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Catalytic flue gas conditioning in electrostatic precipitators of coal-fired power plants

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ABSTRACT

The paper is dedicated to development of the catalytic process for controlled SO_3 production for conditioning of flue gases from coal-fired power plants. On the basis of comparative technological analysis performed for different variants of the process arrangement, it was shown that optimal technological decision is catalytic sulfur dioxide oxidation in synthetic SO_2-containing stream in a separate reactor with two adiabatic beds of catalyst with following introduction of SO_3-containing flow into the main coal boiler gas duct. Undoubted benefits of this process are: complete independence of the process from the flue gases properties; possibility to control SO_3 concentration in the flue gases in the wide range; possibility to process gases with high SO_2 concentration, providing low gas flow rate and low catalyst loading; absence of limitations for the pressure drop of the catalyst bed. Among catalysts on the basis of fiber–glass support the best catalytic performance was observed for platinum-containing catalyst on support modified with zirconium dioxide. It was demonstrated that optimal catalyst solution is combination of conventional granular vanadia and platinum woven fiber–glass catalysts, providing high activity both at high and low temperatures.

1. Introduction

Coal-fired power generation capacity in the Russian Federation is approximately 29 GW, accounting for about 19% of the total electricity generation in the area. Though some decrease of coal consumption in Russia was observed in the 1990s, it is projected that coal's share of fuel usage in the country will be increased due to the fast rise of natural gas prices. With a large amount of the coal used in Russian power plants having an ash content that exceeds 40 wt.%, particulate matter (PM) retention in the flue gas is still a rather urgent problem [1].

Almost a half of such power plants are equipped with electrostatic precipitators (ESPs) for controlling the PM emissions from boilers. The collection efficiency of the ESP partially depends on the electrical resistance of the fly ash. Ash that is too resistive is difficult to charge and collect, and once collected, is difficult to remove from the ESP collection electrodes. High resistance ash can also cause "back corona," in which corona is generated on the collection electrodes, further degrading precipitator performance [2]. Estimates indicate that at typical flue gas temperatures of 140–150 °C, the combustion products of about 40% of the coal fired in Russian and ex-USSR power plants possess unfavorable electro-physical properties.

Therefore, there is great value in increasing the efficiency of ESPs by lowering the resistance of fly ash. This may be accomplished by an ESP upgrade technique known as flue gas conditioning. Injecting small concentrations (2–10 ppm) of SO_3 is a proven way to condition the flue gas for improved ESP performance [3–5]. The surface absorbed SO_3 (or H_2SO_4) is very electrically conductive and effectively lowers the resistance of the bulk fly ash. Controlled catalytic oxidation of SO_2 may be a cost-effective upgrade to condition the flue gas for improved ESP performance.

In general the catalysts and processes for oxidation of SO_2 are well studied [6], but the flue gas conditioning case implies specific requirements that reflect a significant difference from conventional cases. The most important factors are: huge flow rates of flue gases, presence of water vapor and PMs in the flue gas and a tight limitation on duct pressure drop. Additionally, it is important to deliver the SO_3 in a controlled manner, because the lack of sulfur trioxide may lead to insufficient gas conditioning, while excess of SO_3 may cause accelerated corrosion of flue gas duct and ESP. Obviously,

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the conditioning technology should be economically feasible and resource-saving.

In this research an attempt was made to reconsider the conventional SO_2 oxidation technology both in terms of optimal catalysts and optimal process arrangement in respect to flue gas conditioning.

2. Preliminary selection of the catalysts

The following criteria for primary selection of the catalysts were formulated with account of the flue gas conditioning processes specifics:

- Catalysts activity in SO_2 oxidation and the temperature window of their efficient operation.
- Catalysts stability and resistance to deactivation.
- Operation ability in humid and dusty fluids and under low concentrations of SO_2.
- Catalyst price.
- Catalyst market availability.
- Possibility of creation of structured catalyst packings with low-pressure drop.

Existing information on catalysts was analyzed with account of two basic cases of their application in flue gas conditioning processes: in case of their placement directly in the media of flue gases and in case of their placement in the media of separate SO_2-containing stream (see below).

Main attention should be paid to following groups of catalysts (Fig. 1).

2.1. Catalysts on the base of vanadium pentoxide

Such catalysts, containing of V_2O_5 and alkali sulfates, supported at granular porous supports on the base of SiO_2, are the main catalysts of sulfur dioxide oxidation in world commercial practice from 1940s until current time [6]. Such catalysts are characterized with reasonable price and practically unlimited availability at the domestic and world markets. Vanadia sulfuric acid catalysts have appropriate activity and operation stability within the temperature range from 370–400 °C up to 620–650 °C. In relation to the flue gases of coal-fired power plants (provided that process temperature exceeds the dewpoint of formed sulfuric acid) it should be noted, that these catalysts could work in humid streams. But these catalysts: (a) do not have necessary activity and operation stability under low concentrations of SO_2 (below 0.1 :vol.%), (b) may undergo deactivation by components of flue gases (micro-admixtures of volatile compounds of arsenic, selenium and fluorine, and solid components of dust particles) [6] and (c) the technology of production of such catalysts in structured form (for example, in form of monolith honeycombs), giving the way to create the catalysts beds with low-pressure drop and to avoid dust accumulation, is not developed at the commercial level.

