kept in the catalytic reactor, concurrent with a uniform distribution of the flue gases flow and, implicitly, of the temperature. The unbalanced distribution causes the reduction of the NO_x control efficiency, increases the pressure drop on the constructive elements of the catalytic reactor, and increases the amount of unreacted NH_3 (the ammonia slip). An incorrect distribution can be compensated just partially by increasing the catalyst volume, and the pronounced distributions also create difficulties in the injection control of the reducing agent.

The particles deposit of flying ash and ammonium salts on the active surfaces of the catalyst's layers requires their regular cleaning. This operation is made, in the case of large capacity installations, by injecting steam, at a pressure of about 15 atmospheres. The distance between the steam injectors and the catalyst's surfaces is of about 60 cm. The cleaning activity is made without taking the installation out of use, with a periodicity of about 8 hours.

In most cases, the periodic cleaning operation is made also at the layer's level that does not contain, yet, catalyst. In the case of the small reactors, the cleaning of active surfaces can be made manually, using some lances blowing compressed air.

Quarterly, the catalytic surfaces need to be visually inspected and additionally cleaned, in terms of taking the installation out of use. In the case of large installations, the catalyst's surfaces degree of fouling is visually followed with higher frequency. For this purpose, sight windows are made close to the walls of the reactor, that allowing the observation of the catalyst, where the proximity effect determines a lower speed of the gases and, so, the probability of catalytic layers' fouling is greater.

The flying ash particles carried by the flue gas flow have the tendency to clean both the catalyst, and the surfaces of the air preheater. Thus, the risk of fouling the constructive elements with ammonium salts. Even if surprises at the first sight, when the gases have a low content of flying ash, more frequent cleaning of the catalyst is required, especially when particles have a small dimension.

In many cases, the difference between the temperature of the gases that come out of the economizer and the minimal temperature for the catalytic reactor to work does not exceed 10 ^{o}C. This window of temperatures ensures the well operation of the catalytic reactor only in the regime of nominal load of the boiler. For a safe exploitation of the catalyst also in the regime of partially loads, the economizer bypass system is installed. This system made of piping, valves and operating systems, has the purpose to keep the minimal temperature in the catalytic reactor at a level high enough to avoid the formation of ammonium bisulfate. Thus, the positive role of the economizer bypass manifest itself in the conditions of long term operation of the installation in regime of minimal load, minimal load that can reach the level of 50 %.

Even if it is called "economizer bypass system", the system can contain a part of the steam superheater, especially in the case when the gas temperature at the entrance of the economizer is not high enough.

The bypass system has the purpose to interrupt the gas circulation in the reactor, directing them straight to the air preheater. Thus, the catalytic reactor is removed from service, therefore being able to perform its periodic maintenance.

Usefulness of bypass reactor system results from the fact that many of **SCR** systems have a seasonal operation type. These installations operate in the warm season, because high temperatures favor the formation of ozone, through the complex reactions between the nitrogen compounds, volatile organic compounds and ultraviolet radiation. This way, it follows that the inspections are made annually, in the cold season.

The bypass system can be also used for operation optimization of the entire plant. Thus, depending on the NO_x emission level, part of the flue gases can be directed straight to the air preheaters, without being treated in the catalytic reactor. This way, increases the life span of the catalyst, decrease the pressure drops in the reactor and, implicitly, the operating costs are reduced, too.

The reagent, in vapor state, is diluted with a certain amount of hot air to ensure a gas flow as steady as possible and, so, a much better dispersion of the ammonium in the gases to be treaded. The dilution airflow can represent an amount of 2 ÷ 5 % of the reducing agent flow.

❷ *Construction variants of the SCR systems*

The necessity to associate **SCR** systems to different types of combustion installations which operate with a wide range of fossil fuels, as well as the limits imposed to the temperatures inside the catalytic reactor, lead to the fabrication of three constructive types of **SCR** units. At first sight, the three constructive types differ only by the location of the **SCR** unit along the flue gases channels. But in reality, the installation location enforces a series of constructive restrictions.

In practice, there are three placing variants of the **SCR** units:

- ✓ *High dust* (**HDSCR**) – when the catalytic reactor is placed between the economizer and the air preheater (Fig. 3.19.a), operating, thus, in conditions of high concentrations of flying ash and high temperature.
- ✓ *Low dust* (**LDSCR**) – when the catalytic reactor is placed before the electrostatic precipitator, but in the upstream of the air preheater (Fig. 3.19.b), being crossed by hot and dedusted gases.
- ✓ *Tail gas* (*tail end*) (**TGSCR**) – in this case the reactor is placed downstream of a wet desulfurization and particle filtering installations, immediately in the upstream of the stack (Fig. 3.19.c), thus working on desulfurized and dedusted gases, but at a low temperature, result of the placing into the upstream of the wet flue gases desulfurization installation.

In principle, a boiler can be associated with any of the three constructive variants.

Both in the *high-dust* variant, and in the *low-dust* variant, the life span of the catalyst is approximately the same, fact that can be explained through the effect of self-cleaning due to the big flying particles of ash. The *high-dust* variant is preferably to equip the installations for burning liquid and gas fuels, while the *low-dust* option is preferably to equip installations that burn solid fuel.

In first two constructive options, the fouling risk of the catalyst with ammonium bisulfate is not eliminated, especially in the case of burning coals with high content of sulfur and liquid sulfur heavy fuel. In these conditions it seems that placing the **SCR** unit after the desulfurization unit is more favorable. Thus, the *tail-gas* option has the advantage of a smaller volume of catalyst and its bigger life span, as long as the content of flying ash and SO_2 in the flue gases is reduced. But in the same time, the presence of the wet desulfurization installation placed upstream involves the cooling of flue gases at a temperature lower than the optimal operation of the SCR units, in order to reduce the temperature below the boiling temperature of the water, at the atmospheric pressure, necessary for the wet removal of the SO_2 gas.

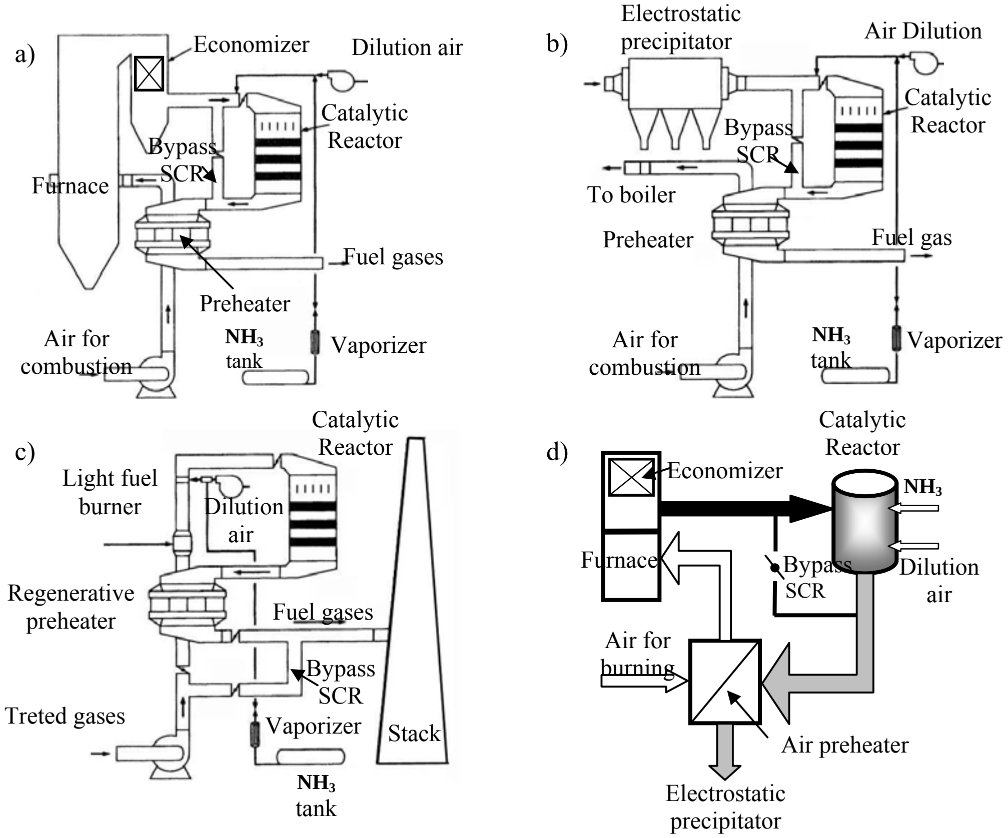


Fig. 3.19. Different types of selective catalytically reduction installations:
a) –High Dust type; b) – Low Dust type;
c) – Tail Gas (Tail End) type; d) – schematic representation of type a).

The reducing concentration of SO_2 from the flue gases make the temperature at witch the ammonium bisulfate strongly precipitate, this remaining, still, much bigger than the temperature of the flue gases at the exhaust of the desulfurization installation (Fig. 3.15). In these conditions, the gases' temperature that goes inside the catalytic reactor must to be increased. In addition, the nitrous oxides reduction reactions have not a satisfactory kinetic at temperatures lower than 100 ^{o}C. From these two reasons, in the *tail-gas* schemes the reheat of the flue gases to the optimum temperature for the **SCR** units operation is required (as results from Fig. 3.16). The low concentration of SO_2 in the flue gases allows the narrow down of the working temperature to a value of approximately 260 ^{o}C.

❸ *The reagent*

In the **SCR** units, the reducing agent is the ammonia (relations 3.6 and 3.7). Catalytic reactors can work both with anhydrous NH_3 (almost pure), and with solutions of 20 ÷ 30 % NH_3 diluted in water. The vaporized reducing agent is introduced in the catalytic reactor with the hot air of dilution.

Ammonia is highly toxic, so that the accidental loss of NH_3 vapors in the atmosphere has to be reduced, to the minimum. The boiling temperature of anhydrous ammonia is of -32^0 C, at the atmospheric pressure. Thus, at ambient temperature the ammonia is in its gaseous state and presents great risk of air pollution. In such conditions, the usage of anhydrous NH_3 must to respect a series of stringent safety requirements as concern the environmental protection. As the majority of the SCR installations operate in areas having large density of population, the safety and the environmental impact requirements have a big share in the decision to install a SCR unit that works with anhydrous NH_3.

Severe rules are imposed both the storage systems, distribution and vaporization, and also on the means of ammonia conveyance. The minimum distances between the related reducing agent installations and the different types of public constructions are imposed by strict regulations, such an example being given in table 3.4, according with the ANSI (*American National Standards Institute*) code K61.1 (Table 3.4).

Table 3.4. Minimum distances for installation of stock containers of NH_3.

Nominal capacity of the container (m^3)	Minimum distance (m) from each container to:		
	Borders of a property; roads; railways;	Places where there are public meetings	Institutional properties
between 2 m^3 - 8 m^3	7,5	45	75
between 8 m^3 - 115 m^3	15	90	150
between 115 m^3 - 380 m^3	15	140	230
over 380 m^3	15	185	300

When is used the aqueous NH_3 solution, the evaporation is negligible at ambient temperature, for this reason the containers set up is not under strict rules. The pressure inside the storage containers for the NH_3 solution is of order 1,5 ÷ 2 atmospheres, when the anhydrous ammoniac is stored at pressures of 15 ÷ 20 atmospheres. However, anhydrous NH_3 is used in more than 95% of the **SCR** operational units, because of some advantages, as follows:

- ✓ lower cost for the reducing agent;
- ✓ storage container volume is 3 ÷ 4 times smaller;
- ✓ the shipping and storage costs are lower;
- ✓ simple vaporization systems, and, thus, lower operating costs.

Besides the eventual loses of NH_3 from the transport and storage systems, **SCR** units are characterized by a continuous loss of NH_3, resulting from the catalytic reactor and named *ammonia slip*. This continuous loss, that can unacceptably change the ecological balance of the thermal power plant, represents in fact the amount of NH_3 that has not reacted with the NO_x.

The unreacted reagent is carried by the flue gases' flow, to the boiler's stack, polluting so the atmosphere.

The ammonia slip cannot be suppressed, but it can be reduced to values lower than 5 ppmv, acceptable from technological point of view.

The NH_3 emission decreases when the volume of catalyst increases, for a given gas flow, with a constant concentration of NO_x. However, the increase of catalytic substance's amount cannot represent a way to reduce the ammonia slip, the catalyst's volume being obtained as an optimum between the technical and economical criterion.

At the present stage of the development of **SCR** technology, the ammonia slip at the moment of facility's commissioning is very low, not exceeding 1 ppmv, but it increases simultaneously with the catalyst's deactivation.

Increasing the ammonia slip is not intended, always, to deactivate the catalyst. Other cases dealing with the degradation of the reactor operation parameters are: poor distribution of the reagent in the flue gases' flow and the uneven distribution of gas flow rates. These disturbances can cause temporary increases into the NH_3 emission of the facility. However, as functional disturbances of nature, they can be corrected without having to change the catalyst.

❹ *The catalyst*

The catalyst is the essential part of a **SCR** unit, also reflected by its cost. Catalyst's cost can reach 20% of the total investment expenses for a SCR unit, given that the specific costs for these units are 20 $/kW – for the case of natural gas combustion and 50 ÷ 70 $/kW – in the case of coal combustion.

To achieve the catalytic layers for the SCR units the following substances can be used: vanadium pentoxide (V_2O_5), iron trioxide (Fe_2O_3), manganese oxide (MnO_2), chromium oxide (CrO_3), titanium oxide (TiO_2), tungsten trioxide (WO_3), as well as compounds based on Ag, Cu, Mo. V_2O_5 has the best reactivity and it is resistant to contamination with ammonium bisulfate, being frequently used for this reason. But at the same time, V_2O_5 is characterized by a high conversion rate of SO_2 into SO_3, thus, especially in the case of the flue gases with high content in sulfur oxides, it is necessary the reduction of vanadium content in the catalyst. In these cases, it is preferable to combine vanadium pentoxide with tungsten trioxide. WO_3 has the property to reduce the available amount of oxygen at the catalyst surface, thus inhibiting the oxidation of SO_2 to SO_3. At the same time, WO_3 improves the mechanical and the thermal stability of the catalyst.

