FEATURES OF SEMI-DRY AMMONIUM DESULFURIZATION

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Abstract – Semi-dry ammonium desulfurization technology is proposed to meet the requirements of Directive 2010/75/EU on reducing sulfur dioxide emissions and obtaining dry product - ammonium sulfate. The peculiarity of this technology is the presence of a gas-phase reaction of sulfur dioxide with ammonia along with the absorption of SO_2 in drops of ammonia water. The efficiency of the absorption of sulfur dioxide by gaseous ammonia (up to 90%) has been experimentally proved, subject to the presence of water vapor in the gas, the volume concentration of which should exceed the volume concentration of ammonia.

Keywords – flue gas, semi-dry desulfurization, sulfur dioxide, ammonia, ammonium sulfate.

Introduction

The issue of environmental protection in the combustion of fuel is becoming increasingly urgent and priority. One of the main pollutants of atmospheric air is sulfur dioxide SO_2, which is the product of oxidation of sulfur as a fuel component. The absence of flue gas cleaning from sulfur dioxide at the Ukrainian TPP leads to significant emissions of it to the atmosphere - more than 1 million tons per year. The direction of European integration of Ukraine's development is set the task of compliance with the requirements of the European Directive 2010/75/EU on industrial emissions [1], which defines emission limit values of sulfur dioxide from large combustion plants (200 mg/m^3 – for existing plants and 150 mg/m^3 – for new ones). Therefore, the task of reducing sulfur dioxide emissions by developing efficient, low-cost and compact desulfurization technologies and in which will be formed a useful product, is urgent.

In the world in branch power industry become the most widespread the wet limestone desulfurization with forced oxidation, which is able to meet the requirements of Directive 2010/75/EU, has high capital and operational costs, uses natural mineral as a sorbent and forms as byproduct gypsum (building material) [2]. Semi-dry lime technology is characterized by lower capital costs. They use as a sorbent a more expensive lime and the byproduct is a dry mixture of calcium sulfite, calcium sulfate and unused lime, which has very limited application.

An alternative to calcium desulfurization techniques can be ammoniacal technologies with the use of ammonia as a sorbent and the production of ammonium sulfate, which is a mineral fertilizer [2]. Wet ammonium sulfate technologies have high efficiency of binding of sulfur dioxide (+ 98%), lower operating costs, but the process of obtaining ammonium sulfate from solution is technologically difficult [3].

The proposed semi-dry ammonium desulfurization method has low capital costs (as semi-dry technology), low operating costs, and high efficiency of SO_2 removal (as ammonia technology), and will be formed the dry sulfate of ammonium. In fig. 1 shows a scheme of semi-dry desulfurization using ammonia water as a sorbent [4].

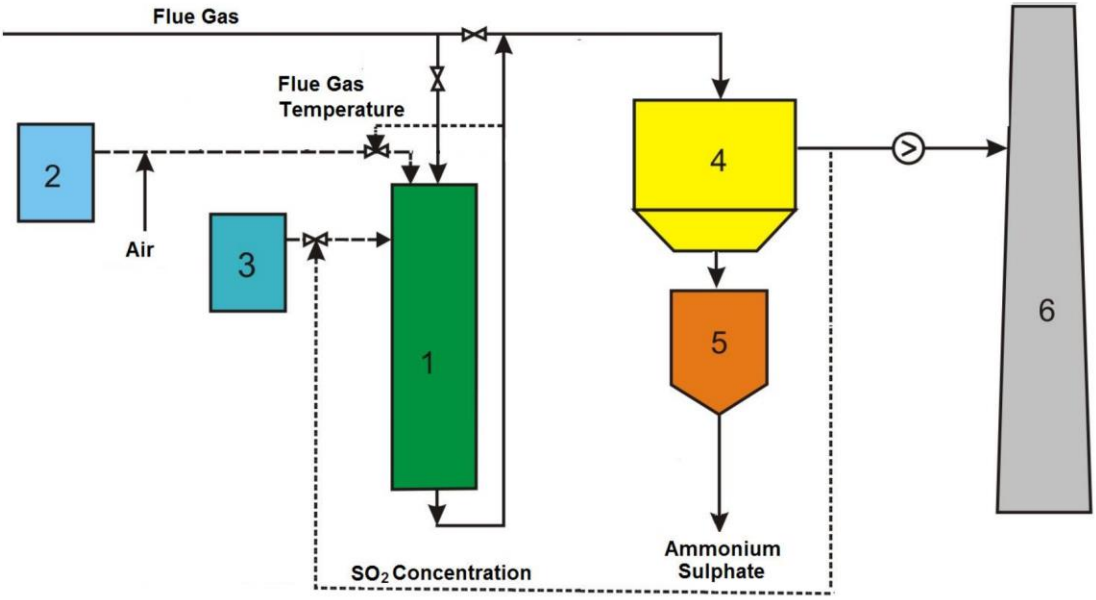

Fig. 1 – Schematic diagram of the semidry ammonium desulfurization
1 – reactor; 2 – technical water tank; 3 – ammonia water tank; 4 – fabric filter;
5 – ammonium sulfate silo; 6 – chimney

