Development of Efficient Technologies for Abatement of Nitrogen and Sulfur Oxides in Flues Gases of Coal Combustion

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Abstract—Results of development of technologies for purification of coal-fired power plants from nitrogen and sulfur oxides in the frame of Russian-Chinese Project No. 14.583.21.0004 are presented.

Keywords—coal combustion, nitrogen oxides, sulfur oxides, sulfur-absorbing reagents

Description of the problem:
At present removal of nitrogen and sulfur oxides from flue gases of power plants is considered an important scientific-technical problem, solution of which is connected with an environmentally safe generation of thermal and electric energy. In many countries, contemporary standards of the design of newly created coal-fired power plants require building treatment facilities for removal of nitrogen and sulfur oxides, and in some countries mercury, from flue gases. Existing domestic coal-fired power plants recover only some part of ash (on filters) from all anthropogenic contaminants. All other toxic compounds, such as NOx, SO2, and SO3 are emitted into the atmosphere without any treatment. That is why a comprehensive approach to the solution of this problem is required, including both incremental modernization of the equipment and implementation of specialized solutions and technologies for the flue gas treatment (deNOx and desulfurization systems at the stages of fuel preparation and gas purification with the use of sorption and catalytic methods, removal of heavy metals, etc.).

In the frame of the realization of Russian-Chinese Project #14.583.21.0004 an original comprehensive technology for efficient purification of flue gases of electric and thermal coal-fired power plants from nitrogen and sulfur oxides was created, which will allow a decrease of the technogenic impact of energy producing enterprises on the environment. This technology was realized in a specially constructed experimental test bench.

The technology, used equipment, results of tests
The technology of purification of coal-fired power plants from toxic compounds involves the combination of various methods:
- lowering of the content of sulfur oxides formed upon the combustion of sulfur-containing fuel by the introduction of sulfur-absorbing reagents (SAR) into the combustion zone;
- a decrease of the content of nitrogen oxides in flue gases by the use of catalytic treatment methods.

The use of sulfur-absorbing reagents is based on the introduction of specially prepared SAR either into the composition of a coal fuel or into the combustion zone. Thus sulfur of fuel or sulfur compounds formed during combustion are transformed into solid compounds that are transferred to ash-and-slag wastes or captured in the composition of fly ash by the dust treatment system of the plant.

Figure 1 presents the site for preparation of coal fuel (including water-coal slurry fuel) and SAR in the composition of the test bench created in the frame of the project.
As the main technology of the fuel preparation for the combustion, the technology of water-coal slurry fuel (WCF) was used [1-3]. The water-coal slurry fuel containing SAR was prepared from the mixture of the filter-cake of "Barzas Association", technical water and a plasticizing additive. For the use as a sulfur absorbing additive, a dolomite mineral \([\text{CaMg(CO}_3\text{)}_2]\) was used, capable of fast and reliable sulfur capture. The water suspension of this SAR was prepared in the shredding installation of periodic performance by wet milling of crushed dolomite marble stone. The SAR consumption was calculated from the sulfur content in fuel and the stoichiometric ratio required for the binding of fuel sulfur, including sulfate sulfur:

\[
\text{CaMg(CO}_3\text{)}_2 + 2\text{SO}_2 \rightarrow \text{CaCO}_3 + \text{SO}_2 + \text{MgCO}_3 + \text{SO}_2 \rightarrow \text{CaSO}_3 + \text{CO}_2 + \text{MgSO}_4 + \text{CO}_2.
\]

The prepared water-coal fuel was fed into the furnace by compressed air supplied into an air-mechanical injector. The rate of fuel supplied into the furnace was regulated in such way as to provide the heat generation of 0.63 MW at the complete combustion of fuel with a lower calorific value of 2681-3167 kcal/kg. The temperature in the furnace was 1000–1100°C. The site of coal fuel combustion is shown in Fig. 2.

Table 1 presents the results of water-coal combustion with the use of SAR. To increase the sulfur content in the fuel the addition of technical carbon was used.