The catalytic substance is fixed at the surface or in the mass of a zeolite ceramic support or made of Al_2O_3. When the active substance is V_2O_5 or the combination of

V_2O_5 and WO_3, the frequently used support is that one made from TiO_2. If the catalytic substance is embedded in the support's substance mass, the catalyst type is homogeneous and it presents as a honeycomb (Fig 3.20).

If the catalytic substance is deposed on the support's surfaces, then the catalyst is heterogeneous type and it presents tabular (Fig. 3.20) or agglomeration nests. When the catalyst elements are in tabular form, the catalyst support is made out of steel.

The catalytic elements are mounted inside of metal frames, forming independent catalytic modules. Many more of these modules form a catalytic layer. A numerical example towards the emplacement of catalytic modules, for an installation with the technical data given in box 3.1, is that given in box 3.2.

Box 3.2. Example towards loading the catalytic layer with independent modules

The 897 m^3 of catalyst, for the installation presented in case 3.1, results by arranging of 144 (12x12) catalytic modules on each of the three active layers of the reactor. The modules have a height of 1.5 m and are made of plate type catalytic elements, the distance between the plates being of 6 mm.

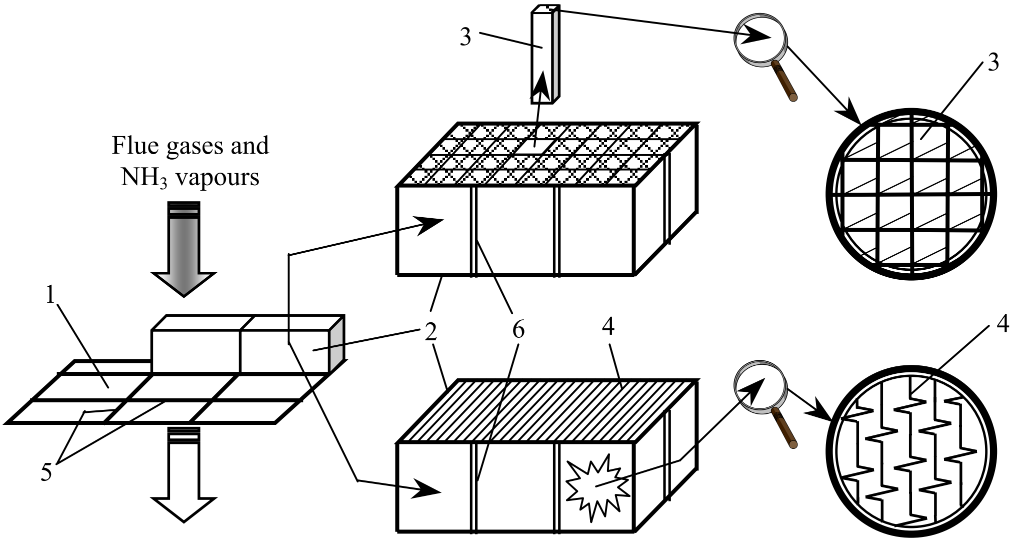


Fig. 3.20. Presentation forms of catalytic layers from units **SCR**:
1) – catalytic layer; 2) – catalytic module; 3) – honeycomb catalytic element; 4) – tabular form catalytic element; 5) – catalytic layer frames; 6) – catalytic module frames.

The catalytic elements made in a honeycomb form, usually, have the contact surface bigger than the catalytic elements in tabular form, for the same catalytic module's volume. Thus, the use of honeycomb catalytic elements involves a smaller volume of the reactor, but at the same time, the mass of any catalytic layer is greater, for the same characteristics of the treated flue gases.

Tabular catalytic elements have an active surface close to that of the honeycomb elements, so the catalyst volume does not depends on the catalytic element type, but on the gases crossing surface. Size that characterizes this area is called *the catalyst step* and represents the distance between the side plates or cell size of the honeycomb type elements.

The catalyst step is chosen depending on the size of the flying ash particles and their concentration in the flue gases. For example, the cell size for the catalytic honeycomb type elements is of 7 ÷ 7.5 mm, when the flying ash is massively present in the flue gases, while, in the case of gaseous fuels combustion, these dimensions are of about 2 ÷ 3 mm. In the case of pulverized coal combustion, the distance between the catalytic elements of tabular type catalysts is of approximately 6 mm.

The choice of a constructive option for the **SCR** installation, the catalyst's type and volume depend on a series of parameters as are the followings:

✓ boiler's type;
✓ physical and chemical properties for the fuel and flying ash;
✓ ash concentration in the treated flue gases;
✓ flue gases' temperature;
✓ NO_x concentration in the flue gases;
✓ allowable emission of NO_x;
✓ NH_3 amount injected in the flue gases;
✓ the amount of oxygen in the flue gases;
✓ the SO_2 concentration in the flue gases;
✓ the flue gases' flow distribution and their velocity;
✓ the admissible rate of SO_2 into SO_3 conversion;
✓ the life span imposed for the catalyst and his deactivation;
✓ the admissible pressure drop on the catalytic layers;
✓ the catalytic reactor impact on the equipment placed in the downstream of it.

In the ideal conditions, the catalyst does not change its reactivity and, so, it could reduce NO_x for an undetermined time. But in reality, the catalyst deteriorates continuously, along its entire operation time, through different physical and chemical means.

The guaranteed life span for the catalyst, a parameter specified by the catalyst's producers, depends on the initial volume of catalyst and on its rate of deactivation. The last parameter depends on an entire series of other parameters, the most important being in close connection with the fuel's type. At the end of the life span, the catalyst performances, both regarding the conversion rate of NO_x and also regarding the ammonia slip, decrease below admissible limits.

Currently, most units that equip pulverized coal boilers have a lifespan of 2 to 4 years guaranteed. Very often, the catalyst lifetime is 3 years of continuous operation (24,000 hours), whether the unit is *high-dust* or *low-dust* type.

The catalyst deactivation is the effect of flying ash deposits, the build up off alkali and alkaline earth metals, the fouling with ammonium sulfate, poisoning with arsenic oxide or other combinations of metals in the coal (Be, Cd, Cr, Hg, Mg, Mn, Pb, U), thermal synthesizing of catalytic substance particles, active substance erosion or even its aging, manifested through micro pore decrease at the contact surface with the treated flue gases.

The main causes of the catalyst's deactivation, as the weight that they have in the deterioration of catalytic layers are given in Table 3.5.

Table 3.5. The main causes for catalyst deterioration

Part / boiler type **Phenomena**	**With ash evacuation in liquid form**	**With ash evacuation in solid form**
Catalyst thermal synthesizing	negligible	negligible
Alkali metals accumulation	low	low
Cover with alkaline earth metals	important	important
Poisoning with As_2O_3	very important in the case of ash recirculation	moderated
Flying ash deposit *)	low	low
Active substance erosion *)	low	low
*) - the phenomenon evolution speed is strictly dependent on the way the **SCR** unit is made.		

For example, in Fig 3.21 is shown a catalyst degradation evolution image.

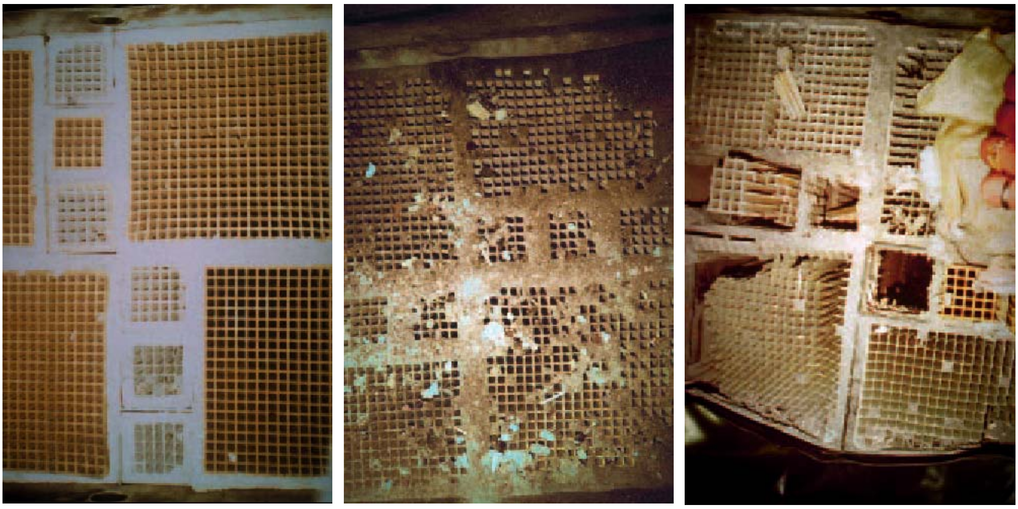


Fig. 3.21. The evolution process in the deterioration of catalyst

Thermal sintering of the catalyst has the effect of increasing particles sizes of active substance that reduces surface contact.

Alkali metals (Na, K) can directly react with the catalytic substance, the resulted compounds being inert. This type of reactions takes place, first, at the catalytic elements' surface, the deactivation rate depending on the alkali metals concentration. If the alkali metals are contained in a soluble solution, they rapidly migrate in the entire catalyst's volume. This type of deactivation is intense when liquid fuels are combusted.

Honeycomb catalytic elements behave better at poisoning by alkali metals, than catalytic elements tabular or plate type.

Arsenic poisoning is due to the diffusion in the catalyst of arsenic trioxide (As_2O_3). As_2O_3 gas results from oxidation at high temperature in the furnace, the complexes of iron, arsenic and sulfur from fossil fuels, according to the reaction:

$$2 \cdot FeAsS + 6\,{}^{1}\!/_{2} \cdot O_2 \rightarrow As_2O_3 + 2 \cdot FeO_3 + 2 \cdot SO_2 . \qquad (3.13)$$

In the gas channels, favorable secondary reactions take place, in witch a part of the As_2O_3 gas is supplementary oxidized, forming arsenic pent oxide:

$$As_2O_3 + O_2 \rightarrow As_2O_5 . \qquad (3.14)$$

As_2O_5 is solid and does not deactivate the catalyst.

The phenomenon of poisoning with Arsenic can be diminished by action at the level of the catalytic or by injecting some additives in the furnace. These additives have the capacity to keep almost the entire quantity of already produced As_2O_3. Good results as additive gives the powder of limestone ($CaCO_3$).

Through a reaction of calcinations, the limestone is transformed into Calcium oxide, as results from the following formula

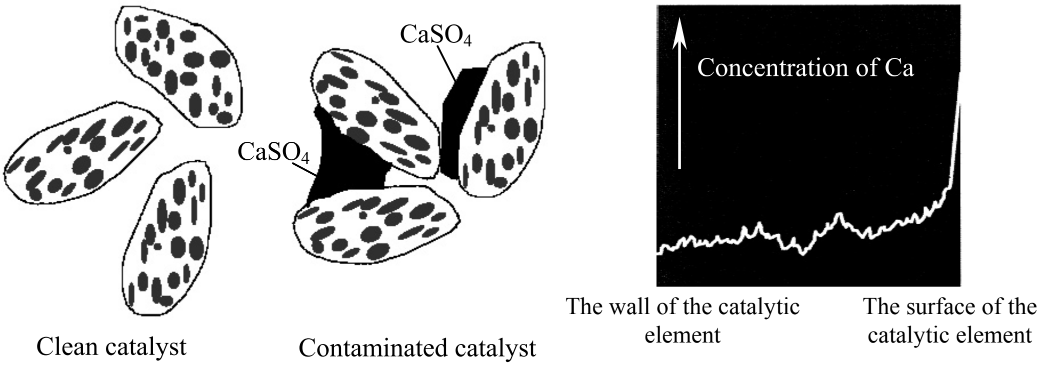
$$CaCO_3 \rightarrow CaO + CO_2\,. \tag{3.15}$$

The particulates of CaO react with the gas As_2O_3, in the presence of the Oxygen, as follows:

$$As_2O_3 + 3\cdot CaO + O_2 \rightarrow Ca_3\left(AsO_4\right)_2\,. \tag{3.16}$$

The solid compound $Ca_3(AsO_4)_2$ should precipitate, similar to the ammonia salts, on the active surfaces of the catalytic reactor. The effects of such a contamination are less dangerous for the activity of the catalyst then the poisoning with As_2O_3.

Calcium and Magnesium existing in the composition of sulfates can precipitate on the active surfaces of the catalyst, restricting the access of NO_x gases and of the reagent HN_3 at these ones, as results from Fig. 3.22. The maximum concentration of Calcium is registered at the expose surface of the catalyst, in its depth the concentration of calcium being smaller by far.



Clean catalyst Contaminated catalyst

Fig. 3.22. The contamination of the catalyst’s surface with $CaSO_4$ and Ca accumulation

If the powder of limestone is injected only with the aim to control the catalyst poisoning with Arsenic, than the injected quantity must be perfectly controlled so that the excess of CaO remains very small. If, in exchange, the powder of $CaCO_3$ is injected into the furnace to control the emission of Sulfur oxides, resulting so an important quantity of Calcium sulfate $CaSO_4$, is better to use *low-dust* type **SCR** units.

The erosion of the catalyst’s surface is the effect of the permanent collision of the flying ash with the exposed surfaces. The erosion speed is a function of the following:

- ✓ the velocity of the flue gases,

- ✓ the physical and the chemical proprieties of the flying ash,
- ✓ the angle between the direction of the flying ash movement and the catalyst's plane,
- ✓ the catalyst's proprieties.

An incorrect distribution of the flue gasses flows can lead to a severe erosion of the leading edge, taking into account the high velocity of the flying ash particulates. Later, even in these zones the erosion phenomenon is accelerated because the predominant directions of the flue gases flows are oriented through the surfaces already affected by the erosion.

