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State of the art in the field of emission reduction of sulphur dioxide produced during coal combustion

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Abstract

The need for clean coal technologies to reduce the adverse environmental impact of coal combustion products has been grounded. The article deals with information concerning present and future technologies, directed towards the struggle against air pollution by SO_2, produced during coal combustion. Their classification and critical rating from economical and technological points of views (including those developed by authors) have been performed. The method of comparing the effectiveness of flue gas desulphurization (FGD) processes and technologies of coal preventive desulphurization were offered.

Key words

Desulphurization technology; coal; sulphur; sulphur dioxide; flue gas.

1. Introduction

Today, oil, natural gas and coal are the main sources of energy in the world. Their shares in the structure of primary energy consumption in 2015 were 32.9; 23.8 and 29.2%, respectively (BP Statistical Review, 2015). On the other hand, the world's coal reserves considerably exceed oil and gas reserves and the predicted period of coal use is at least twice as large. Table 1 presents data on proven reserves of coal at the end of 2015, its share in total energy resources and terms of proven reserves use.

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Depending on the level of the industry development, the amount of produced coal used for heat and power generation varies from 60 to 90 % in different countries (coal is burned at thermal power stations (TPS) or large combustion plants (LCP)). Generally, 40.4 % of world electricity is generated from coal (Trushina and Schypachev, 2011; European Commission, 2016). Taking this fact into account, as well as the above-mentioned data and worldwide tendency to abandon nuclear energy (IEA, 2012), one can predict the sustainable usage of coal for several decades (IEA (Technology roadmap), 2012).

During the combustion gas or coal, which are mainly used as fuel to produce electric and thermal energy, carbon monoxide, water vapour and a small amount of other oxides are formed. During the combustion, natural gas that contains a small amount of sulphur and nitrogen, CO_2 is mainly formed, whereas in the case of coal a large amount of harmful substances gets into the atmosphere, the main of which is sulphur dioxide (SO_2). The residence time of SO_2 in the atmosphere is short: 15-20 days in the relatively clean air. During this time SO_2 may be partially oxidised to SO_3 under the effect of oxygen, (Krawczyk et al., 2013), dissolved together with it in water and fall in the form of the so-called "acid rain". Final products are distributed as follows: in the form of precipitates on the lithosphere surface - 43%, on the hydrosphere surface - 13%; they are absorbed by plants - 12%, by the hydrosphere - 13% (Malyarenko, 2008). The precipitates have a harmful effect on human and animal health, the productivity of crops; they destroy materials and protective coatings. For instance, SO_2 emission can cause diseases in the exposed humans which incur medical costs drawn from the governmental budgets. It has been calculated that depending on the level of economical development of a given country, such costs vary from 566 to 11,096 EUR per tonne of SO_2 (Sevenster et al., 2008).

To reduce the adverse environmental impact of combustion products a series of regulatory and technological arrangements is employed. During the last decade, a lot of attention was paid to the improvement of the environmental properties of motor fuels (diesel and gasoline). First of all the content of sulphuric compounds which form sulphur dioxide during combustion should be reduced. This led to the development of new regulations (The clean air act, 2004; Worldwide fuel charter, 2006), improvement of the industrial process (hydrocleaning) (Babich and Moulij, 2003; Yolshin et al., 2010; Aliev and Yolshin, 2013) and the development of new technologies of sulphuric compounds removal from petroleum products (Babich and Moulij, 2003; Paniv et al., 2006; Jiang et al. 2009; Javadli and de Klerk, 2012; Pysh'yev, 2012; Pyshyev et al., 2013; Farsh and Shiralizadeh, 2015). However, SO_2 emissions from vehicles is a small part of the total emissions of this harmful compound. Therefore, the above-mentioned measures allowed to reduce sulphur oxide emissions from motor-cars only by few tenths of a percent and from total vehicle – about two percents (see Table 2). Data from Table 2 confirm that heat and electric power production is the main environmental pollutant by SO_2 in the world. The dominant position is occupied by thermal power plants, which use mostly coal.

The reason for such a trend of SO_2 emissions in the atmosphere is extremely high (compared to other fuels) sulphur content in coal. If the sulphur content does not exceed 1.0-1.5 wt. % in coal, it is regarded as a low-sulphur one (Yurovskyy, 1960; Kawatra and Timothy, 2001) (for comparison, the sulphur content in gasoline and diesel fuel, on average, is 0.00010-0.00005 wt.% (ICCT, 2014). There are many fields with a high sulphur content (up to 8-11 wt.%) (Yurovskyy, 1960; Pysh’yev, Gunka et al., 2012). Some countries, including Ukraine, have reserves of only sulphur and high sulphur coal (Pysh’yev et al., 2012; DKUE, 2015; Pysh’yev, Prysiazhnyi et al., 2015).

In view of the above, the energy sector has also developed and implemented a number of documents normalising emissions of harmful flue gas from power stations, including sulphur dioxide, though works were started in this directions as early as in the 30s of the last century (see. Fig. 1).