<table>
<thead>
<tr>
<th>Type of fuel</th>
<th>Content of sulfur oxides in flue gases, mg / nm3</th>
<th>Reduction of harmful emissions into the atmosphere, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>WCF (Cf:= 59.5 % - filter-cake + 0.3 % type T)</td>
<td>250</td>
<td>0</td>
</tr>
<tr>
<td>WCF (Cf:= 58.0 % filter-cake + 0.3 % type T + 1.06 % CaMg(CO_3)_2)</td>
<td>76</td>
<td>70.5</td>
</tr>
<tr>
<td>WCF (Cf:= 59.5 % filter-cake + 0.3 % type T + 1.06 % CaMg(CO_3)_2)</td>
<td>77</td>
<td>70.2</td>
</tr>
<tr>
<td>Filter-cake &quot;Barzas Association&quot; + technical coal</td>
<td>830</td>
<td>0</td>
</tr>
<tr>
<td>WCF (Cf:= 32.0 % filter-cake + 20.7 % technical carbon + 0.3 % type T)</td>
<td>158</td>
<td>81</td>
</tr>
<tr>
<td>WCF (Cf:= 29.5 % filter-cake + 19.6 % technical carbon + 0.3 % type T + 3.8 % CaMg(CO_3)_2)</td>
<td>153</td>
<td>82.3</td>
</tr>
</tbody>
</table>

As can be seen from the results of the combustion tests, the reduction of harmful emissions into the atmosphere formed upon the fuel combustion, achieved by the use of sulfur absorbing reagents in the combustion zone is equal to 70.2 – 82.3%.

Then the flue gases were directed to the catalytic treatment system.

The catalytic purification of flue gases from nitrogen oxides is conducted most efficiently by the use of monolithic catalysts working at high space velocities and low contact times. Monolithic catalysts are widely used in the gas treatment practice of Western countries and Japan. The supports used for the preparation of these catalysts are \(\text{Al}_2\text{O}_3\) [4-5], \(\text{TiO}_2\) [6-8], \(\text{ZrO}_2\) and their mixtures, zeolites, [9-14], prepared as honeycomb monoliths.

The existing methods of catalytic purification of flue gases from nitrogen oxides are based on \(\text{NO}_x\) reduction by the following reducing agents: ammonia, hydrocarbons, carbon monoxide, etc. [15-17]. The literature analysis shows that the most promising catalytic systems are individual or mixed transition metal oxides. In multi-component systems,
one metal usually modifies the catalytic properties of another one as a result of the mutual electronic and structural effects.

For the tests of gas purification from NO\textsubscript{x} in the pilot flue gas cleaning unit, experimental samples of monolithic Fe-Cr-Zn/Al\textsubscript{2}O\textsubscript{3} catalysts were prepared.

The catalytic flue gas cleaning unit is shown in Fig. 3.

The treated gas before the supply to the catalytic reactor (Fig. 4) is heated to the temperature 350-400°C by a flow heater. The design of the catalytic reactor includes a thermocouple well with a chromel-alumel thermocouple installed in the center of the catalyst bed for the measurement of the gas temperature. At the inlet of the reactor, the gas is mixed with ammonia. For the supply and measurement of the ammonia flow, a standard rotameter is used. Ammonia supply was regulated manually by the rotameter. The amount of the supplied ammonia depends on the NO\textsubscript{x} content in the treated gas (NH\textsubscript{3}/NO\textsubscript{x} = 1/1). For the measurement of the concentration of nitrogen oxides in gas flows and evaluation of the efficiency of the flue gas cleaning unit, three gas sampling points were provided: at the reactor inlet, in the reactor after ammonia supply and at the reactor outlet. The analysis of the treated flue gas was performed using a quadrupole mass analyzer QMS 300 permitting the measurement of low concentrations of pollutants [18-19].

The results of the tests in the experimental test bench showed that the efficiency of flue gas purification from pollutants attained the following values:
- removal of sulfur oxides using dolomite as a SAR was equal to 70.2 – 82.3 %;
- removal of nitrogen oxides using the catalytic treatment attained 94 %.

Thus, the results of the work allow concluding that the technology of abatement of pollutants formed in the flue gases of coal-fired power plants developed under the project is sufficiently efficient and can be recommended for the implementation at the existing and designed energy-generating enterprises.

References