In the case of homogenous honeycomb catalysts type, the erosion is faster than in the case of plate type catalysts. Since the most catalyst erosion occurs at the catalyst leading edge, which is exposed to the direct impingement of the dust particles, the catalyst may be hardened at entrance region to provide further protection (Fig. 3.23).

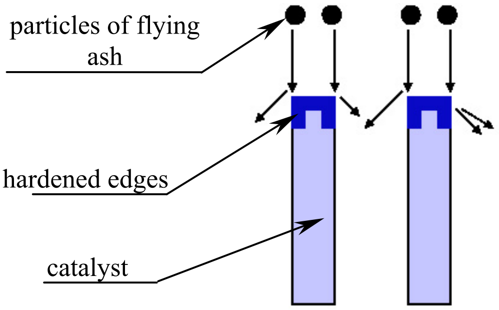


Fig. 3.23. Honeycomb catalyst with hardened edges

In order to maintain a **SCR** system as long as possible into its nominal parameters, in what is concerning the NO_x emission and the ammonia slip, and in order to minimize the costs of upgrading the catalyst's layers a *catalyst management plan* is designed for each **SCR** unit. The long-term maintenance of the catalyst is dictated initially by this plan, which represents the best estimate of when catalyst upgrades will be needed during the future life of the facility. The catalyst management plan gives information referring to the moment of loading of the spare layer, to the moments of the replacing the catalyst on the oldest catalyst layers in the reactor, as well as necessary instructions as concern the storage and the recycling of the deactivated catalyst.

For a proper decision of catalyst upgrading (the load of spare layer and the replacement of used catalyst) the estimated timing of the *catalyst management plan* is corrected with some test results on the catalyst performances at a given moment. In this aim, the catalyst producers' install into the catalytic reactor some *test elements* that are analyzed accordingly the timing specified in the *catalyst management plan*.

Most **SCR** reactor associated with coal-fired facilities have one or two spare layers, which are unused at the initial start-up of the facility. When the catalyst reaches its end-of life it can no longer achieve both its deNO$_x$ and ammonia slip performance requirements. Thus for a particular installation, catalyst life is determined by the point at which ammonia slip reaches its allowable maximum. The reaching of this ammonia slip maximum allowable point for the entire reactor do not means that the entire volume of the catalyst must be replaced, because not all the layers reach the end-of-life simultaneously. The most disposed to the deactivation is the layer placed near to the inlet of gases into reactor. In the first stage of the reactor's upgrading, the spare layer is loaded with fresh catalyst. In this way there is not exposed additional catalyst to a deactivating environment.

As results from Fig. 3.24, representing the timing of a *catalyst management plan* for a given facility, the load of the spare layer leads to the increase of the catalyst's relative activity over its initial level. If the guarantee catalyst's life is of 24000 hours, the spare layer is loaded after a roughly 26000 hours from the initial start-up of the facility. The difference of 2000 hours represents the interruptions for the periodical maintenance of the boiler and of the **SCR** system.

The next stage of the facility's operation is the load of the second spare layer, if such a layer exists. Otherwise, the catalyst of the first layer is replaced, its deactivation being the most advanced. The replacing activity is repeated, at the appropriate timing, at the second layer, thus when all the catalyst layers in a reactor were loaded they will be replaced by turns. In this way, there are reached the nominal performances of the catalyst in long-term operation of the facility.

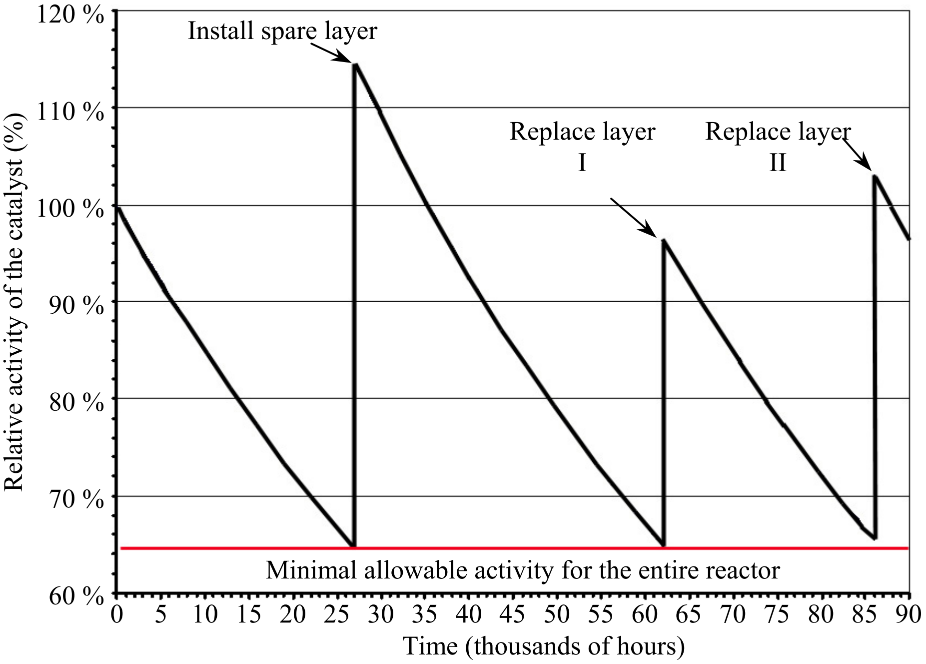


Fig. 3.24. Example of catalyst management plan for a three layers reactor

As results from Fig. 3.24, the installation of the catalyst on the spare layer and the replacement of the catalyst on the first and the second layers ensure an operational time of ten years. Even the entire cycle of catalyst management plan is long enough, the replacement of the catalyst implies costs that can reach 50 % of the total operational cost of the **SCR** unit, for the entire operational cycle.

As concern the storage and recycling of the deactivated catalysts, the actual environmental standards do not refer to the materials included in the structures of the catalytic elements as being industrial wastes with environmental risk. Even so, is recommended that the deactivated catalyst to be returned to the producer, that one being in the position to perform an adequate treatment of the resulted wastes.

❺ *SCR Reactors*

As a result of the preponderant use of the **SCR** systems to control NO_x emissions from industrial gases, many developed countries from Europe, USA, Japan, Canada and Australia produce such systems. The main producers of complete SCR system or of good quality catalysts are the following: ABB, Siemens, Von Roll, Comertech Inc., Haldor Topsoe A/S, Babcock & Wilcox Company, Johnson Matthey, Hitachi Zosen, Nippon Shokobai, W.R. Grace & Co., Mitsubishi Heavy Industries.

3.2.2.2. Selective Non-Catalytic Reduction (SNCR)

Nowadays, the **SNCR** units are frequently associated to the boilers burning coal in the technology of fluidized-bad, where the permanent recycling of the ash ensures a adequate time of fuel combustion at that temperature which is ideal for NO control and reduction.

❶ *The Principle of the deNO$_x$ Method*

As a principle, the method of selective non-catalytic reduction implies the injection of a reduction agent (re-agent) in the flow of the flue gases. The reduction reaction is not facilitated by a catalyst, a good kinetic of the reduction reaction being provided by the contribution of thermal energy. The re-agent is injected in a boiler's zone where the temperature is between 850 ÷ 1150 ^{o}C.

As a re-agent in **SNCR** systems may be used ammonia (NH_3) – very similar to the case of the **SCR** systems, urea ($CO(NH_2)_2$), cyanide salts, and some organic compounds (methylamine, ethyldiamine). The most frequently used re-agents are NH_3 and $CO(NH_2)_2$, the others being used especially for comparative studies.

When the used re-agent is NH_3, the technology is known as "Thermal DeNO$_x$", and when the used re-agent is $CO(NH_2)_2$, the commercial available technology is known as "NO$_x$OUT™". In the first stage of the development of the **SNCR** systems it was preferred aqueous ammonia (NH_4OH) as re-agent. Nowadays, as a result of the reduced environmental impact of the aqueous this re-agent is preferred.

In the condition of an adequate reaction time in the boiler's area where the temperature is optimal for the evolution of the reduction reaction and a good mixing between flue gas and re-agent, the efficiency of the **SNCR** systems can reach a level of 70 ÷ 80 %, with an ammonia slip of 10 ÷ 50 ppm, irrespective if the re-agent is NH_4OH or $CO(NH_2)_2$.

The increase of the control level of NO over 80 % is theoretically possible, but the ammonia slip can reach unacceptable values.

Similar to the case of **SCR** systems, the process chemical reactions can be classified into predominant, base, reactions and undesirable reactions.

The main reactions are thermally based exothermic reactions between re-agent and NO_x. The following are the predominant reactions for ammonia and urea based systems :

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O + caldura\uparrow, \qquad (3.17)$$

$$4NO + 2CO(NH_2)_2 + O_2 \rightarrow 4N_2 + 2CO_2 + 4H_2O + caldura\uparrow. \qquad (3.18)$$

As a difference from the **SCR** systems, the **SNCR** systems only remove NO from the flue gas and do not remove NO_2 emissions from the flue gas stream. In the case of the boilers of fossil fuel fired power plants the main quantity in the total NO_x emissions is that of NO, especially in the area of above the combustion chamber, where the re-agent is injected. It is anticipated that the NO_x emissions from most boiler applications would typically consist of approximately 95 % NO and 5 % NO_2. In such conditions, there is not a major deficiency the lack of NO_2 reduction, but is a reason why the global efficiency of **SNCR** system is smaller than that of the **SCR** systems.

With the exception of the oxidation of SO_2 to SO_3 (reaction 3.9), facilitated by the catalysts of the **SCR** systems, all of the undesirable reactions that can occur for **SCR** systems occur for **SNCR** systems too. In such conditions, result ammonia salts which precipitate on the facility's equipment (from overheater to boiler's stack).

In the category of secondary, unwanted, reactions there are the reactions between NH_3 and the acid gases.

In addition of ammonia salts forming, in **SNCR** systems are developed another secondary reactions. The following reactions can significantly affect the performance of the **SNCR** system:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad \rightarrow \text{ammonia thermal decompozition}, \qquad (3.19)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad \rightarrow \text{ammonia oxidation to NO}, \qquad (3.20)$$

$$4NH_3 + 7O_2 \rightarrow 2NO_2 + 6H_2O \quad \rightarrow \text{ammonia oxidation to } NO_2, \qquad (3.21)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad \rightarrow \text{nitrous oxide emissions}. \qquad (3.22)$$

All the unwanted reactions lead to an extra-consumption of NH_3, thus a supplementary ammonia injection being necessary for the same NO reduction.

❷ *The parameters that affect the efficiency of the **SNCR** systems*

The performances of the **SNCR** systems are highly dependent of a series of parameters that belong to the steam generator and to the constructive elements of the system itself. Thus, parameters as are the type of fuel, the boiler’s capacity, the characteristics of the thermal transfer and the quality of the combustion can reduce the system’s efficiency with 50 to 60 %, especially in the case of pulverized coal-fired boilers having nominal powers higher than 150 MW.

The main parameters influencing the efficiency of the **SNCR** systems are:

✓ the temperature,
✓ the injected quantity of re-agent,
✓ the concentration of CO,
✓ the O_2 excess in the flue gases,
✓ the velocity of the gases in the downstream of the re-agent injection points.

For the usual powers of the steam boilers, the parameters having the higher importance on the efficiency of NO control are the temperature and the molar ratio NH_3/NO_x. In the decreased importance it follows the initial NO_x concentration in the flue gases, the concentration of and the concentration of O_2 in the furnace.

The highest sensitivity of the SNCR systems main reactions to the temperature is highlighted in Fig. 3.25, the curves being drawn for the initial concentration of NO_x = 950 g/MWh, the concentration of CO = 100 ppm, the concentration of O_2 = 4,5 % in the furnace and for the residence time of 0,3 s. That can be observed the existence of an window of optimum temperatures; for this window the efficiency is higher than 90 %, obviously when the molar ratio NH_3/NO_x is bigger than 1.

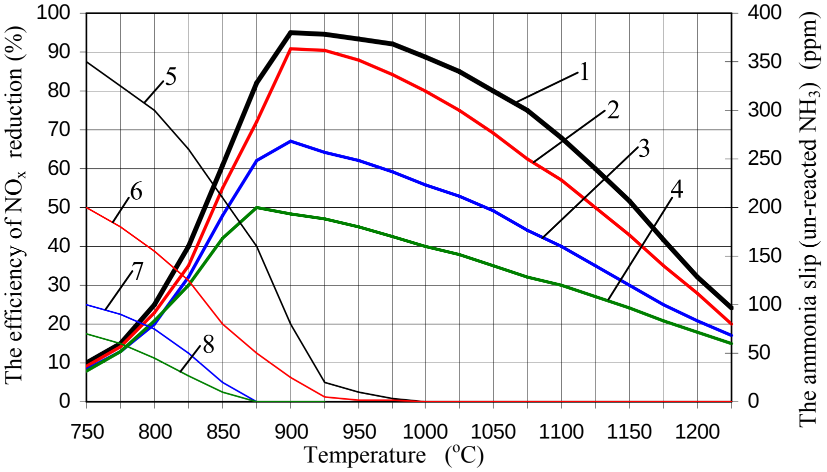


Fig. 3.25. The dependency of NO_x control efficiency (curves 1 ÷ 4) and of ammonia slip (curves 5 ÷ 8) by the temperature, for different values of NH_3/NO_x molar ratio:
1 and 5 - $NH_3/NO_x = 2.0$; 2 and 6 - $NH_3/NO_x = 1.2$; 3 and 7 - $NH_3/NO_x = 0.7$; 4 and 8 - $NH_3/NO_x = 0.5$.

The reduction of the **SNCR** systems' efficiency at the left side of the optimal window is the effect of the reduction of the chemical kinetics of the reduction reaction due to the lack of thermal activation energy (reaction 3.17 or 3.18).