2.2. Carbon-based catalysts

The catalysts for oxidation of sulfur dioxide on the base of activated carbons are also known [7]. Evident advantages of such catalysts are: (a) very low value of lower operation temperature (~120–150 °C), (b) relatively high activity and operation stability under low SO_2 concentrations, and (c) ability to work in humid fluids. Theoretically, the oxidation of sulfur dioxide is possible using inexpensive conventional types of granular activated carbons. But, as it was shown by our special research performed earlier, conventional carbons with large fraction of micro- and mesopores (1–10 nm) in the porous structure have a strong capillary pressure inside the pores, which leads to condensation of sulfuric acid, which may form in the media of humid gases. It results in the practical absence of sulfur trioxide in gaseous reaction products, and the catalyst quickly loses activity because of pore blocking. Further, conventional activated carbons have quite low mechanical strength.

It is possible to overcome all these complications by application of specific types of activated pyrocarbons with high fraction of mesopores (~10–40 nm) and practical absence of micropores, example being carbon materials Sibunit [8,9]. At the same time such materials are characterized by a much higher price and are produced in limited amounts, complicating their wide commercial application in the conditioning process. Additional problem, similar to the case of vanadia catalysts, is lack of experience of commercial production of such catalysts in form of honeycombs and other structured forms. It is possible to conclude, that carbon materials on the base of Sibunit may be further considered placement directly in the media of flue gases at low temperatures (120–200 °C), though such application should be considered in more detail. Concerning application of carbon catalysts in streams with high SO_2 concentration, it should be noted that performance of exothermic reaction of sulfur dioxide oxidation is connected with significant adiabatic heat rise; therefore, even at moderate inlet temperature the maximum temperature in the catalyst bed may reach 250–300 °C. Such temperatures make possible the interaction of carbon with oxygen and sulfur dioxide, resulting in carbon burning and formation of undesirable by-products (CO, CO_2, COS, CS_2, and elemental sulfur). Due to that reason application of carbon-based catalysts in concentrated SO_2-containing streams does not seem reasonable.

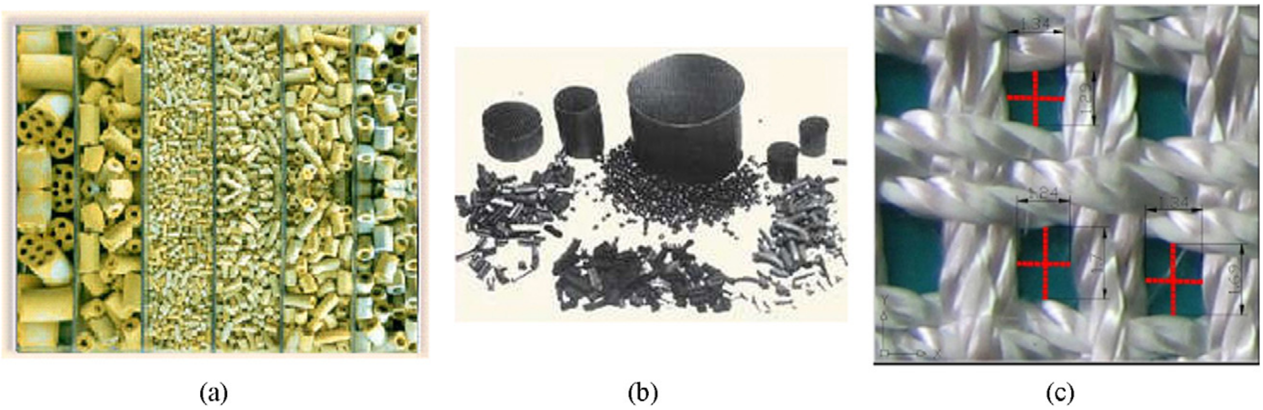

Fig. 1. Catalysts for oxidation of sulfur dioxide: (a) sulfuric acid vanadia catalyst, (b) Sibunit carbon, and (c) platinum on fiber–glass.

2.3. Platinum-based catalysts

Catalysts using platinum are known since the end of 19th century, when they were applied in sulfuric acid industry, until they were finally replaced by vanadia systems [6]. Advantages of such catalysts are: high activity, relatively low minimum border of temperature window (~300 °C), their working ability under low concentrations of SO_2 and the ability to produce them in a form of honeycombs. On the other hand, these catalysts are characterized with very low resistance to deactivation, high platinum losses and extremely high cost, being a result of big platinum content (up to few mass%).

New generation of platinum catalysts on the fiber–glass supports was developed recently [10–12]. In these catalysts the glass micro-fibers, structured in form of threads in glass fabric of various structures, are used as supports for active components. In relation to sulfur dioxide oxidation the most prospective types of active species are platinum and vanadia. Such catalysts contain the catalytically active nano-sized structures, where platinum exists in highly dispersed state with size less than 1 nm [10,11]. Such a platinum state provides its unique catalytic properties, which cannot be realized with the other types of supports. In many reactions such catalysts demonstrate high activity and selectivity and extremely high stability and resistance to deactivation of such catalysts is observed in different aggressive media. A very important advantage of these catalysts is the low platinum content (at the level of 0.01–0.05 mass%), resulting in their relatively low cost. Preliminary tests of fiber–glass catalysts in SO_2 oxidation reaction showed their high activity, high resistance to deactivation, wide temperature window of efficient operation (300–800 °C) and ability to work in humid fluids and under low concentrations of SO_2. A very important characteristic of fiber–glass catalysts is their original geometrical structure and mechanical flexibility, opening unique possibilities for creation of new types of structured beds with low-pressure drop which are useful with heavy dusty fluids (though, the latter requires the additional check and experimental confirmation). In summary Pt/fiber–glass catalysts are of interest for cases of catalysts positioned in flue gases and in separate SO_2-containing stream. Moreover, it is reasonable to consider the fiber–glass catalysts on the base of vanadia as well.