Flue gas after dust precipitation is introduced into the reactor, which is usually supplied with drops of ammonia and technical water. In drops of ammonia solution NH3, dissociation occurs with the formation of ammonium cation [5]:

$$NH_3{\times}H_2O \leftrightarrow NH_4OH^+ + OH^- \quad (1)$$

Sulfur dioxide as a component of flue gas is dissolved in water, with the formation of mainly anion of hydrosulfite [5,6]:

$$SO_2 + H_2O \leftrightarrow HSO_3^- + H^+ \quad (2)$$

$$HSO_3^- \leftrightarrow SO_3^{-2} + H^+ \quad (3)$$

In the presence of oxygen in flue gas, the reaction of conversion of the anion of hydrosulfite into anion sulfate with the release of sulfur dioxide occurs [6]:

$$2\ HSO_3^- + O_2 \leftrightarrow SO_4^{-2} + SO_2 + H_2O \quad (4)$$

Ammonium cation will react with anions of hydrosulfite and sulfate by reactions:

$$NH_4OH^+ + HSO_3^- \leftrightarrow NH_4HSO_3 + H_2O \quad (5)$$

$$2\ NH_4OH^+ + SO_4^{-2} \leftrightarrow (NH_4)_2SO_4 + H_2O \quad (6)$$

Simultaneously with the chemical reactions in the reactor, there are processes of heat and mass transfer between hot flue gas and cold droplets - heating and evaporation of moisture due to the heat of flue gas. By the definition of semi-dry technology in the reactor there should be complete evaporation of the introduced moisture, and the temperature of the treated flue gases should be at least 10 °C above the water dew point [2, 4, 6]. After evaporation of the moisture, NH_4HSO_3 and ammonium sulfate molecules $(NH_4)_2SO_4$ will form aerosols which will precipitate on the surface of bags of fabric filter in the form of particles of up to 5 microns in size, with the reaction of conversion of ammonium hydrosulfite to ammonium sulfate

$$2\ NH_4HSO_3 + O_2 \leftrightarrow (NH_4)_2SO_4 + H_2O \quad (8)$$

The part of the ammonia enters the flue gas from drops of ammonia water in the molecular form. The ammonia concentration in the gas phase depends on the content of ammonia NH_3 in the drops of ammonia water and their temperature [7]. The formation of aerosols of ammonia and sulfur dioxide of submicron size occurs in flue gas containing sulfur dioxide. The main component of such aerosols is amido-ammonium sulfite $(NH_3)_2 \times SO_2$ [8] which in the presence of water vapor and oxygen in the flue gas on the surface of the bags of fabric filter is converted to ammonium sulfate:

$$(NH_3)_2 \times SO_2 + H_2O + \frac{1}{2} O_2 = (NH_4)_2SO_4. \quad (9)$$

A certain part of the gaseous ammonia is absorbed by the drops of technical water due to a high absorbing property of NH_3 [7]. The end-product of the absorption of sulfur dioxide and ammonia in the drops of technical water is ammonium sulfate.

Material and Methods

The peculiarity of ammonium semi-dry desulfurization is the presence of a gas-phase reaction between ammonia and sulfur dioxide. To test this hypothesis, a series of experimental studies was conducted.

In fig. 2. the scheme of experimental laboratory installation for the study of gas-phase reactions is presented. Model gases $N_2 + SO_2$ and $N_2 + NH_3$, as well as pure N_2, are fed to a gas heater in which the separated gases are heated. Next, the model gases $N_2 + SO_2$ and $N_2 + NH_3$ are directed to the gas-phase reactor. Nitrogen passes through a humidifying chamber, where it adds a water vapor.