At the temperatures higher than the optimal window, the reduction of the systems' efficiency can be explained by the increased weight of the unwanted reactions of thermal decomposition of the re-agent and of its oxidation (reactions 3.19 ÷ 3.22).

At lower temperatures, in the left side of the optimum window of the **SNCR** systems, but in the conditions of a greater than 1 molar ration NH_3/NO_x (specific for a normal operation of the system), the efficiency of NO control is less affected by the molar ration NH_3/NO_x. The influence of this ratio is more important for higher temperatures, specific for the normal operation of the majority of the **SNCR** systems. In the same time, the reduction of the NH_3/NO_x molar ratio does not modify the position of the optimal temperatures window but reduces its size.

As results from Fig. 3.25 (the curves 5 ÷ 8), the ammonia slip can became unacceptable high if the re-agent is injected in a boiler's zone having relatively low temperature. The ammonia slip increases when the molar ration NH_3/NO_x increases, too. In the optimal temperatures window, the ammonia slip is small because the re-agent is consumed, in a very big weight, by the main reactions of reduction. At the right side of the optimal temperature window, the ammonia slip became negligible, as a result of the increased chemical kinetics of the main reaction and of the increased weight of the secondary reactions of thermal decomposition and ammonia oxidation.

The molar ratio NH_3/NO_x and, implicitly, the injected quantity of re-agent must not exceed 2 ÷ 3 per units. If the quantity of re-agent is higher than this, the ammonia slip increases in a dangerous way and the increase of the NO control efficiency does not increase important enough. This last conclusion is put into evidence by the typical dependency of the NO_x emission of the boiler by the molar ratio NH_3/NO_x, as result it from the curve given in Fig. 3.26.

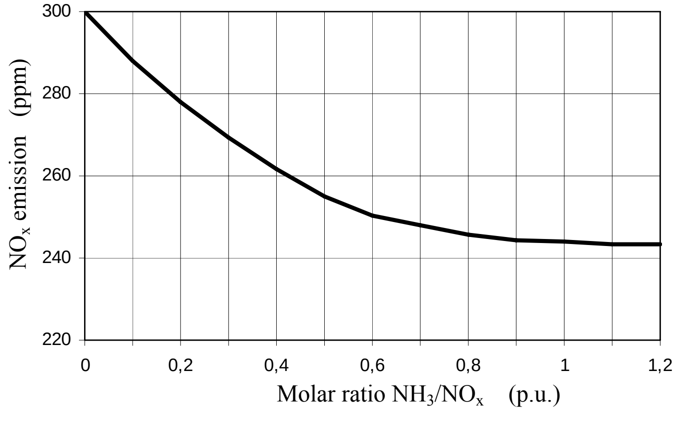


Fig. 3.26. The dependency of NO_x emission by the injected quantity of re-agent

As results from Fig. 3.27, long residence time can lead to a translation of the optimal temperature window toward small values, but for a residence time higher than 0,4 s and at the usual temperature of the **SNCR** systems' operation is not registered a significant increase of the efficiency of the NO control.

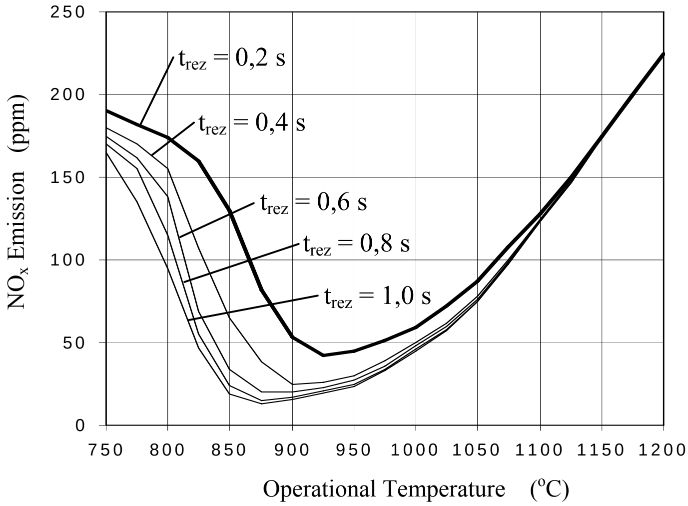


Fig. 3.27. The dependency of NO_x emission by the temperature and the residence time

The usual residence time at the optimal temperature is of 0,2 ÷ 0,3 seconds, and is practically independent by the injected quantity of re-agent.

In the normal conditions of the boilers' and **SNCR** systems' operation, the distribution of the temperatures inside the boiler does not significantly affects the efficiency of the NO reduction. In the same time, the global efficiency of the system can decrease when the boiler works at partial loads or when the re-agent is injected at the highest level of the boiler's furnace.

The specific dependency between the efficiency of NO control and temperature (Fig. 3.25) shows that the highest values of the efficiency are obtained only for a small window of temperatures. In the real operational conditions, there appear modifications of the temperature's distribution as a result of the boiler's requested load, thus the **SNCR** systems does not constantly work at theirs maximum efficiency. Moreover, the ammonia slip can frequently overpass the acceptable limits.

The technical solution to overstep this major disadvantage is that of the injection of an additive, simultaneously with the re-agent. Thus, when ammonia is used as re-agent, the additive is the molecular Hydrogen (H_2). The optimal window of the temperatures can be displaced from the vicinity of 900 °C, toward the vicinity of 700 °C, as results from Fig. 3.28. The curve corresponding to the ammonia slip is displaced toward lower temperatures too. As a secondary effect, the injection of the additive leads to a certain reduction of the optimal temperatures window.

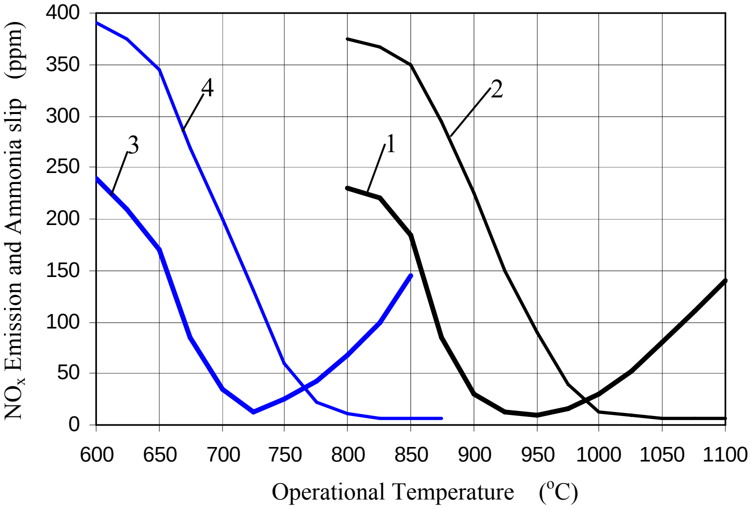


Fig. 3.28. The dependency of the NO$_x$ emission and of the Ammonia slip by temperature and by the additive injection: 1 - NO$_x$ emission without H_2 injection; 2 - NH_3 slip, without H_2 injection; 3 - NO$_x$ emission with H_2 injection; 4 - NH_3 slip, with H_2 injection.

❸ *System Configuration and Capabilities*

As was previously presented, the optimal window of operational temperatures of the **SNCR** systems is between 900 ÷ 1150 °C, the injection of an additive leading to the displacement of this window toward a mean value of 700 °C.

Usually, the temperature in the furnace of the coal-fired boilers of the power plants is of 1350 ÷1650 °C. In such conditions, results that the optimal temperatures for the **SNCR** systems are those from the superior part of the boilers' furnaces or even in the first horizontal channel of the flue gases, in the vicinity of the overheater.

In the case of the boilers having nominal power greater than 100 ÷ 200 MW, it is practically impossible to have temperatures uniformly distributed into the entire furnace, impossible to realize a uniform distribution of the re-agent in the entire transversal area of the furnace and a long residence time of the re-agent, exactly in the window of optimal temperatures. In such conditions, the re-agent injectors are very important as design and as position into the furnace. Constructively, the injectors can be of two types, as follows:

- ✓ fixed (wall-mounted) injectors, placed into furnace's walls;
- ✓ retractable injectors, cooled with steam.

The wall-mounted injectors do not have a good spraying efficiency in the case of big furnaces, this being the reason why there are used retractable injectors or combinations of wall-mounted injectors and retractable ones.

Multi-level injection uses different kinds of injectors, meaning different operational types of injectors and different geometries of the spraying nozzles. Thus, on the inferior levels are installed retractable injectors, that are retracted when the boiler works with partial loads and on the superior levels are installed wall-mounted injectors, especially when the nominal power of the boiler is smaller than 100 MW.

When the used re-agent is ammonia, the transportation medium through injector is the steam or a flow of air. In the case of boilers equipped with intra-combustion systems of NO_x control, can be used as transportation medium the over-fire air, anyhow necessary to be introduced into the furnace in the aim of realize a complete combustion, or even the recirculated flue gases.

The ratio of volume flows NH_3/transportation medium mast be chosen in an appropriate way to ensure a temperature of the injector lower than 500 ^oC, for all the operational regimes of the boiler.

When the re-agent is urea, the transportation medium is the water, in the furnace being injected a solution of 40 ÷ 70 %. The dilution degree must be chosen in the right way to ensure the appropriate cooling of the injector and, in the same time, to affect in a minimum way the burning conditions (boiler's efficiency).

The main components of a urea-based **SNCR** system are sown in Fig. 3.29.

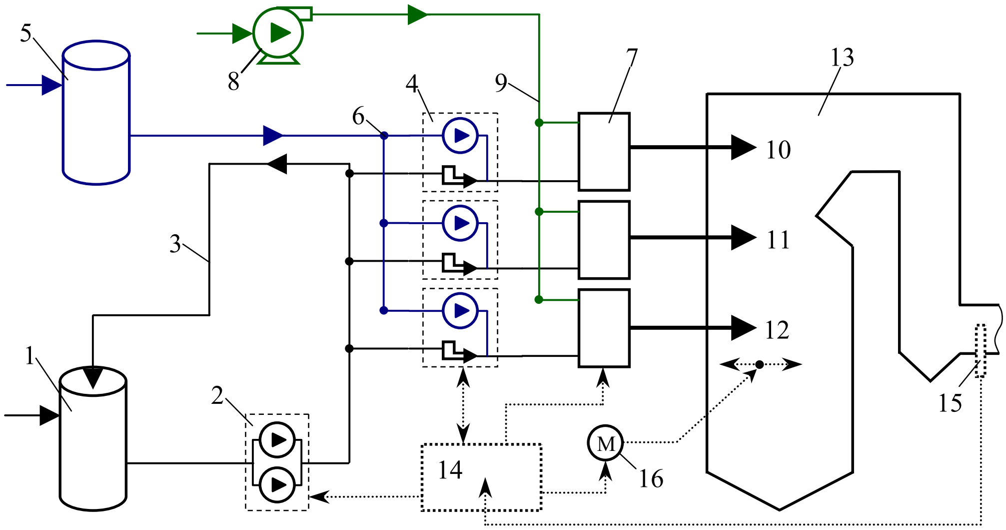


Fig. 3.29. The principle scheme of a urea-based **SNCR** system:
1 – Re-agent storage tank; 2 – Re-agent circulation module (pumps); 3 – Recirculation loop; 4 – Metering and Dosage modules; 5 – Water tank; 6 – Water distribution circuit; 7 – Distribution modules; 8 – Air compressor; 9 – Air compressed distribution circuit; 10 – The injector of the third zone; 11 - The injector of the second zone; 12 – Retractable injector of the first zone; 13 – Steam boiler; 14 - Automation; 15 - NO_x emission continuous monitoring system; 16 – Actuator of the retractable injectors.

A 50 ÷ 70 % by weight urea solution is delivered by truck and loaded into the storage tank (1). At this weight, the re-agent must be kept at a temperature above 15,5 ^{o}C, to prevent urea crystallization into a solid state. In this aim, the re-agent storage tank must be thermal insulated and heated by external electrical pads. Most of the heat required is supplied by an in-line heater that is integrated into the Circulation module (2).

The recirculation module contains the circulation module (2) and the recirculation loop (3). The main function of the recirculation module is that to supply the metering and dosage modules (4). At the same time, the recirculation loop (3) helps to prevent no flow conditions and maintains the re-agent in a well-mixed state inside the storage tank (1). However, the primary function op the recirculation module is to deliver the required urea for injection to the metering and dosage modules (4).

At the metering and dosage modules (4), the urea is regulated and then diluted with water to allow greater coverage across the boiler. The necessary water is supplied through the water distribution circuit (6) from water tank (5). The pressure of the urea solution at the outlet of the metering and dosage module is of 7 ÷ 10 atm. The metering and dosage module can have a common distribution circuit, in this case one of the module being kept as operational reserve (one module is in stand-by).

At the outlet of the metering and dosage modules, the urea solution is directed to the distribution modules (7). To the distribution modules is send a air compressed flow, supplied by a dedicated compressor (8) and distributed to the each module through a distribution circuit (9). The distribution modules regulate the flow of the diluted urea and air to each injector. Flow rates and pressures are set manually during the start-up.

The compressed air is used to atomize the diluted urea with the aim of obtaining a good mixing urea solution – flue gases. At the same time, the injected air has the role to cool the injectors. In the case of steam-cooled injectors, the steam can take the role of solution atomization, thus the compressed air circuit became not necessary. If the re-agent is mixed with a part of the warm air for the complete combustion or with recirculated flue gases, it results a very good and homogenous dispersion of the urea solution into the furnace.

The flows of urea solution and compressed air are sent toward the injectors, in each injection zones existing more such injectors (five ore six such injectors). The injector of the third zone (10) and of the second zone (11) are intended for operation at mid and high boiler loads. The injectors of the firs zone, 12 (in many cases there are four such injectors), are designed to operate at low loads and they must be retractable type. These injectors are automatically retracted from the furnace via a pneumatic mechanism during higher loads, to protect and to extend the injectors' life.