3. Choice of optimal process flow sheet

In development of the process flow sheets two basic routes for process performance were considered:

1. *Oxidation of SO_2, present in the flue gases of coal-fired boilers, directly in the flue gases* [9,13–15]. Sulfur dioxide, being the product of oxidation of sulfur–organic compounds, present in coal, is a common component of flue gases from coal-fired boilers. Therefore, it seems attractive to use this SO_2 for production of SO_3. Except the conditioning of flue gases to improve dust removal in ESPs, this case seems to be useful as a way to decrease sulfur emission to atmosphere.
2. *Oxidation of SO_2 in separate stream with high concentration of SO_2* [16–18]. In this case it is proposed to perform sulfur dioxide oxidation in separate reactor and to introduce afterwards the reaction products, containing SO_3, into boiler gas duct. It is proposed to use synthetic SO_2-containing streams (for example, produced by combustion of elemental sulfur), as a way to maintain high enough concentration of sulfur dioxide.

For the first route different positions for the catalysts in the flue gas streams were considered (see Fig. 2):

- 1a. Directly in the gas duct in the low-temperature zone between air-heater and ESP.
- 1b. In the bypass duct in the low-temperature zone between air-heater and ESP.
- 1c. Directly in the gas duct in the high-temperature zone between economizer and air-heater.
- 1d. In the bypass duct in the high-temperature zone between economizer and air-heater.

For comparative analysis of these cases the standard Russian boiler TPP-210A with steam productivity of 950 tonnes/h, which is used at coal-fired power plants in Russia and ex-USSR countries in energy blocks with electrical power of 300 MW was considered. The flow rate of flue gases in such boiler under nominal loading is equal to 1.2 mln.m^3/h). The average temperature of flue gases in the low-temperature zone (between air-heater and ESP) is 130–160 °C, and in high-temperature zone (between economizer and air-heater) 420–430 °C. In case of combustion of Kuznetsk and Ekibastuz coal the content SO_2 in flue gases is equal to 600–900 mg/m^3 (~200–300 vppm). The reserve of the gas duct pressure drop (the limit value of hydraulic resistance of devices, which may be positioned inside the duct) depends upon the boiler technical condition, but in common for currently operating boilers it does not exceed 50 mm WC.

Optimal concentration of SO_3 was defined on the base of calculated and experimental data for typical coal used at Russian power plants. It was shown, that for Kuznetsk and Kaschimsk coal at typical ESP operation temperature (130–160 °C) the optimal concentration is equal to ~10 vppm SO_3, while for Ekibastuz coal it may be as high as ~70 vppm.

For high-temperature cases (1c and 1d) the application of conventional vanadia and fiber–glass catalysts was considered, for low-temperature (1a and 1b) carbon catalysts on the base of Sibunit were studied.

3.1. Route 1: in-duct catalyst positioning

Calculation results for route 1 for different types of coal are given in Tables 1 and 2. For calculations the average SO_2 content in flue

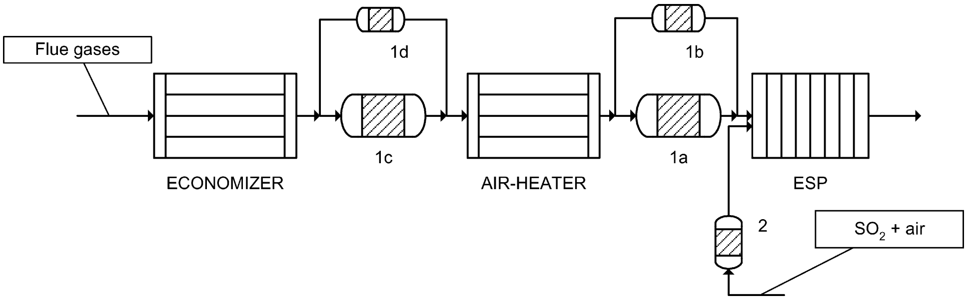

Fig. 2. Flow sheets of catalyst positioning in the sulfur dioxide oxidation process.

Table 1
Process parameters for Kuznetsk coal.

Case	Catalyst	Required level of SO_2 conversion, %	Flue gases flow rate in the catalyst bed, st.m^3/h	Required catalyst loading, m^3/tonnes	Catalyst bed pressure drop, mm WC
1a	Sibunit, granular	4	1,200,000	330/200	>3000
1b	Sibunit, granular	100	48,000	27/16	>1000
1c	V_2O_5/SiO_2, granular	4	1,200,000	233/180	>2000
1d	V_2O_5/SiO_2, granular	100	48,000	30/24	>1000
1c′	Fiber-glass catalyst	4	1,200,000	160/20	~250
1d′	Fiber–glass catalyst	100	48,000	24/8	~150

gases equal to 250 vppm was used. Required level of SO_2 conversion was calculated from the value of final sulfur trioxide concentration of 10 ppm for Kuznetsk coal and 70 ppm for Ekibastuz coal. Calculations of bypass cases 1b and 1d were based on ~100% conversion of SO_2 (with account of sulfuric acid formation).