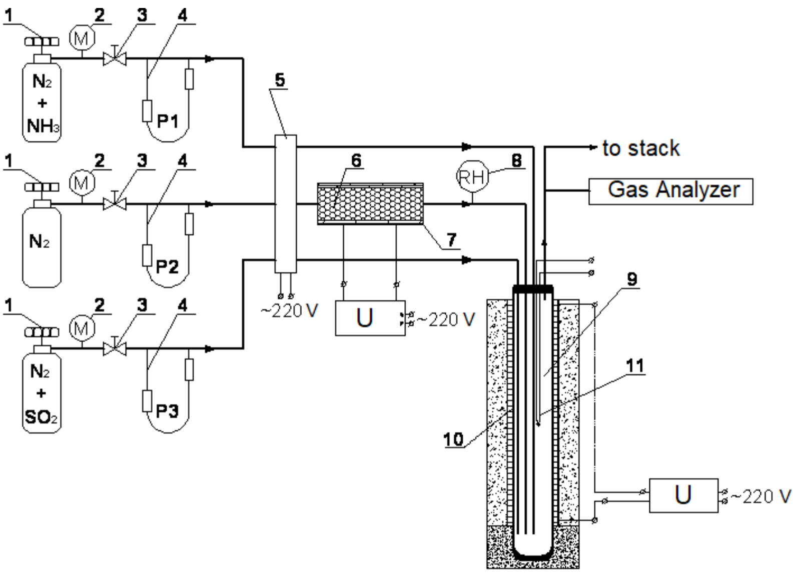

Fig. 2 – Scheme of installation of gas-phase reaction of ammonia and sulfur dioxide in humid conditions.
1 – balloons with nitrogen and mixtures; 2 – gearboxes; 3 – fine control valves; 4 – rheometers; 5 – gas heater; 6 – evaporator; 7 – heater; 8 – a moisture meter; 9 – reactor; 10 – reactor heater; 11 – thermocouple.

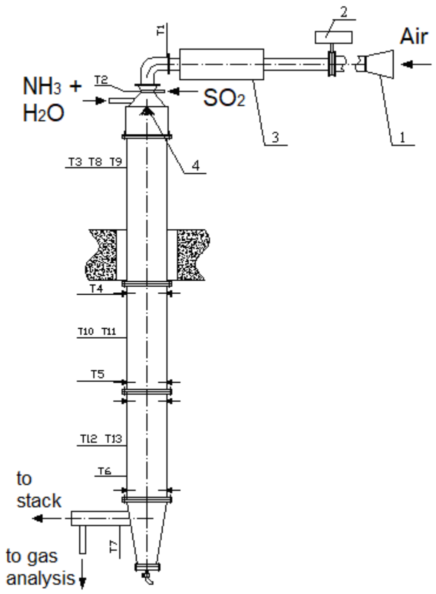

Fig. 3 – Scheme of installation of semi-dry cleaning
1 – air flow regulator,
2 – micromanometer, 3 – electric furnace for air preheating,
4 – ammonia solution atomizer,
T1-T13 – thermocouple.

Experiments were conducted in two modes: mode 1 (the water vapor content in the gas mixture is determined by the final moisture contained in the technical nitrogen balloon) and mode 2 (the water vapor content in the gas mixture is determined by the flow of water supplied to the humidifying chamber). The temperature of the gas mixture in the reactor was higher than 100 °C, which eliminates the absorption of sulfur dioxide in droplets.

A series of experiments were carried out to obtain a complex result of absorption of ammonia sulfur dioxide, in which a solution of ammonia was introduced into the hot gas stream containing sulfur dioxide using a pneumatic nozzle. That is, in the absorption of sulfur dioxide ammonia, dissolved in water droplets, and ammonia, which passed through the desorption from the solution into the gas phase, was involved.

Experimental pilot installation for the study of the process of semi-dry cleaning of flue gases from sulfur dioxide (Fig. 3) is a vertically placed cylindrical reactor with a height of 2600 mm and an internal diameter of 320 mm. To the outlet pipe of the reactor is connected a ID fan, which creates the movement of air through the reactor in the chimney. The air velocity in the reactor is regulated by the change in the passage through the channel. The heating of the air is made using an electric furnace, which is a ceramic tube in which the heating elements are located. The reactor and the supply path of hot air outside have thermal insulation.

Results and discussion

As a result of experiments of the gas-phase reaction of ammonia and sulfur dioxide, the average values of SO_2 concentration after the reactor were obtained and the removal efficiency of sulfur dioxide in mode 1 (with the content of water vapor in the gas mixture determined by moisture contained in the technical nitrogen cylinder) and mode 2 (with the content of water vapor in the gas mixture is determined by the flow of water vapor formed in the chamber of moisture) [9]. In each of the modes, three experiments were performed with a mole ratio of NH_3/SO_2 = 0.89; 1.5; 2.23. According to the results of the research, the dependence of the efficiency of the sulfur dioxide removal on the ratio NH_3/SO_2 was obtained (Fig. 4).