Because it is difficult to realize devices monitoring the small quantities of NH_3 (ammonia slip must be of 2 ÷ 10 ppm), the automation of the **SNCR** systems is realized based on the continuous monitoring of the NO_x into flue gases, using the monitoring system 15. It is relatively difficult to realize a very precise tuning of the urea solution injection only based on NO_x continuous monitoring and without ammonia slip monitoring.

The tuning of the **SNCR** system at the operational parameters of the boiler is realized into two steps.

The primarily tuning is based on a *feed forward* type loop, the input data being parameters as are the fuel and the steam flows, and set the urea pumping rate to a pre-defined range of values to meet the required target of NO_x emissions. This setting loop establishes the initial position of the retractable injectors too.

The fine-tuning, realized by the automation module 14, is a feedback type loop. A NO_x signal from the continuous emission monitoring system is used to regulate the positions of the retractable injectors, the pumping rate, the flows of urea solution and air and the concentration of the re-agent to maintain the emission of NO_x at setpoint.

In the case of the boilers having high nominal powers, there are retractable injectors installed also in the second or even in the third zone of the furnace, each such injector being positioned through electromechanical or hydraulical actuators (16).

❹ *Examples of **SNCR** Technologies*

World wide there are many producers of **SNCR** systems. Some examples of producers of ammonia based **SNCR** systems, without ranking them, are the following: Babcock & Wilcox Company - Deutsche Babcock, Götaverken Miljō, Exxon Research and Engineering Company, LAB, Procedair, LGI, Von Roll.

The German company named Nalco Fuel Tech GmbH, from Essen, has the world license of a urea based **SNCR** system, named NO_xOUT® SNCR. Fuel Tech, Inc., Batavia - Illinois, has also good results in the development of the system NO_xOUT® SNCR and in the combined use of **SNCR** and **SCR** systems, in a so-called NO_xOUT CASCADE® SCR. Important results in the development of the urea-based **SNCR** systems were obtained and published by Research-Cotrell and Electric Power Research Institute, the last one being the owner of the license of **RRI** system (Rich Reagent Injection).

The technique **Von Roll** uses as re-agent aqueous ammonia (NH_4OH). The re-agent is injected using the steam, in a furnace's zone where the temperature is of 850 ÷ 1000 ^{o}C. Obviously, in order to obtain a good NO control efficiency, the injected re-agent must be in excess.

The originality of the Von Roll technique consists in the method of ammonia slip recuperation, as results from Fig. 3.30. Thus, after the reactions of NO reduction, the excess of ammonia is in the composition of the liquid byproducts resulting from the humid flue gases treatment. In a first reactor for liquid effluents treatment, the solution of ammonia is separated from ammonia salts. After this, the liquid effluents are neutralized using a basic solution (solution of Calcium hydroxide), and, finally the ammonia is separated injecting steam into a striping reactor. After the condensation of vapours, the aqueous ammonia is recirculated.

The recuperation of the ammonia slip give the possibility to operate with an important excess of re-agent, so the efficiency of NO control can reach the level of 90

%, similar to the **SCR** systems. These are good reasons to the frequently use of the systems Von Roll in the case of wastes' thermal treatment and recycling.

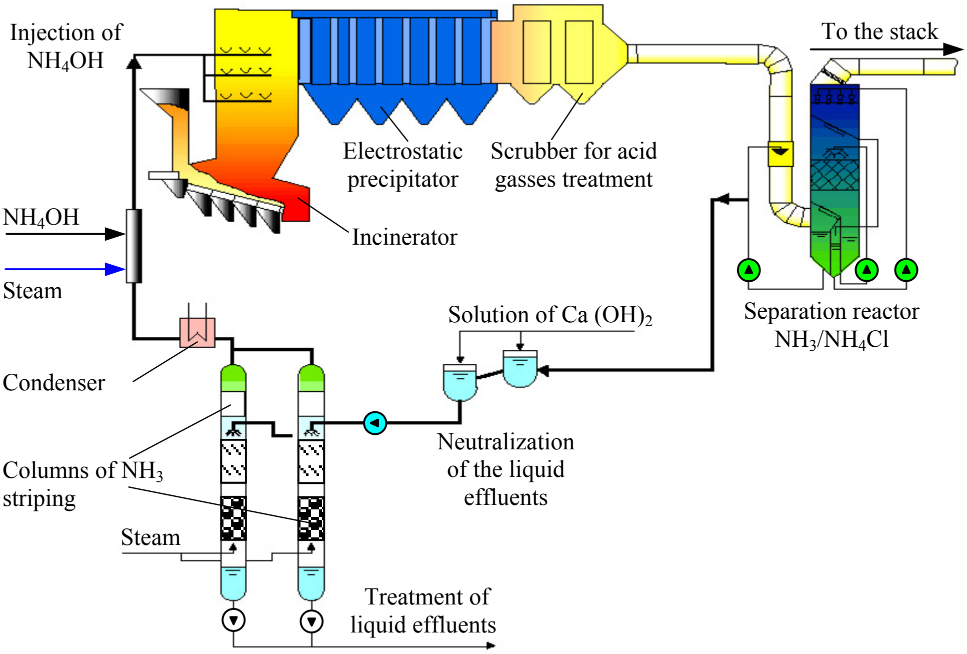


Fig. 3.30. The scheme of the **Von Roll SNCR** system, with ammonia slip recirculation

The technique **NO_x OUT® SNCR**, realized by Fuel Tech, Inc., uses as re-agent the urea solution. Usually, these facilities operate with NO control efficiencies of 40 ÷ 60 %, without producing dangerous gaseous emissions and without producing solid byproducts.

The system implies a very good control of urea solution injection, in that window of temperatures in which the efficiency of NO control is maximum, the chemical activity of urea being optimal in a domain of between 900 °C and 1150 °C.

The injection of the urea solution is realized on several levels into the furnace and is very well tuned with the boiler's load, in this way the domain of temperatures in the injection zones being from 870 °C to 1370 °C.

The parameters that affect the pollution control efficiency are the following:

- ✓ the initial quantity of NO_x into flue gases,
- ✓ the distribution of the flue gases' temperatures into the furnace,
- ✓ the distribution of the flue gases' velocities,
- ✓ the weight of the Sulfur oxides and of CO in the flue gases,
- ✓ the internal geometry of the furnace.

The technique NO_xOUT® **SNCR** may operate in association with all the power plants' boilers, irrespective of the kind of burned fossil fuel. At the same time, this technique can be used in the case of boilers burning biomass, in the case of wastes incinerators as well as in the case of the furnaces in siderurgy or in the case of the kilns (for the production of building materials).

One of the major advantages of the NO_xOUT® SNCR technique is that of the flexibility and of the adaptability into the operation together with other techniques for NO_x control. A good example is that of the technique NO_xOUT CASCADE®, realized by the company Fuel Tech, too, and which can reach a NO control efficiency of 80 %, in the condition of the use of two deNO_x stages. Thus, in the first stage the urea solution is injected into the furnace, very similar to the technique NO_xOUT®, but controlling the urea solution's injection in such a way that not all the injected quantity reacts with the pollutant. The excess of urea is transformed into ammonia, which will be used in the second stage of NO_x control as re-agent in a small **SCR** unit, placed in the zones of lower temperatures of the boiler.

Such a hybrid technique leads to a better control of the NO_x emissions and, maybe more important, leads to a drastic reduction of ammonia slip. In this way increase significantly the chemical efficiency of the re-agent. Usually, this technique does not imply the use of a special catalytic reactor. The catalyst's layers may be installed directly into the existing flue gases tubing, with them minimal modification and without modifying the extractor fan.

3.2.2.3. Copper Oxide Process

Most current power plants use two separate facilities or technologies to reduce SO_x and NO_x emissions. The Copper Oxide Process is a cleanup technology that can reduce both SO_x and NO_x in a single unit. Thus, this new technology has the potential to have lower costs than the separate technologies.

The Copper Oxide Process is a dry regenerable process that has many advantages over wet scrubbers. Thus, the chemical absorption on Copper Oxide (CuO) does not produce landfill wastes, thus avoiding concerns over the limited landfill space, increasing landfill costs, and public awareness of the environmental impact. Moreover, the Copper Oxide Process provides an effective way to use the sulfur as a byproduct. The technology turns the captured SO_x into high valued byproducts as sulfuric acid, elementary sulfur, ammonia sulfate, fertilizers and concentrated SO_2 gas. The flexibility of the technology enables to be considered the local market conditions when choosing the byproduct type and can further compensate the costs for operating the process. Lastly, because the Copper Oxide Technology is a dry and regenerable process, it will not generate solid waste requiring landfills.

Besides the economical aspects, the Copper Oxide Process is remarkable through the high efficiency into the emissions control. Thus, it can reduce more than 95 % from the SO_2, more than 90 % from NO_x and 50 % from the particulate emissions.

The Copper Oxide Technology was originally developed at the US Department of Energy – Federal Energy Technology Center (FETC).

As a principle, the control of gaseous pollutant has the following evolution: CuO reacts with SO_2, in a boiler's area where the temperatures are between 340 and 400 ^oC. It results copper sulfate ($CuSO_4$). $CuSO_4$ then can be reduced to Cu by methane (CH_4) or other reducing gases. Thus, the gas SO_2 is released in a concentrated form that can be used in various processes.

The regenerated sorbent is exposed to the flue gases, the elemental copper is cover to copper oxide that can be again used to react with SO_2.

The main reaction can be expressed as follows:

$$CuO + SO_2 + \tfrac{1}{2}O_2 = CuSO_4\,; \qquad (3.23)$$

$$CuSO_4 + \tfrac{1}{2}CH_4 = Cu + SO_2 + \tfrac{1}{2}CO_2 + H_2O\,; \qquad (3.24)$$

$$Cu + \tfrac{1}{2}O_2 = CuO\,. \qquad (3.25)$$

Until this stage, only the emission of SO_2 is controlled. A special characteristic of the Copper Oxide Process is that of NO_x control, transforming Nitrogen Oxides into molecular Nitrogen and water, using ammonia as re-agent.

In the domain of temperatures where operates the reactor, the reduction reactions of NO_x cannot be developed without a catalyst. In the case of Copper Oxide Process, the role of catalyst is taken over by the $CuSO_4$ and, in a small measure, by the CuO. From this point of view, the reduction of NO_x emissions is quite similar to that developed in the **SCR** systems, explaining so the high efficiency of NO_x control (90 %). As a conclusion, by injecting NH_3 into the flue gases before it contacts CuO impregnated sorbent, both NO_x and SO_2 in the flue gases can be removed.

The reduction reactions are similar to (3.6) and (3.7), developed in the classically catalytic reactors. At the same time can be developed more efficient reactions, implying smaller quantities of re-agent, as are the following:

$$6NO + 4NH_3 = 5N_2 + 6H_2O\,; \qquad (3.26)$$

$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O\,. \qquad (3.27)$$

The basic schematic flow diagram of the Copper Oxide Process is that given in Fig. 3.51.

In the schematic flow diagram there are three main flows, as follows:

- ✓ for pollution control – simultaneous treatment of SO_2 and NO_x,
- ✓ for the sorbent regeneration,
- ✓ sulfur recovery process.

The flue gases enters into the reaction column (1) where SO_2 is removed by CuO (the reaction column having so a role of dry scrubber), and NO_x are reduced by the NH_3, in the presence of the catalyst $CuSO_4$ + CuO (the reaction column having the role of a catalytic reactor). Cleaned flue gases can be evacuated, after the recuperation of their residual heat in a heat exchanger, and the spent sorbent, containing a big quantity of $CuSO_4$, is discharged toward the sorbent regenerator (2).

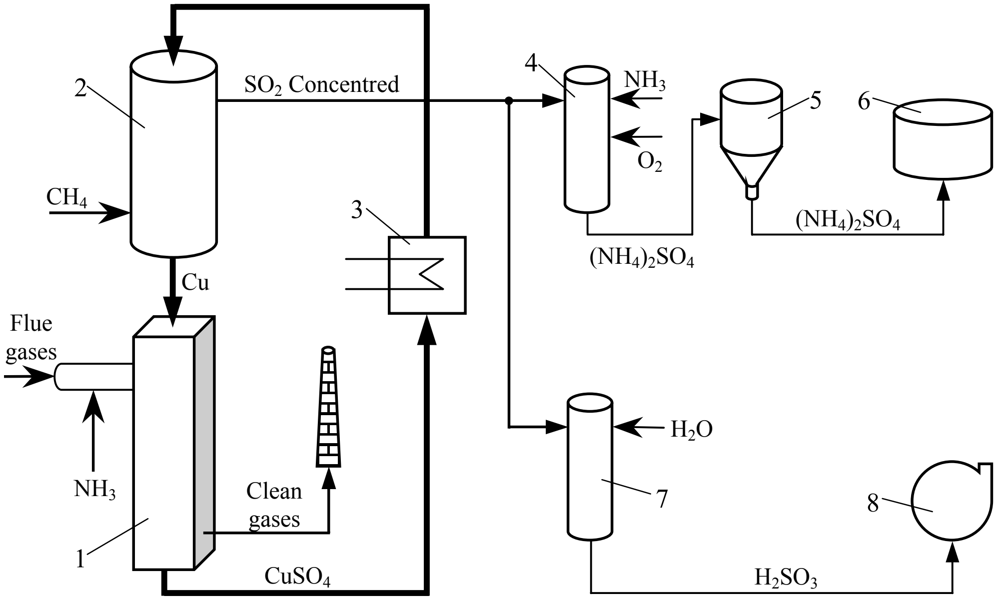


Fig. 3.31. The flow diagram of the Copper Oxide Process:
1 – The main reaction column; 2 – Sorbent regenerator; 3 - Heater;
4 – Ammonia absorption; 5 - Crystallizer; 6 – Fertilizer storage;
7 – Column absorbtion SO_2; 8 – Steep acid storage.