From the presented information it is possible to make the following conclusions:

- Cases with positioning of carbon and vanadia catalysts in the main flue gas duct (1a and 1c) require extremely high catalysts loadings (up to 500 m^3). Except the high cost of loaded catalysts, such cases are practically inappropriate due to absence of space of necessary volume in the duct. Concerning Sibunit-based catalysts it should be also noted that such volume (up to 300 tonnes per one boiler) exceeds the volume of its today's commercial production, what significantly limits its practical prospective in respect to described application.
- In all cases of granular catalysts (1a–1d) application, the inadmissibly high level of catalyst bed pressure drop, significantly exceeding the limiting level (50 mm WC), is observed. Another, even more serious, problem is possibility of dust deposition in the bed of granular material, leading to fast bed blocking by dust and, in fact, to boiler shutdown. Theoretically, it is possible to decrease the catalyst pressure drop and to provide their workability in the conditions of dusty fluid by application of structured catalysts (in form of honeycomb monoliths), however, in the current commercial practice the production of vanadium-oxide and Sibunit monoliths is practically absent.
- It is possible to solve to some extent the dust deposition and pressure drop problems by application of structured beds of fiber–glass catalysts.
- The positioning of all types of catalysts in the main flue gas duct (1a, 1c and 1c′) are different from others in that they provide no practical possibility for the control the sulfur trioxide concentration in flue gases, as well as no possibility of any process control in course of operation in general. Theoretically, some control systems may developed (for example, by means of controlled shielding of a part of the catalyst bed from contact with gas), however, actual application of any such devices will lead to the rise of the duct pressure drop above the admissible level.
- It is possible to overcome the problems with pressure drop in the flow sheets with gas bypassing (1b, 1d, and 1d′) provided that bypass contour will include the gas pump for pumping of bypassed flue gases. In this case it is necessary to take into account the additional energy consumption for such pumping (for granular catalysts such consumption may reach 250 kW for Kuznetsk coal and up to more than 1.5 MW for Ekibastuz coal). The only acceptable case that of with fiber–glass catalysts (1d′), where energy consumption does not exceed 40 kW (for Kuznetsk coal). Notably, in all these cases there exists the issue of reliable gas pump operation under high dust content and its elevated temperature (above 400 °C), solution for which does not look evident.
- The advantage of bypass cases (1b, 1d, and 1d′) is the opportunity to control the flow rate of flue gases in the bypass and, consequently, the possibility to control the concentration of SO_3 in flue gases.
- Bypass flow sheets (1b, 1d, and 1d′) offer a way to decrease the catalyst loading and, correspondingly, its cost. However, it is necessary to take into account that for positioning of the catalysts in the bypass stream the creation of separate reactor is necessary. Cost of such reactors may be quite high, thus reducing the positive impact of the decrease of catalyst cost.

In summary, it is possible to exclude from further consideration all cases, connected with direct positioning of the catalyst inside the main flue gas duct (1a, 1c, and 1c′), as well as all cases connected with application of granular catalysts (1a–1d). The only one relatively promising case from all cases of oxidation of SO_2, contained in the flue gas, is case 1d′, proposing the application of fiber–glass catalyst in the separate bypass reactor. However, the final conclusion on workability of such process may be made only after the performance of direct experiments on filtration of dusty flows through the structured beds of such catalysts.

3.2. Route 2: separate stream oxidation

Fig. 3 shows the flow sheet of the process, realizing the technological route 2. In this case the initial SO_2-containing mixture is formed by combustion of elemental sulfur, then this mixture goes through the reactor, where oxidation of sulfur dioxide into trioxide takes place, and afterwards the SO_3-containing flow is fed into main boiler duct (preferably: directly before the ESP).

Calculated parameters for this process are given in Table 3. The calculation was made for fiber–glass catalyst for the gases of elemental sulfur combustion, containing 10 vol.% SO_2.

It is seen that in all significant parameters this process is much more advantageous than all processes of technological route 1. Particularly, the required catalyst loading volume in this case is 100

Table 2
Process parameters for Ekibastuz coal.

Case	Catalyst	Required level of SO_2 conversion, %	Flue gases flow rate in the catalyst bed, st.m^3/h	Required catalyst loading, m^3/tonnes	Catalyst bed pressure drop, mm WC
1a	Sibunit, granular	28	1,200,000	500/300	>3500
1b	Sibunit, granular	100	336,000	190/114	>1000
1c	V_2O_5/SiO_2, granular	28	1,200,000	350/280	>2500
1d	V_2O_5/SiO_2, granular	100	336,000	200/160	>1000
1c′	Fiber–glass catalyst	28	1,200,000	240/30	~250
1d′	Fiber–glass catalyst	100	336,000	140/18	~150

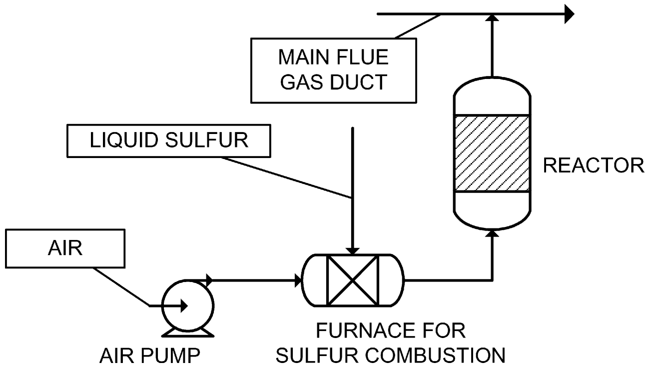

Fig. 3. Flow sheet of the process corresponding to technological route 2.

times less than this value for case 1d′. The similar ratio relates to reactor capital cost and to required energy consumption.

Undoubted benefits of this process route are:

- complete independence of the process from flow rate, composition and temperature of the flue gases;
- possibility to control SO_3 concentration in the flue gases in the wide range;
- complete absence of dust in the gas flow;
- possibility to process gases with high SO_2 concentration, thus providing low gas flow rate and low catalyst loading;
- absence of limitations for the pressure drop of the catalyst bed.