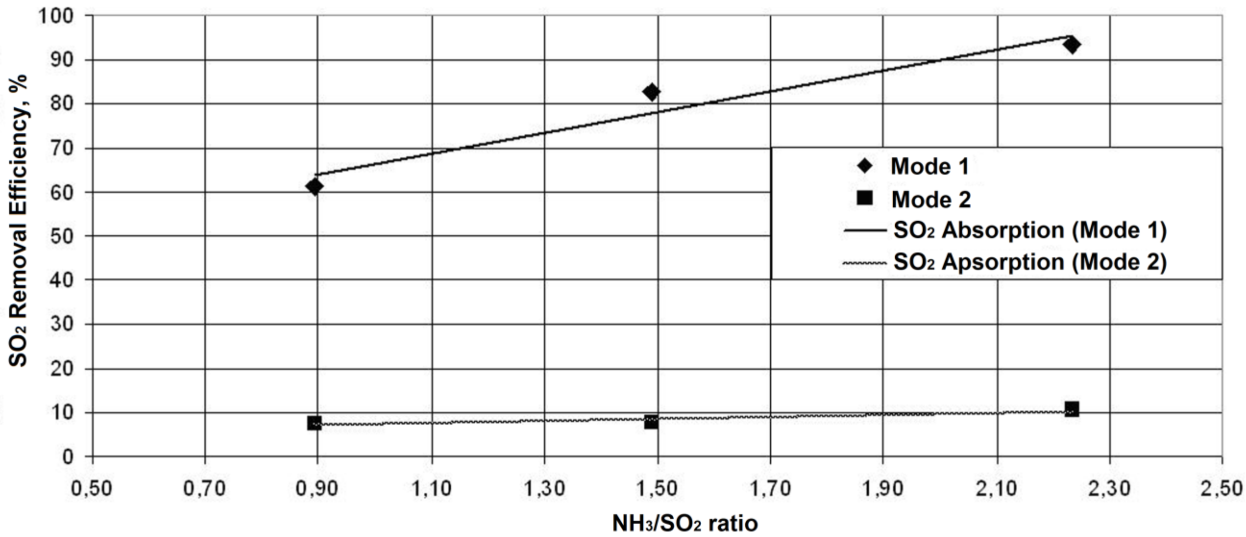

Fig. 4 – Dependence of the efficiency of sulfur dioxide reduction from the molar ratio NH_3/SO_2

These experiments showed that the increase in the water vapor content (change in the molar ratio of H2O / NH3 from 0.21 to 1.08) significantly improves the efficiency of binding of sulfur dioxide to gaseous ammonia (change from 7.9% to 82.8% at the initial molar ratio NH_3/SO_2 = 1.5). This is due to the catalytic effect of water vapor on the reaction of coupling sulfur dioxide with ammonia in the gas phase.

Thus, it has been experimentally proved, that for the gas-phase absorption of sulfur dioxide ammonia, the volumetric concentration of water vapor should exceed the volume concentration of ammonia.

The results of tests of the complex absorption made it possible to experimentally confirm the presence of gas-phase absorption by ammonia and determine the total efficiency of absorption of sulfur dioxide by a solution of ammonia. In all experiments, when the ammonia solution is fed to the reaction zone, the absorption of sulfur dioxide is observed. Input and output parameters of experiments are shown in Table 1.

Table 1

Parameters of experiments on the installation of semi-dry cleaning

Parameter	A	B	C
The gas temperature at the inlet to the reactor, °C	95.4	95.4	88.7
Concentration of SO_2 at the reactor inlet, ppm	600	850	1000
Model gas consumption, l/min	2526	1656	1284
Mass consumption of ammonia solution, g/s	1.72	1.72	1.72
NH_3 mass concentration in solution, %	1.24	1.24	1.24
Initial molar ratio NH_3/SO_2	1.5	1.6	1,7
Concentration of SO_2 at the reactor outlet, ppm	179	215	239
Desulfurization efficiency, %	70.2	74.7	76.1

The obtained data showed that the total efficiency of sulfur dioxide reduction is at the level of 70-76% with a molar ratio of NH_3/SO_2 = 1.5-1.7, which excludes the release of ammonia in ambient air.

The efficiency of removing SO_2 can be greatly increased by increasing the inlet temperature of the gas phases. This will increase the amount of ammonia solution introduced into the reactor and dissolved sulfur dioxide in the liquid. Another leverage for increasing efficiency (by 20%) is an increase in the molar ratio of NH_3/SO_2 to stoichiometric (up to 2).

Conclusions

1. In order to comply with the requirements of Directive 2010/75/EU, it is necessary to promptly implement desulfurization technologies that ensure high efficiency of removal of sulfur dioxide (97% +), are economical and form a useful by-product. Such technology is semi-dry ammonium desulfurization to yield dry ammonium sulfate.

2. The peculiarity of semi-dry ammonium desulfurization is the presence of sulfur dioxide in drops of ammonia solution and the gas-phase reaction between ammonia and sulfur dioxide. Experimentally, the degree of removal of sulfur dioxide (up to 90%) was obtained by reacting SO_2 with ammonia in the gas phase. The determining condition for this effect is the presence in the gas medium of water vapor, the volume concentration of which must exceed the volume concentration of ammonia.

3. Experimental studies of complexly semi-dry ammonium desulfurization confirmed the high efficiency of this technology, even in conditions of low input temperature of gas and molar ratio NH_3/SO_2 less than 2.

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