$CuSO_4$ is reduced to Cu using methane or other reducing gas, and SO_2 is released in the off gas stream. The regenerated sorbent is fed back to the absorber and so the cycle of the sulfur removal is completed.

Because the Copper regeneration is efficient only at the temperatures higher than 450 ^{o}C, the spent sorbent must be heated in (3). The necessity of the supplemental heating is justified by the specific dependency of the regeneration efficiency by the temperature and by the residence time of the sorbent in the regenerator's column. As results from Fig. 3.32, a regeneration degree higher than 80 % can be obtained only at temperatures higher than those existing in the main reaction column (1) and for a residence time of approximately 2 ÷ 3 hours.

Even initially were used reaction columns with fixed bed configuration, nowadays there are used, practically in exclusivity, reactors in moving bad configuration, taking into account them constructional and operational advantages. Thus, in the reactors with fixed bad configuration the absorption and the regeneration were developed alternatively, in the same chamber, reason why it were necessary more columns simultaneously and a complex system of ducts and gas valves. Besides, because of the large amount of necessary sorbent to achieve high sulfur removal efficiencies, the sorbent attrition is considerable high.

In the case of moving bad reactors, both the pollutants removal efficiency and the sorbent operation are better. Besides, in the case of moving bad configuration, the absorption and the regeneration can be developed at the optimal temperature for each process, regime very difficult to be achieved in the case of the fixed bad configuration. As a result, the recirculation rate can be increased and, implicitly, the molar ratio of Cu/SO_2, resulting so a higher desulfurization degree.

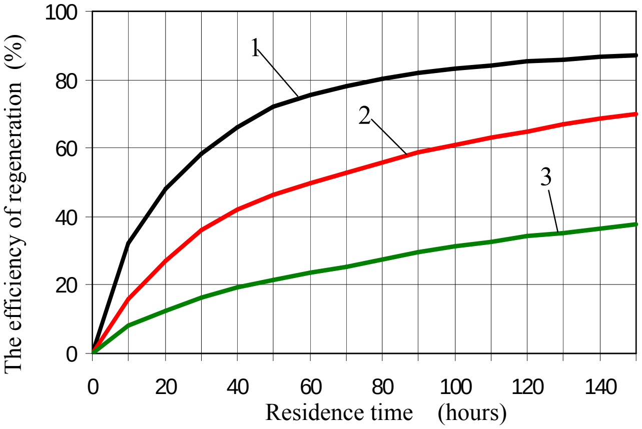


Fig. 3.32. The dependency between the sorbent regeneration efficiency, temperature and residence time: 1 - θ = 470 °C; 2 - θ = 435 °C; 3 - θ = 400 °C.

The sorbent is delivered as alumina spheres impregnated with CuO and having the diameter between 1,5 ÷ 6 mm. The mass of the Copper represents approximately 6 ÷ 7 % from the mass of such a sphere. The realization of some spheres with a bigger weight of Copper is not advantageous because the fouling of the pores limit the access of the gas SO_2 to the sorbent, a quantity of Copper remaining so unreacted. Moreover, a bigger quantity of Copper into the sorbent spheres reduces theirs mechanical endurance. The particles resulting from the broken spheres can lead to the reactors' plugging and can foul the tubing in the same way as the flying ash.

The sorbent prepared as previous described has a specific cost of 4 ÷ 6 $/kg. A possibility to reduce the sorbent's cost is that to use alumina spheres impregnated with $CuSO_4$. As long as $CuSO_4$ impregnated sorbent can be easily prepared by soaking the alumina spheres into a $CuSO_4$ solution, the cost of producing sorbent can be dramatically reduced. It must be mentioned that if such a sorbent is used, it is mandatory that the first operation is the activation of the sorbent in the regenerator.

There are both mechanical and pneumatic transportation methods for the sorbent. The second solution is advantageous because the spheres' erosion through friction with the transporter's elements is reduced. Because a large amount of sorbent is used, it is important to keep the sorbent attrition small. Careful design and testing of pneumatic sorbent transport system include using of appropriate velocity of the carrying gas and reducing sorbent's damage into the system's valves.

The SO_2 recovery and valorization process can have different flows, as a function of the byproducts that is intent to be obtained. In Fig. 3.31 there are given examples of the flows of production of the fertilizers and of the steep acid. Thus, in the column of the ammonia absorption (4) there are developed the following reactions:

$$SO_2 + H_2O = H_2SO_3\,; \tag{3.28}$$

$$H_2SO_3 + 2NH_3 = (NH_4)_2SO_3\,; \tag{3.29}$$

$$(NH_4)_2SO_3 + 1/2O_2 = (NH_4)_2SO_4\,. \tag{3.30}$$

The SO_2 gas reacts with water producing the sulphurous acid. This one reacts with ammonia producing a solution of ammonium sulphite. The solution is oxidized and so results a solution of ammonium sulphate. In the aim of the usage of the ammonium sulphate as fertilizer, the solution must be treated in a crystallizer, the solid state so obtained being delivered toward a storage tank (6).

Even the reduction reaction of NO_x is developed in a molar ratio $NH_3/NO_x = 1$, the eventually existing ammonia slip participates in reactions like (3.29) is, this technology having, in addition, the advantage of zero pollution with ammonia.

When the production of sulfuric acid is intended, the concentrated SO_2 gas is delivered toward the absorber (7), where in reaction with the water is obtained the sulphurous acid (reaction 3.28). The diluted solution of H_2SO_3 is stored into the tank (8), following to be used for the sulfuric acid (H_2SO_4) production.

3.2.2.4. The Adsorption on Charcoal

The technique of the adsorption on charcoal (activated carbon) or on coke obtained from lignite has a good efficiency into removal of various pollutants, from acid gases to heavy metals. Because the efficiency is not very high and the process is not a selective one, this technique is used only as complementary pollution control system associated to the classical ones.

As principle, the technique consists into the adsorption (physical binding) of the pollutants by a reactive (adsorption support). The adsorption support must have a very big specific surface, as the charcoal and the coke have.

The coke obtained from lignite is more attractive for industrial scale applications then the charcoal being ten times cheaper. Even the adsorption capacity of the coke obtained from lignite is lower the ratio efficiency/price is on its side.

The coke obtained through thermal treatment of the lignite, at a temperature of 950 ^{o}C, has the characteristics given in Table 3.6. By the heating process there are eliminate the volatile organic compounds (VOC) and there are obtained very porous and hygrophobic particles having a good potential of adsorption.

Table 3.6. The characteristics of the lignite-coke produced by Rheinbraun Brennstoff GmbH

Granulometry	< 1,25 mm	**The contain of S**	0,5 % - mass unit
Water contain	0,5 % - mass units	**Inferior calorific power**	29,9 MJ/kg
VOC	3,0 %	**Specific surface**	300 m^2/g
Carbon	87,5 %	**Volume of the pores**	50 %

An adsorbent with a lower capacity of self-combustion than the classical charcoal or coke has the commercially name of SORBALIT® and is obtained by mixing the the charcoal with Calcium hydroxide $Ca(OH)_2$.

Taking into account the pollutant that will be removed, the adsorption support can be put into a fixed bad, into a circulating bad or in the filtration system of the particles resulted from a fluidized bad furnace. Irrespective of the constructive type, the operating temperature must be maintained between 100 and 150 °C, higher than the acid dew point and lower than the self-ignition temperature of the adsorbent.

These systems are integrated into the boilers flow after the particulate filter, in order to avoid the adsorption support fouling, and the gases' velocity must be chosen in a manner to avoid the adsorbent particles' take over.

In the case of flue gases treatment, this process was initially used to remove sulfur gases. Later, the charcoal was used as catalyst for the reduction of NO_x, the re-agent being the ammonia. As a conclusion, this process ensures the physical binding of the acid gases (SO_2, SO_3, HCl, HF) and heavy metals (Hg) and the selective catalytic reduction of NO_x.

As a difference from the **SCR** and **SNCR** systems, this process has not any ammonia slip, all the unreacted NH_3 being adsorbed by the charcoal.

At the optimal temperature, between 120 and 140 °C, the ammonia reacts especially with sulfur oxides. Toa void the excessive consumption of ammonia, the system is separated into two zones:

- ✓ the first zone removes the residual SO_x (the main SO_x removal being realized in a previous stage, using a classical sulfur removal process),
- ✓ the second zone reduces NO_x, immediately after the ammonia injection.

As an example, in the case of a unit installed at Düsseldorf and which process a flow of 7000 Nm^3/h, the flue gas pass initially through a desulfurization scrubber, after this it pass through six moving beds of active coke and through two fixed beds of charcoal. The first two beds are for residual SO_x removal, the ammonia injection being realized in the third bed, the participation of each bed being that in Fig. 3.33.

After its use, the adsorbent loaded with the pollutants must be neutralized or recycled. The chosen way depend on the characteristics of the adsorbed pollutants and, implicitly, on the technological process associated to the pollutant removal facility.

Thus, in the case of the incineration of the household wastes it is preferable to destroy the adsorbed organic materials through thermal high temperature processes. In such a case, the charcoal takes the role of a fuel, if the environmental standards permit it.

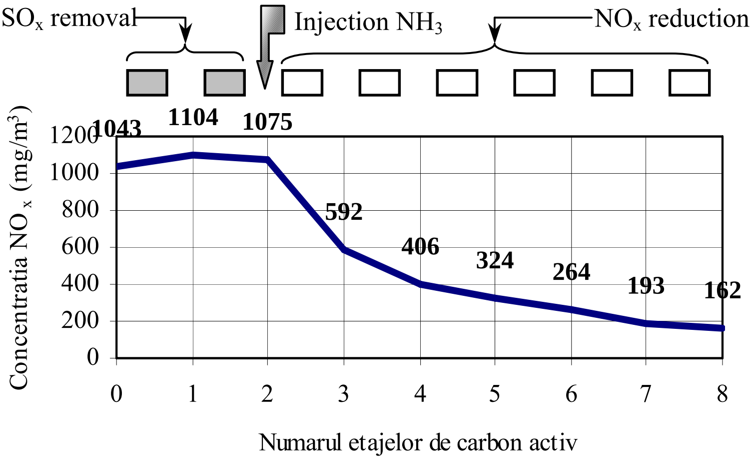


Fig. 3.33. The efficiency of the charcoal beds in the process of NO_x reduction

The regeneration of the charcoal is realized through controlled desorption, at a temperature between 200 ÷ 350 °C. Obviously, the charcoal regeneration implies the existence of the necessary technologies to put into value the adsorbed pollutants, nowadays existing some difficulties into mercury recovery.

3.2.2.5. Electron Beam Technology

The electron beam technology is a very efficient method to remove the SO_x and NO_x in flue gas from coal-fired power plants. The Electron Beam Technology presents many advantages comparing with conventional methods: simultaneous removal of SO_x and NO_x, dry process without waste water, no need of a catalyst, low capital costs, by-products can be utilized as fertilizers.

The operational costs are relatively small when the electron accelerator works with current pulses (pulsed corona discharge, non-thermal plasma discharge). When the electron accelerator is supplied with direct current, the energy consumption of the facility can reach 3 % from the energy production of the power plant.

As a principle, the Electron Beam Technology is a dry method for SO_x and NO_x removal, based on the creation of some active species, as are O, OH and HO_2 resulting in the electron beam irradiation process of the flue gas. These active species are chemically very active and supplementary oxidize the sulfur oxides and nitrogen oxides existing in the flue gases of the coal-fired power plants. The injection of a quantity of ammonia finalizes the pollutants' removal process, resulting solid and dry ammonia salts that can be used in the fertilizers industry.

The stages of the removal process are the following:

- ✓ The removal of the flying ash from the flue gases.
- ✓ Generation of the active species; By collision of the electron with the molecules of SO_2, NO_x, CO_2 and H_2O, there are continuously generated active species as are O, OH, HO_2. Such a reaction is as follows

$$O_2,\ H_2O \xrightarrow{e^-} O, OH, HO_2. \tag{3.31}$$

- ✓ Oxidation reaction of SO_2 and NO_x; SO_2 and NO_x are oxidized and converted into sulfuric and nitric acid respectively, by these active species generated by electron beam irradiation of the flue gases, in the presence of the water vapor:

$$SO_2 \xrightarrow{O,\, OH,\, HO_2} H_2SO_4; \tag{3.32}$$

$$NO_x \xrightarrow{O,\, OH,\, HO_2} HNO_3. \tag{3.33}$$

- ✓ Neutralization reaction; Nitric acid and sulfuric acid produced by the oxidation reaction react with the ammonia injected into the reactor and ammonia salts, as results from the following reactions:

$$HNO_3 + NH_3 \rightarrow NH_4NO_3; \tag{3.34}$$

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4. \tag{3.35}$$

The efficiency of the process is higher than 90 %, as concern the SO_2 removal, and of 80 %, as concern NO_x removal.

If ammonia is not injected there results the nitric acid and the sulfuric acid, but the removal efficiency dramatically decrease, reaching only 10 m%, in the conditions of the increase of the electron beam energy consumption.

The scheme of such a facility with two stages irradiation is that given in Fig 3.34.

If the facility serves a coal-fired boiler (1), before acid gases removal the flue gas must be filtrated into an electrostatic precipitator to avoid the main reactor (5) fouling and to realize a partial neutralization of the acid in the presence of the basic components of the flying ash. In this aim is not necessary a special investment, the existing electrostatic precipitator (2) having usually a good enough efficiency.

The flue gas is cooled in a cooling tower (3) by spraying with water. This washing of the gases partially removes acid gases and residual very fine flying ash. In the main reactor of irradiation and reaction (5), there are developed all the specific reactions of the process, from the active species generation to the ammonia salts production.

The beam accelerator (6) is a multi-stage irradiation type, the energy of the electron beam being of 500 ÷ 700 keV and the penetration depth of 1000 mm.