A disadvantage of this case is consumption of side feed (liquid sulfur), though, as it is seen from Table 3, the overall demand for sulfur appears to be appropriate.

Some anxiety may be expressed to the fact, that incomplete conversion of sulfur dioxide in the reactor will lead to the rise of SO_2 discharged into atmosphere with flue gases. However, this rise will not exceed 2–3 vppm for Kuznetsk coal and 15–20 vppm for Ekibastuz one, which, for background concentration of SO_2 in flue gases of 200–300 vppm, does not seem to be a critical value.

4. Fiber–glass catalysts investigation

4.1. Synthesis of fiber–glass catalysts samples

The synthesis of Pt/FG and V/FG catalysts, different in composition of glass support (in content of Al, Zr, and Na), type of weave, nature and content of active component (Pt or VO_x) was performed.

Platinum-containing catalysts were prepared by impregnation of FG textiles by water solutions of platinum precursors. Depending upon the impregnation solution concentration and method of synthesis the samples contained 0.01–0.05 mass% of platinum.

Vanadia-containing catalysts were prepared by impregnation of Al–Si support by water solution of vanadyl oxalate VOC_2O_4. Depending upon the concentration of impregnation solution and conditions of preparation the samples contained 0.34–0.77 mass% of vanadium.

4.2. Catalyst characterization

The properties of SiOH groups were studied by the method of infra-red spectroscopy (IRS) diffusion reflectance [10] using Shimadzu 8300 spectrometer equipped with diffusion reflectance prefix DRS-8000 in the range 400–7000 cm^{-1} with resolution of 4 cm^{-1}.

The IRS in the standard variant appeared to be not appropriate for the study of fiber–glass materials. After stirring of fibers into powder their structure is destroyed and this leads to doubts about the adequacy of obtained data and properties of initial fibers. The use of IRS microscopes makes possible to work with samples down to 50 μm in size, while the size of studied fibers is below 10 μm. Transmission methods allowing the study of the plates with the thickness down to 100 μm with the size of not less than 10 mm × 10 mm, which can hardly be produced from fibers. Diffusion reflectance methods do not contain quantitative analysis possibilities.

In this research we used semi-quantitative analysis method, combining transmission and diffusion reflectance techniques. For registration of IR-spectra the fibers (20–40 mg) were maximally uniformly placed in a form of a circle with diameter of 15–20 mm at the aluminum mirror, which was positioned in the diffusion reflectance cell. In this case it was possible to record the sum of the light, transmitted through the sample and diffusionally reflected from the layer of known thickness. Finally, the accuracy of concentration of OH groups measurement was ±30%.

The state of supported Pt in catalysts was estimated by means of UV–vis spectra of diffusion reflectance, recorded by a Shimadzu 4501 spectrometer, equipped with ISR-250 attachment, after calcination of samples in air at 350 °C with following reduction at 350 °C during 1 h and cooling in the hydrogen flow down to ambient temperature.

The study of fiber–glass supports by IRS of adsorbed OH groups showed that in spectra of Al–Si glass supports the absorption band 3740 cm^{-1}, typical for traditional silica gels and relating to isolated OH groups at the external surface, is absent. It seems that this absence is caused by the small value of the unit surface of glass fabric. IR spectra contains the wide band ca. 3400 cm^{-1}, which may be referred to superposition of bands of three types of hydrogen-bonded OH groups: molecular water, SiOH groups, connected with water by hydrogen bond and also neighboring OH groups, con-

Table 3
Technological parameters of the process for the route 2.

No.	Parameter	Meas. unit	Value	
			Kuznetsk coal	Ekibastuz coal
1	Gas flow rate	st.m^3/h	155	1085
2	SO_2 conversion in the reactor	%	78	
3	Production capacity in respect to SO_3	st.m^3/h	12	84
4	SO_3 content in flue gases	vppm	10	70
5	Gas temperature at the reactor inlet	°C	350	
6	Gas temperature at the reactor outlet	°C	580	
7	Catalyst loading	l/kg	50/6	350/40
8	Reactor pressure drop	mm WC	Not higher than 250	
9	Energy consumption of the air pump	kW	0.2	1.4
10	Liquid sulfur consumption	kg/h	22	154
11	Annual sulfur consumption	Tonnes	176	1232

nected by strong hydrogen bond in the fragments SiOH·OHSi. Despite the similarity in chemical composition to traditional silica gels, the IR spectra of silica fiber–glass supports contain relatively narrow band at 3640 cm^{-1} with half-width of 65–75 cm^{-1}, corresponding to OH groups in the volume of glass fibers. The total amount of OH groups in Al–Si glass–fiber support dried at 110 °C is equal to ∼5000 μmol/g.

IR spectra of Zr–Si glass fabric are similar to those for Al–Si samples, i.e. instead of the typical band for usual silica gels absorption ∼3740 cm^{-1} the intensive and narrow band shifted to the low-frequency area of 3590 cm^{-1} is observed. Presumably, this support, like the Al–Si one, contains significant amount of OH groups, localized in the volume of glass fibers or in microcavities, formed during leaching.

According to presented UV–vis spectra of diffusion reflectance it is seen that platinum in Pt/SiFG catalysts may exist in three states:

- Pt^{2+}: in form of two-valent ions (bands 22,000–26,000 cm^{-1}),
- Pt^0: in form of metallic particles (bands in the region 49,000–52,000 cm^{-1}),
- $Pt^{\delta+}$: $2 < \delta < 0$, in form of charged metal clusters (bands in the region 34,000–42,000 cm^{-1}).