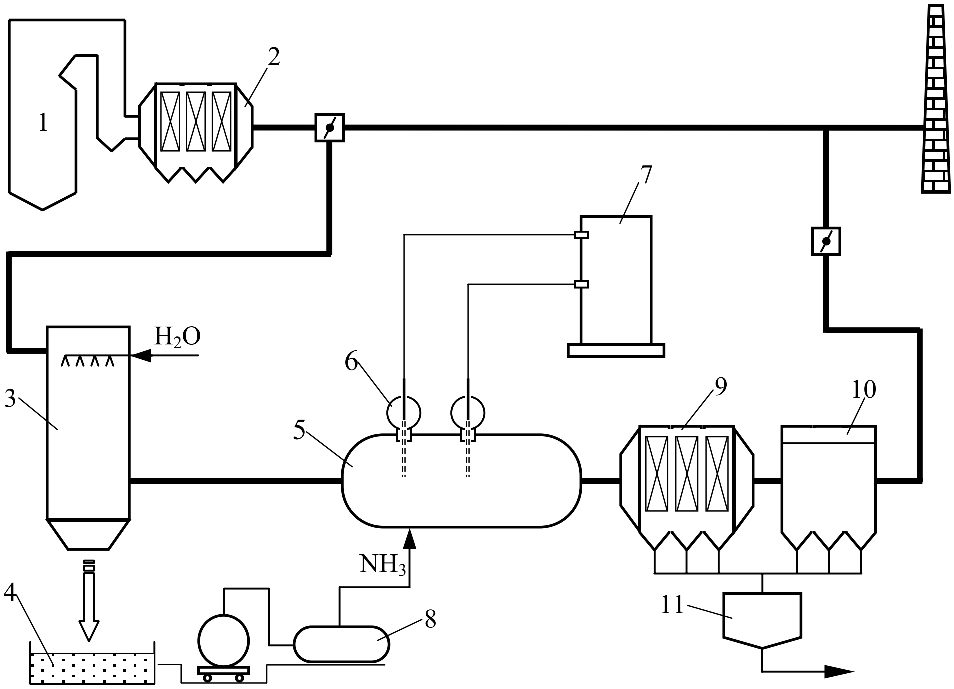


Fig. 3.34. The scheme of the facility designed to remove SO_2 and NO_x using accelerated electron beam: 1 – steam boiler; 2 – electrostatic precipitator for flying ash; 3 – cooling tower; 4 – water collection tank; 5 – main reactor for irradiation and chemical reactions; 6 – electron curtain accelerator; 7 – pulse voltage generator; 8 – ammonia storage tank; 9 – electrostatic precipitator ammonia salts; 10 – bag filter; 11 – storage by-products (fertilizers).

In the acceleration systems with only one accelerating stage, electron can attain energies as high as 0.5 MeV, suitable for some industrial applications as are: surface treatments, pant and ink on the metals, wood and plastic. The irradiation in multiple stages can lead to electron energies of 10 MeV and is necessary in the case of pollutants removal, in the case of medical sterilization and food pasteurization.

The operating life of the cathode realizing the electron thermal emission is of about 8000 hours, and the thickness of the accelerating window material is of 30 μm. Thicker materials increase the energy loss in it.

The nominal voltage of the pulse generator (7) is of some tens of kV. The nominal power is relatively small, the magnitude of the current pulses being of 500 ÷ 1000 mA and the pulse width of 0,1 ÷ 10 μs. The repeating frequency is adjustable in the domain of 50 Hz ÷ 1 kHz.

All the restrictions as concern ammonia are the same at the **SCR** systems.

The ammonia salts are obtained as very fine particles that must be collected from the flue gas. The relatively big quantity of such particles and their very small dimensions can lead to the necessity of using a combined filtration system: electrostatic precipitator (9) and bag house filter (10).

The increase of the irradiation dose leads to the increase of the removal efficiency of SO_2 and NO_x (Fig. 3.35,a), the same trend being observed in the case of the irradiation stages increasing (Fig. 3.35,b).

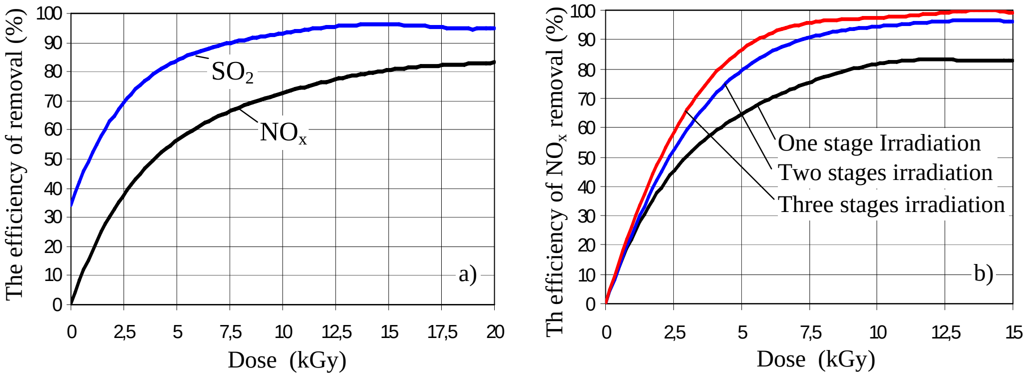


Fig. 3.35. The dependency between pollutants removal efficiency, the irradiation dose and the number of the irradiation stages.

As results from Fig. 3.35,a, the efficiency of SO_2 removal is higher than those of NO_x reduction. The increase of the irradiation dose over a level of approximately 15 kGy does not lead to a significantly increase of the removal efficiency, resulting only an increase on energy consumption for electron acceleration.

The two-stages irradiation leads to an important increase of the pollutants removal from flue gases. The irradiation in three stages does not lead to significant increase of the pollutants removal efficiency, both for NO_x reduction and for the SO_2 removal.

The introduction of electron beam ob both reactor's sides implies the increase of the removal efficiency of SO_2 and NO_x, with an approximately 6 ÷ 8 %, irrespective of the irradiation dose, as results from the curves drawn in Fig. 3.36,a.

As results from Fig. 3.36,b, the removal efficiency of SO_2 is very sensible at the temperature. The increase of the temperature over the threshold of 62 ÷ 64 ^{o}C leads to an important decrease of the SO_2 removal efficiency.

The electron beam technology is appropriate and will be developed especially for the pulverized coal-fired power plants having the power of the boilers between 100 ÷ 300 MW, especially as result of the following advantages:

- ✓ the efficient and simultaneously removal of two dangerous pollutants,
- ✓ the operation without ammonia slip,
- ✓ the costs of investment are smaller with 30 ÷ 40 %,
- ✓ relatively long operational life,
- ✓ the obtained by-product can be used for the production of the fertilizers.

The disadvantage of the relatively high energy consumption, of about 1 ÷ 2 % from the energy produced by the power plant equipped with such a facility, can be diminished through the irradiation into two stages and from both reactor's sides, in this case the energy consumption decreasing with approximately 20 ÷ 30 %.

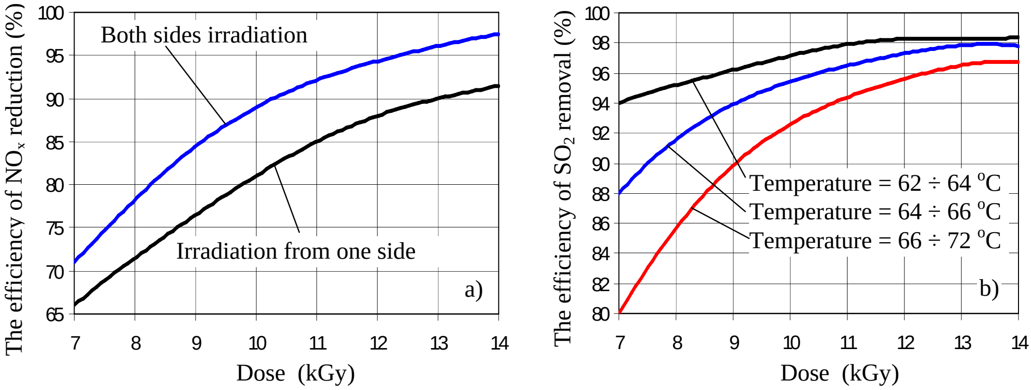


Fig. 3.36. The dependency between the pollutants removal efficiency and the irradiation dose, as a function of the electron accelerators position (a) and of the temperature of the flue gas (b).

3.2.3. Hybrid methods for NO_x reduction

The hybrid methods for NO_x reduction consists into the simultaneously use of at least two NO_x control techniques, some of them being of intra-combustion type and at least one of them being a post-combustion type. Another possibility to imagine the hybrid NO_x removal is that of simultaneously using of two post-combustion methods, as are **SCR** and **SNCR**. In the last case, the global efficiency of the pollutant's removal is given especially by the synergism of the two post-combustion methods.

As concern the simultaneous use of intra-combustion and post-combustion NO_x reduction methods, practically every of the post-combustion methods can be associated with the staged combustion, realized individually or for the entire furnace. Such an example is the association of staged combustion with a **SNCR** system (Fig. 3.37).

The intra-combustion method consists into the use of low-NO_x burners, but in the conditions of an insufficient primary air. Thus, the effect of the individual staged combustion is accentuated by the global staged combustions, the combustion being finished by the flow of the over fire air (**OFA**). The intra-combustion systems are designed to reach theirs maximum NO_x reduction efficiencies. Such a hybrid method has a NO_x reduction efficiency of 69 ÷ 70 %, even in the conditions of using a classically **OFA** system and not an advanced one (**AOFA**).

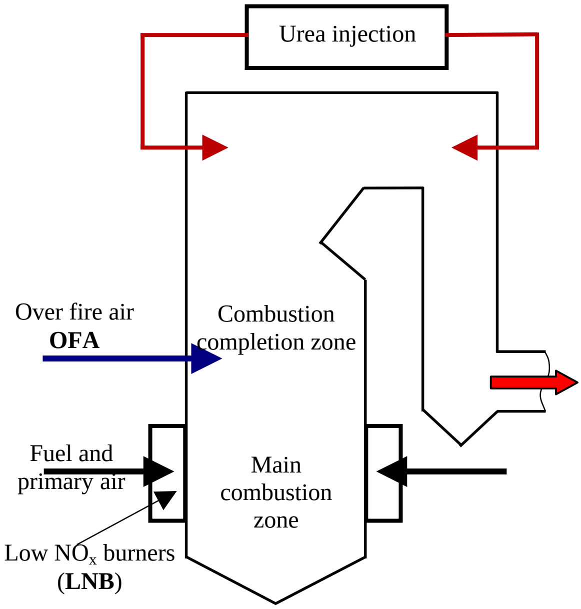


Fig. 3.37. The principle scheme of the NO_x reduction hybrid method obtained by the simultaneously use of the staged combustion and the urea-based **SNCR**

The **SNCR** system is not designed to the work at its maximum NO_x reduction efficiency. The re-agent is injected only in the upper part of the furnace at most on two injection levels. The injectors of the first level are usually wall-mounted injector and of the second one are of retractile type.

The system is so operated thus, in this stage, the NO_x reduction efficiency is of 30 ÷ 50 %. In injection of the re-agent in the upper zone of the furnace has the disadvantage of an important ammonia slip (10 ppm, the maximum admissible ammonia slip being of 2 ÷ 5 ppm). The ammonia slip can be reduced if the boiler is equipped with a wet flue gas desulfurization facility.

The association of staged combustion and **SNCR** reaches a NO_x reduction efficiency of approximately 80 %, irrespective of the boiler's load. When the load decreases, the efficiency of the primary methods decreases too, SNCR being designed to compensate this decrease.

In the case of steam boilers based on liquid fuel or gas combustion, an important decrease of the NO_x emission can be reached if one of the methods which control the NO_x emissions through the operative parameters of the boiler is associated with **SNCR**. Such an application can be that consisting into the injection of water vapors in the furnace, as a primary method, and a urea-based **SNCR** system, as secondary method. If the flue gas recirculation is used only in the upper part of the furnace, as a method to control the temperature of the steam, this method can be extended toward the lower part of the furnace, obtaining an additional reduction of the NO.

The intra-combustion method consists into the injection of a very fine pulverized water flow in the main combustion area, furnace's zone in which results the biggest quantity of NO. This water jets are introduced at the level of the every burner, simultaneously with a compressed air flow.

Before of the water injection, this is very carefully processed to remove all the suspensions that can foul the injection nozzle. Such a filtration is highly important because the nozzles for water injection are constructive parts of the burners, resulting so a very difficult maintenance. In the water circuit of the **SNCR** system the pressure is of about 10 ÷ 15 atm. If this water is used also for the combustion tempering the pressure must be reduce to 7,5 ÷ 8 atm, using some pressure reducing devices.

The reduction of the temperature, in the zone of the primary pyrolysis, leads to the reduction of the NO emission. There are industrial scale applications that reduce the NO emission with at most 37,5 % - in the case of the gas fuel combustion, and with approximately 15 % - in the case of the liquid fuel combustion, the NO reduction essentially depending by the injected water flow and by the water drops' fineness.

The secondary method of the process is of $NO_xOUT^{®}$ **SNCR** type, the re-agent being a 50 % weigh urea solution into water. In this solution it is introduced a small quantity of additives having the role to reduce the corrosion rate of the SNCR system and of the boiler. The zone of the urea injection is quite specific for each type of boiler, the appropriate position being chosen in order to maintain the re-agent as long as possible in the optimal temperatures window, reaching so an efficiency of 60 %.

Exactly as in the case of stand alone urea-based **SNCR** systems, the urea tank must be protected against low temperatures, in order to avoid the re-agent solidify. The urea storage tank is placed into boilers' room is thermal insulated and a little heated, in order to maintain the concentrated urea's temperature at least at 20 ^{o}C.