An estimation of the ratio of integral intensity was performed following the decomposition of observed spectra into individual Gauss components. Intensity was defined as area under Gauss curves outlining the contours of selected absorbance bands 38,000 ± 4000 cm^{-1} and 50,000 ± 4000 cm^{-1}.

Comparison of spectra for different catalysts shows that increase of platinum content in the sample leads to increase of Pt^0 fraction in from of metallic particles with constant fraction of platinum in clusters.

UV–vis spectra for a zirconium-containing sample with platinum, reduced at 300 °C and obtained from solutions with different platinum concentrations: 1 and 3 g/l are given in Fig. 4. It is seen that amount of platinum clusters, obtained during impregnation of fiber–glass fabrics by solutions with different Pt content, is equal. Increase of platinum concentration has led only to formation of metallic particles localized at the external surface of the fibers. For the sample with increased platinum content there are also clearly evident bands in the region 20,000–25,000 cm^{-1} being an evidence of partial oxidation of small metal particles in contact with air atmosphere.

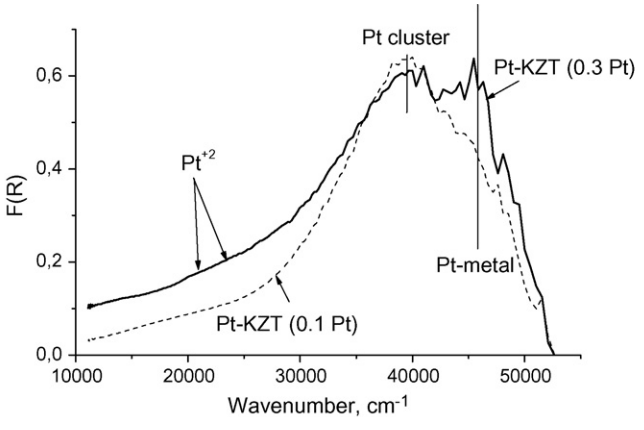

Fig. 4. UV–vis spectra for Zr-containing sample with platinum, reduced at 300 °C and obtained from solution with different platinum concentration: 1 g/l (marked as 0.1) and 3 g/l (marked as 0.3).

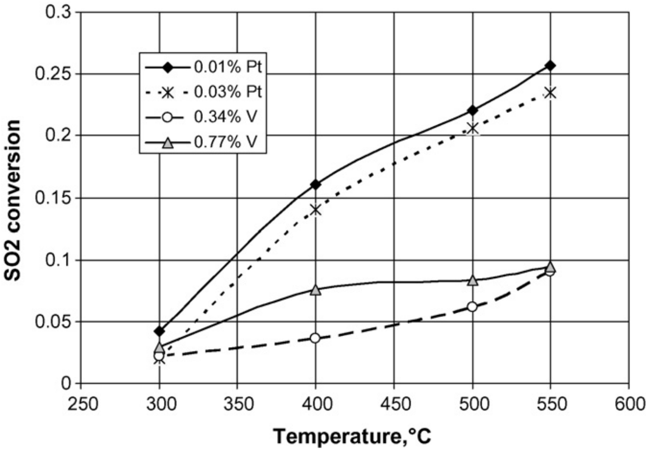

Fig. 5. Dependence of sulfur dioxide conversion upon reaction temperature at platinum (Pt) and vanadia (V) fiber–glass-based catalysts. Notations show the concentration of active component calculated for metal in mass%.

4.3. Catalyst samples screening

The testing technique included loading of the catalyst sample (in form of separate fibers) into the reactor. The testing was performed in the temperature range 250–600 °C (with initial temperature increase from minimum to maximum and then vice versa). At each temperature the testing was held until an achievement of the steady-state catalyst performance. Sulfur dioxide concentration was maintained at the level of 1.0–2.0 vol.%, oxygen: 3.0–4.0 vol.% (with helium as balance). Catalyst loading in each experiment was 0.17 g, reaction mixture flow rate 51 ml/min.

During the preliminary screening the catalysts on the base of silica and silica–alumina fiber–glasses were excluded from consideration since they lacked sufficient thermal stability.

Other results on conversion of sulfur dioxide with different catalysts using zirconia fiber–glass supports upon temperature are represented in Fig. 5.

Thus the paradox of higher activity of the sample with lower Pt content (0.01%) was discovered. Notably, the highly dispersed platinum in charged clusters is dominating in the sample with low platinum content, while in the sample with higher Pt loading such domination belongs to metallic platinum. Therefore, the initial theoretical proposition that platinum clusters are the most catalytically active type of platinum [10,11] was finally confirmed.

Regarding vanadia catalysts, the sample with higher vanadium content was predictably found to be more active. Anyway, activity of both these samples was too low for inclusion in the final consideration.

An additional line of experiments was preformed for comparison of platinum fiber–glass catalysts with conventional granular vanadia catalysts, such as Russian commercial catalyst IC-1-6, with results represented in Fig. 6. It is seen that conventional vanadia catalyst has high activity at temperatures above 400 °C, much exceeding platinum fiber–glass activity starting from ∼420 °C.

From the other hand, the platinum catalyst has higher activity in low-temperature area. This factor is very important, because low-temperature activity offers the way to decrease minimum operation temperature in the sulfur dioxide oxidation process. In adiabatic catalyst beds it will lead to decrease of maximum process temperature, a benefit for increasing the equilibrium conversion of SO_2.

The simple combination of advantages of both catalysts may be provided by mechanical mixture of two catalysts. Fig. 6 demonstrates the results of experiments on research of catalytic activity

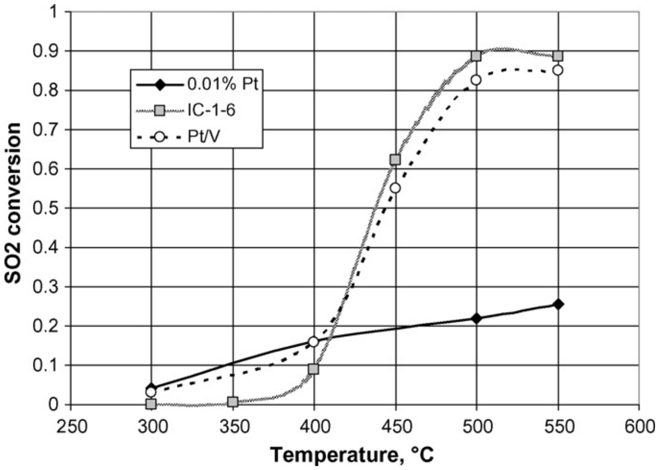

Fig. 6. Dependence of sulfur dioxide conversion upon reaction temperature with different catalysts. Notations: 0.01% Pt: platinum sample on zirconia-containing fiber–glass with Pt content of 0.01%; IC-1-6: conventional commercial granular vanadia catalyst; Pt/V: mixture of mentioned catalysts (in mass ratio 1:1). Experiments held with equal total mass of samples.

of the combined catalytic system, consisting from mixture of platinum-containing glass fibers and crushed pellets of vanadia catalyst IC-1-6. It is seen, that a combined system can successfully unite the positive features of both catalysts.

5. Process simulation and optimization

At this stage of the research the development and preliminary optimization of the sulfur dioxide installation flow sheet was performed. The flow sheets with one, two and three adiabatic catalysts beds were considered (Fig. 7) with application of an equilibrium simulation approach. For each case the variation of reaction gas temperature at the inlet to each catalyst bed was simulated. Afterwards, the mixing of the product stream with flue gas stream was simulated (flue gas flow rate 1.2 mln.st.m^3/h, sulfur dioxide content in flue gas 250 ppm). The system parameters necessary to achieve a sulfur trioxide concentration in flue gases equal to 10 ppm were calculated.

The simulation showed that optimal temperature of the reaction gas at the inlet to the catalyst bed is ~350 °C for all catalyst beds. The simulation results for different flow sheets are represented in Table 4.

It is seen form Table 1 that in all cases the residual concentration of sulfur dioxide in flue gases is almost constant and its variation is negligible compared to its basic concentration. However, a significant (almost 20%) decrease of sulfur consumption is observed during the transfer from one-bed flow sheet (I) to two-bed scheme (II). The further increase of number of beds to three (flow sheet III) does not introduce significant changes into process characteristics. Therefore, it may be stated that the two-stage flow sheet is optimal for this process.

The kinetic modeling of the sulfur dioxide oxidation process in the two-stage flow sheet was performed. A common two-temperature one-dimensional adiabatic plug flow reactor model [19] was used in simulation. Data on SO_2 oxidation kinetics at conventional vanadia catalysts was taken from literature [6].

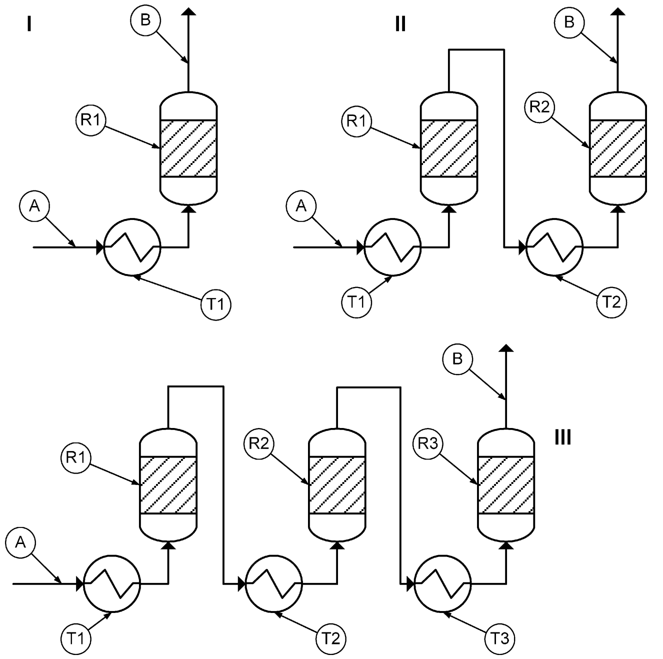

Fig. 7. Flow sheets with one (I), two (II) and three (III) adiabatic catalyst beds: (A) initial SO_2-containing mixture and (B) product SO_3-contining mixture: T, heat exchangers; R, catalyst beds.

For a description of reaction kinetics at fiber–glass catalysts and combined Pt/V system we used experimental data, obtained in current research. It was found that reaction rate might be described with the linear kinetic equation in respect to SO_2 and O_2 concentrations with account of reaction reversibility:

$$W = k_0 \exp\left(-\frac{E}{RT}\right) C_{SO_2} C_{O_2} \left(1 - \frac{C_{SO_3}}{C_{SO_2} C_{O_2}^{0.5} K_P(T)}\right) \tag{1}$$

where k_0 is the kinetic pre-exponent (st.ml of SO_2 per g of catalyst per sec), E the activation energy (kJ/mol), R the universal gas constant (kJ/(mol K)), T the temperature (K), C_i the concentration of reacting species (molar fractions), and K_p is the equilibrium constant.