A good way to increase the NO_x control efficiency, as concern the pollutants reduction as well as the investment and operational costs, is that of the combined use of the **SNCR** type process with the **SCR** type, in the so-called NO_xOUT $CASCADE^{®}$ installations. This type of NO_x reduction installations was designed by Nalco Fuel Tech, in collaboration with Electric Power Research Institute.

The association of these two dry post-combustion techniques leads to a very efficient use of the re-agent, in a large window of the boiler's loads.

The first stage of pollutant reduction is one of **SNCR** type, the re-agent being urea as well as ammonia. When the **SNCR** system is operating as stand-alone process, its performances are limited by the necessity of the re-agent injection at high temperatures, in order to avoid unacceptable high ammonia slip.

The second stage on NO_x control is a **SCR** process, but this facility being designed to operate only simultaneously with the **SNCR** system and in the downstream of it. Such an operational way leads to small catalytic reactors having small pressure and speed drops and small velocities of catalyst's poisoning.

The hybrid system **SNCR/SCR** implies the operation of the **SNCR** system at a lower temperature then in the case of the boilers equipped only with a **SNCR** system. The operating temperature is shifted toward the minimal limit of the optimal window of the temperatures. In these conditions, the NO control efficiency is very close to the maximum one, but in the condition of an important ammonia slip, as results from Fig. 3.28. When the flue gases leave the treatment **SNCR** zone, the quantity of NH_3 is unacceptable high to allow the evacuation of the gasses to the stack. The residual ammonia is used as re-agent in the second stage of the hybrid process (**SCR** system).

The fact that the **SCR** system operate only with the ammonia slip of the **SNCR** system leads to a much smaller quantity of the necessary catalyst than in the case when the **SCR** system operates as stand-alone NO_x control technology, as results from the curves given in Fig. 3.38.

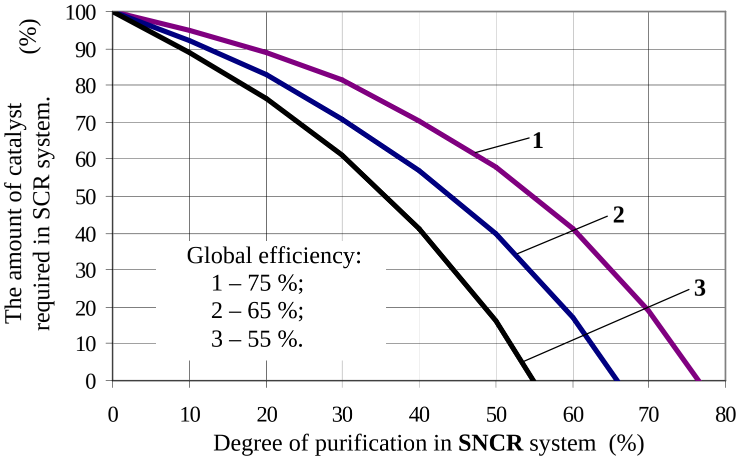


Fig. 3.38. The necessary catalyst in the hybrid NO_xOUT CASCADE® systems

Ad an example, if the **SNCR/SCR** cascade is designed for a $deNO_x$ efficiency of 65 %, 50 % in the **SNCR** stage and 30 % in the **SCR** stage, the volume of the catalyst is lower with approximately 60 %, than in the case when **SCR** system should reach a control efficiency of 65 %, working as stand-alone $deNO_x$ system. In such conditions, the operational requests are different comparing with those of the classical **SCR**:

- ✓ The degree of the re-agent use can be smaller (of only 60 ÷ 80 %), without obtaining an increase of the ammonia slip in the flue gases;
- ✓ The NO_x reduction efficiency can be temporarily reduced, at one level of 10 ÷ 30 %, knowing that the **SCR** systems reach a NO_x reduction efficiency of 90 %.

These operational requests are reflected into the construction of the **SCR** system imagined to operate into a cascade. Thus, the small volume of the catalysts permits its installation even in the flue gases tubing, being not necessary special catalytic reactors. Another attractive technical solution is that of the installation of the catalytic layers directly on the hot surfaces of the regenerative air preheaters, in this boilers' zone being appropriate conditions for the operation of the V_2O_5/TiO_2 catalysts, as follows:

- ✓ optimal temperature window for the reduction reactions (300 ÷ 400 °C);
- ✓ a big enough contact surface.

The small dimensions of the catalyst imply small investment costs and only some minor modifications of the boiler, even in the case of a supplementary ammonia injection in the area of the **SCR** system (Fig. 3.39). In this last case, the re-agent is injected through a single nozzle grid.

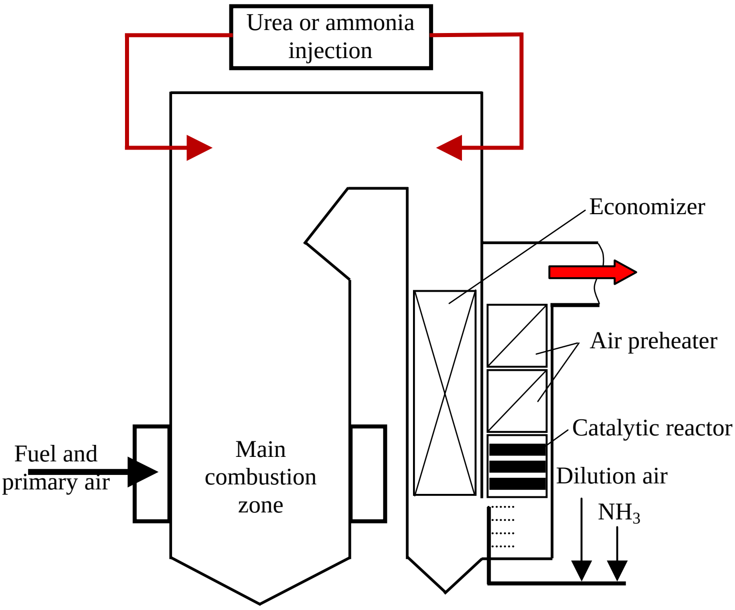


Fig. 3.39. The schematic diagram of the hybrid NO_x control system cascade **SNCR/SCR**

The small size of the catalyst involves low values of pressure drop in the catalytic layers and a small catalytic conversion of SO_2 into SO_3, this being proportional with the reduction of the catalyst's size. If there are added the reducing storage costs for used catalyst, it results in low costs to operate with the cascades than those of the application of each technique separately.

The purification degree of **SNCR/SCR** cascades is higher than that obtained by summing the efficiency of the two systems, working separately, while the global technological and NH_3 slip are smaller. This is due to carry out the chemical reactions in those parameters that lead to the reactions' maximum kinetic.

The **SNCR/SCR** cascades are characterized by a more flexible operation than either of the systems considered separately, being able to easily adapt to the frequent changes of the operation conditions caused by the changes in boiler's load. The cascade is sized to the maximum load of the boiler and when the load decreases, the reducing agent flow from the **SNCR** system is reduced, even up to a complete stop. The stop limit of the first stage depends on the capacity of **SCR** to reduce emissions below the maximum allowable limit.

All these advantages recommend the use of **SNCR/SCR** cascades at industrial scale, good results being obtained in the boilers' retrofit too.

Even if such **SNCR/SCR** cascades have a very high efficiency in terms of relatively low investment costs (15 ÷ 25 USD/kW), the boiler's NO_x emissions control with low costs, still represents a technical challenge. The overall efficiency of the selective reduction afterburner catalytic or non-catalytic techniques, can be overcome only by unconventional systems, a possible example being that the use of wet electrostatic precipitators, for collecting fly ash as well as for acid gas control.

The electrostatic precipitators have a very high efficiency in the collection of flying ash from the flue gases, the constructive version of dry collection being basically used in coal-fired power plants' boilers. The electrostatic wet collection variant could be used for simultaneous NO_x and SO_x emissions control, in terms of low investment costs and smaller size plants compared with the classical association of secondary wet desulfurization with **SCR** facilies. In addition, the advantages of wet particle collection (avoiding reverse corona discharge, the disruptive discharge and retraining of settled dust phenomenon) and some constructive simplification can reduce the operating costs of the pollutants' control facilities.

The dry electrostatic precipitators can reduce NO_x emissions as a result of intense ionization of the gas in the presence of corona discharge, but this reduction is more important when wet electrostatic precipitators are used, due to the chemical reactions involving water and its radicals that are produced in the presence corona discharge. In addition, the presence of water decreases the ammonia slip, this fact being an effect of pollutant absorption in the aqueous solutions.

The phenomena involved in the simultaneous treatment of particles and NO_x emissions, in an electrostatic precipitator, are the followings:

- ✓ the ionization of particles and molecules of the pollutant gases;
- ✓ the oxidation of some gases by the ozone;
- ✓ the oxidation of some gases by the free radicals;
- ✓ obtaining of some ammonium nitrate aerosols (NH_4NO_3), by NH_3 vapor injection;
- ✓ the collection of the particles and aerosols.

The corona discharge, having reached its stage of streamer - cold plasma (in which only the electrons are strongly accelerated, without being accelerated and heated the ions), generates electrons which are sufficiently energized in order to produce ionization processes, either by attaching to particles in suspension and to the gas molecules, or by dissociation of gas molecules, followed by attachment processes. Thus, if the free electrons are attached to molecules of NO, negative ions NO^- are formed, which will be separated by the action of electrostatic force. These phenomena also occur in dry electrostatic precipitators, but the degree of control of NO_x emissions is far from being satisfactory.

Compared to the classic case of DC corona discharge, there are observed the increasing degrees of desulfurization and denitriding, even if in dry conditions, when the electrode systems are powered by voltage impulse. The corona impulse discharge causes only the acceleration of the electrons up to energy levels large enough to generate free radicals, while ions with significantly higher masses and thus greater inertia, cannot be accelerated so much, this fact leading to a small amount of energy consume.

The impulse corona discharge can be used to both negative and positive polarities. The corona discharge at negative polarity occurs only in the proximity of emission electrodes, while positive polarity corona discharge is characterized by greater length streamers (even up to 10 times), which penetrate deep into the gas flow, thus ionizing larger volumes of gas, at the same discharge energy. In this way, the impulse corona discharge at positive polarity is more effective in retaining the NO_x emissions. However, taking into account the low power consumption of an electrostatic precipitator, which operates with impulse voltage, the supplementary reduce of energy consumption is not very important, especially when the risk of disruptive discharge, at the positive polarity, is higher.

In electrostatic precipitators there is a certain amount of ozone formed by reactions as following:

$$\begin{cases} e^- + O_2 \to 2O + e^- \\ e^- + O_2 \to O + O^- \\ O^- + O_2 + M \to O_3 + M \end{cases} . \tag{3.36}$$

In classical plants, the emission of ozone represents a disadvantage and in some applications there must be taken special measures for decomposition of ozone. On the other hand, NO is much less soluble in water than NO_2 and the ozone can be used for a rapid (less than 0.1 s) of NO to NO_2 conversion, by reaction of the form:

$$\begin{cases} NO + O \to NO_2 \\ NO + O_3 \to NO_2 + O_2 \\ 3NO + O_3 \to 3NO_2 \end{cases} . \tag{3.37}$$

Ozone, due to its strong oxidizing character, continue the oxidation reactions of NO and NO_2 to nitrogen trioxide (NO_3) and nitrous oxide (N_2O_5), as follows:

$$\begin{cases} NO_2 + O_3 \to NO_3 + O_2 \\ 2NO + 3O_3 \to N_2O_5 + 3O_2 \end{cases} , \tag{3.38}$$

compounds that easily react with water, thus, resulting in the formation of nitric acid, which can be retained in a controlled manner. Simultaneously, SO_2 and SO_3 oxidation reactions occur, increasing the risk of developing of a large amount of H_2SO_4 that would lead to rapid corrosion of the electrostatic precipitator's internal equipment. In fact, the SO_2 oxidation reaction is much slower than for the oxidation of nitrogen compounds.

The phenomena of oxidation in the presence of free radicals are generated implicitly by the corona discharge. Thus, by collision of accelerated electrons with neutral molecules in the flue gas (N_2, O_2, H_2O, CO_2), there are formed free radicals (O, N, H, OH), positive and negative ions and excited molecules. Subsequently interactions, as are those of electron-ion and ion-ion, as well as the detachment phenomena create the secondary radicals (HO_2). These radicals oxidize gaseous NO_x, facilitating their reaction with water, or react with nitrogen oxides, in the sense of formation of some aerosols that can be trapped by the electrostatic precipitator.

Nitrogen oxides can be reduced to N_2 and H_2O by free radicals of NH and NH_2 types, produced by corona discharge even in dry electrostatic precipitators. The efficiency of these reactions decreases when the concentration of O_2 increases.

Ammonia used as a reducing agent in **SCR** and **SNCR** facilities and in air-accelerated electron reduction beam, can be used in wet electrostatic precipitators in oreder to convert NO_x into the ammonium nitrate aerosol (NH_4NO_3). The reactions involve an intermediate step, in order to transform the NH_3 in radicals NH, NH_2 and H, NH_3 by molecules collision with free electrons generated by corona discharge.

In dry electrostatic precipitators, for temperatures between ambient temperature and 150 °C, the reactions for obtaining NH_4NO_3 aerosols involve only nitrogen dioxide, the converted amount of NO being negligible.

At DC voltage, the corona discharge can oxidize up to 67% of the existing NO in flue gases, in the presence of oxygen and water vapor. This level of pollution control can be achieved only at electric field intensity bigger than that of the classical electrostatic precipitators (4.5 ÷ 9 kV/cm).

In conclusion, the existing wet electrostatic precipitators that use impulse corona discharge, in which is injected an additional quantity of ozone and ammonia, can hold simultaneously the flying ash and a large quantity of NO_x from the flue gases.

The NO_x control efficiency increases with the increasing residence time of the gas, with the initial NO_x concentration, with the intensity of corona discharge and with the amount of ozone injected from the outside, the ozone produced in the electrostatic precipitator being insufficient for a supplementary oxidation of the nitrogen oxides amount existing in the typical flue gases.

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