Data fitting have shown that optimal description of experimental results is achieved with the following kinetic parameters: $k_0 = 4.53 \times 10^2$ st.ml$_{SO_2}$/(g$_{cat}$ s), $E = 51.6$ kJ/mol. In this case the proposed kinetic equation provides good agreement between experimental and calculated data in the wide area of sulfur dioxide and oxygen concentrations (Fig. 8). Nevertheless, the given kinetic model is preliminary and performance of more detailed investigation in this area seems reasonable.

Fig. 9 shows the simulated dependence of sulfur dioxide conversion from gas temperature at the inlet to each of two catalyst bed sections for following conditions: initial concentration of sulfur dioxide: 10 vol.%, oxygen: 13%, balance: nitrogen; height of each catalyst section: 0.6 m.

Table 4
Comparative characteristics for flow sheets I, II and III.

Flow sheet	Total degree of SO_2 conversion	Consumption of elemental sulfur, kg/h	Residual content of SO_2 in flue gases, ppm
I	84.1%	19.9	252
II	99.1%	16.6	250
III	99.5%	16.5	250

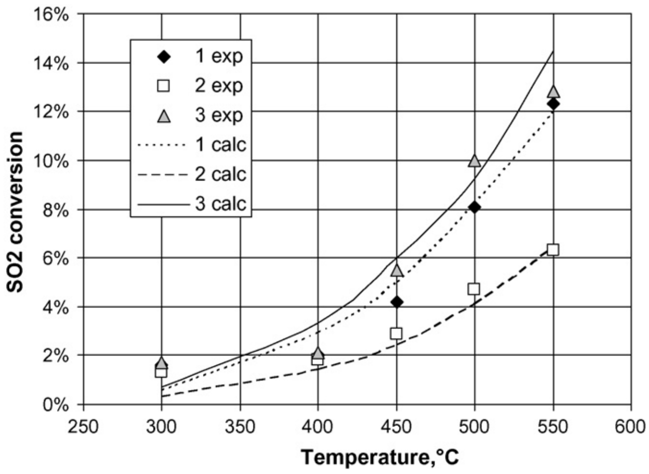

Fig. 8. Data on sulfur dioxide conversion vs. temperature for different inlet mixture compositions: (1) 1.6 vol.% SO_2 and 3.4 vol.% O_2, (2) 3.4 vol.% SO_2 and 1.7 vol.% O_2, (3) 1.0 vol.% SO_2 and 4.0 vol.% O_2. Points correspond to experimental data, lines: to calculations via Eq. (1).

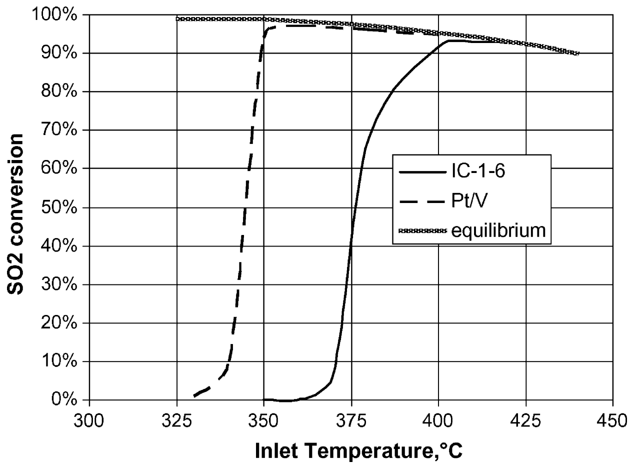

Fig. 9. Dependence of achievable sulfur dioxide conversion from inlet gas temperature for different types of catalysts (IC-1-6, conventional granular vanadia catalyst; Pt/V, combined system; green line shows the equilibrium conversion limits).

It is seen that for each catalyst the conversion rises with the rise of temperature, leading to reaction rate increase. However, with further temperature rise the conversion reaches the equilibrium level and starts to decrease. It results in existence of an optimal value of inlet gas temperature for each catalyst. Due to higher low-temperature activity of the combined system this optimum is visibly shifted to areas of lower temperatures in comparison with pure conventional vanadia catalyst (ca. 350 °C for Pt/V instead of ~405 °C for IC-1-6). This temperature shift leads to improvement of equilibrium limitations in the case of the combined system and corresponding increase of SO_2 conversion.

6. Conclusion

The comparative technological analysis performed for different variants of the flue gas conditioning process arrangement has shown that optimal technological decision is catalytic sulfur dioxide oxidation in synthetic SO_2-containing stream in a separate reactor with two adiabatic beds of catalyst with following introduction of SO_3-containing flow into the main coal boiler gas duct. The undoubted benefits of this process are: complete independence of the process from the flue gases parameters (flow rate, temperature, SO_2 content, limitations on pressure drop, etc.); possibility to control SO_3 concentration in the flue gases within a wide range; possibility to process gases with high SO_2 concentration, providing low gas flow rate and low catalyst loading; absence of limitations for the pressure drop of the catalyst bed.

New SO_2 oxidation catalysts on the base of platinum supported on glass fibers were investigated. Among such catalysts the best catalytic performance was observed for low-platinum (Pt content 0.01–0.03 mass%) catalyst on zirconia-containing fiber–glass support, showing good activity in low-temperature area. It was demonstrated that optimal catalyst solution is combination of conventional granular vanadia and platinum woven fiber–glass catalysts, providing high activity both at high and low temperatures.

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