According to Directive EC (2001), the SO_2 content in the flue gas of new plants should be 200 mg/nm^3 (approx. 160 ppm or 0.007 vol.%), while for the modernized plants with a capacity above 500 MWth and those with a capacity up to 500 MWth, the respective limit values were set at 400 mg/nm^3 (approx. 320 ppm or 0.014 vol.%) and 400-2000 mg/nm^3 (approx. 320-1600 ppm or 0.014-0.07 vol.%). In order to achieve the SO_2 contents in flue gas of 200, 400 or 400-2000 mg/nm^3, the amount of sulphur in raw material should not exceed 0.1, 0.2 and 0.2-1.0 wt.%, respectively.

Compliance with the above requirements of regulations regarding SO_2 emissions at thermal power stations is rather complicated from the technological and economic points of view. The reduction of sulphur dioxide emissions with the flue gas produced during coal combustion can be achieved directly at TPS (by removing SO_2 from combustion products) or by the preventive removal of sulphur from coal. So this work is dedicated to reviewing the mentioned processes (both industrial and those that are developed/implemented).

2. Methods of reducing pollutions while coal combustion

Obtaining of liquefied SO_2, sulphuric acid or sulphur by well known and technologically simple methods (Rozenknop, 1952; Rameshni and Santo, 2005; Javorskyj, 2010; Dzhonova-Atanasova et al., 2013) would seem the most feasible methods of sulphur dioxide removal from TPS flue gas, since the liquefied SO_2, sulphuric acid or sulphur are widely used in industry. However, the content of sulphur dioxide in TPS flue gas does not exceed 0.1-0.3 vol. % (2860-8570 mg/nm^3) (ICPS, 2011; Syhal, 1988). When using coal with the content of sulphur up to 3.0 wt. % at TPS or LCP (European Commission, 2016), the concentration of sulphur(IV) oxide in flue gases will be 0.2 vol. % (6000 mg/nm^3). Therefore, in such a case the known methods to produce liquid SO_2, sulphuric acid or sulphur are sufficiently expensive (see Subsection 2.4) and sometimes even technically impossible.

The methods of SO_2 removal can be divided into two groups: SO_2 removal from the flue gas after and directly during raw material combustion. According to the mentioned division, the technological processes of flue gas desulphurization (FGD) can be divided into non-regenerative (non-cyclic) (wet, semi-dry and dry) and regenerative (cyclic) technology (EPA, 2004; European Commission, 2016). The essence of wet desulphurization process is sulphur dioxide binding in the liquid phase through its dissolution, dissociation and interaction with the sorbent. The resulting waste water with wet by-products requires treatment. Semi-dry desulphurization technology includes two phases of interaction between the sorbent and SO_2 – absorption on liquid droplets, which eventually evaporate, and adsorption on the surface of the sorbent and the product after the complete evaporation of drops. Dry desulphurization is characterised by sulphur dioxide adsorption on the sorbent surface and formation of products over it. Taking into account the above-mentioned complications arising during the use of regenerative (cyclic) technologies, the share of these processes does not exceed 5 %, while they are practically absent in the USA. Among the non-regenerative technologies, wet systems are dominated (80-85 %); the quantity of semi-dry (spray-dry) and dry (sorbent injection) processes is 10-12% and 3-4 %, respectively (EPA, 2004; Córdoba, 2015; European Commission, 2016).

2.1. Technologies of wet desulphurization

The most common desulphurization technology is wet desulphurization using sorbents with alkaline properties – limestone, lime, sea water, ammonia water, etc. The process using calcium compounds (limestone/lime methods) dominates among all wet desulphurization processes. Currently, more than a half of wet desulphurization processes in the world (56-88 %) use a limestone/lime method (Schnelle and Charles, 2001; Zevenhoven and Kilpinen, 2004; Rosemount Analytical, 2014; Córdoba, 2015; European Commission, 2016). For lime wet desulphurization the following reactions are typical:

- dissolution and dissociation of sulphur dioxide in water:

$$SO_2 + H_2O = H_2SO_3 \quad (1)$$

$$H_2SO_3 = H^+ + HSO_3^- \quad (2)$$

- limestone dissolution in the acid medium:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad (3)$$

- the formation of calcium sulphate and removal of carbon dioxide:

$$Ca^{2+} + HSO_3^- = CaHSO_3^+ \quad (4)$$

$$CaHSO_3^+ = CaSO_3 + H^+ \quad (5)$$

$$HCO_3^- + H^+ = H_2O + CO_2 \quad (6)$$

- the formation of acid salts of calcium bisulphite in the zone of low pH:

$$CaSO_3 + H^+ = CaHSO_3^+ \quad (7)$$

$$CaHSO_3^+ + HSO_3^- = Ca(HSO_3)_2 \quad (8)$$

If forced oxidation takes place, the reaction (9) occurs:

$$CaHSO_3^+ + \tfrac{1}{2}\, O_2 = CaSO_4 + H^+ \quad (9)$$

If the saturated solution is formed, the crystals of gypsum are formed:

$$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O \quad (10)$$

During natural oxidation, the calcium sulphite is partially oxidised by oxygen of the flue gas. With an excess of lime, sulphite quickly saturates the solution, adds water and precipitates in the form of small crystals of calcium sulphite hemihydrate:

$$CaSO_3 + H_2O = CaSO_3 \cdot \tfrac{1}{2}H_2O + \tfrac{1}{2}H_2O \quad (11)$$

Thus, gypsum or a mixture of calcium sulphate and sulphite can be formed depending on the oxygen concentration in the reaction zone. After the process ends, the products are dehydrated. FGD by-products obtained during natural oxidation poorly give back water (small size of the crystals) and have no markets. During forced oxidation, the dehydration is easy due to the large size of the gypsum crystals. In Table 3, both modes are compared.

Limestone (mainly $CaCO_3$) is most often used as a sorbent due to the prevalence of its world's deposits and low price (3-10 times cheaper than other sorbents) (Zevenhoven and Kilpinen, 2004; European Commission, 2016). Lime (CaO or $Ca(OH)_2$) was used earlier because it has higher reactivity in comparison with that of limestone. Sometimes lime is used to obtain a high-quality by-product (e.g. gypsum) because natural limestone and chalk contain calcite ($CaCO_3$) and other components. When using limestone the lime calcination by carbon dioxide of the flue gas and harmful release of energy in the absorber are eliminated. The modern design of limestone scrubbers allows efficient sulphur removal. Generally SO_2 reduction rate according to limestone/lime method is 92-99 %.

Seawater scrubbing process can be considered as the second most popular process (Tokumura et al., 2006; Andreasen et al., 2007; European Commission, 2016). The technology is based on the absorption of sulphur dioxide by alkaline components of sea water (primarily, carbonates) with the formation of sulphites and sulphates:

$$SO_2 + 2HCO_3^- = SO_3^{2-} + 2CO_2 + H_2O \qquad (12)$$

$$SO_2 + 2HCO_3^- + \tfrac{1}{2}O_2 = SO_4^{2-} + 2CO_2 + H_2O \qquad (13)$$

The resulting sulphates/sulphites return with water into the sea. It is clear that seawater scrubbing process can be installed only near the springs of seawater. The effectiveness of SO_2 removal in such processes is slightly lower and comes to 85-98 %.

The next method is an ammonia (ammonium-sulphate) wet method (Maripuu et al., 2006; Marsulex Environmental Technologies, 2009; European Commission, 2016) based on the reactions of SO_2 and SO_3 with aqueous ammonia, followed by oxidation of formed by-products to obtain stable ammonium sulphate $(NH_4)_2SO_4$. The main chemical reactions are:

- absorption of dissolved SO_2 by NH_4OH:

$$2NH_4OH + H_2SO_3 = (NH_4)_2SO_3 + 2H_2O \quad (14)$$

$$(NH_4)_2SO_3 + H_2SO_3 = 2NH_4HSO_3 \quad (15)$$

- oxidation of ammonium sulphite and ammonium bisulphite to ammonium sulphate:

$$(NH_4)_2SO_3 + ½ O_2 = (NH_4)_2SO_4 \quad (16)$$

$$NH_4HSO_3 + ½ O_2 = NH_4HSO_4 \quad (17)$$

$$NH_4HSO_4 + NH_4OH = (NH_4)_2SO_4 + H_2O \quad (19)$$

If ammonia is constantly added to the solution while maintaining the ratio of neutral and acid salts within acceptable limits, it is possible to obtain crystalline ammonium sulphate, which is used as a fertiliser.

The efficiencies of ammonia wet method, as a rule, are by 2-4 % higher than that of limestone/lime process. General SO_2 reduction rate according to this method is 95-99 %; it is possible to reduce the SO_2 content in the flue gases down to 200 mg/nm^3 (0.007 vol.%).

To remove sulphur dioxide the solutions of sodium and magnesium hydroxides (carbonates), as well as hydrogen peroxide are also used (Vanderschuren, 2004; European Commission, 2016). The efficiency of these processes is generally higher than 90 %.

2.2. Technologies of semi-dry desulphurization

Semi-dry (spray-dry) methods occupy the intermediate position between the wet and dry methods. According to these methods sulphur dioxide is binding both in the liquid phase, on the droplets of moisture introduced into the stream of flue gas (whereby the amount of introduced fluid is much smaller than that of washing liquid for wet scrubbers) and on the surface of solid sorbents (Ma et al., 2001; European Commission, 2016).

Slaked lime ($Ca(OH)_2$) which is in the form of powder or slurry introduced to the reaction zone is the main sorbent used in semi-dry desulphurization technology. In the reaction volume (single reactor or part of flue), a series of parallel-sequential processes takes place: SO_2 dissolution in droplets of moisture, heat and evaporation of the droplets of moisture, the chemical reaction of sulphur dioxide and the sorbent. When using the suspension of slaked lime, the mixture of dry mixture of calcium sulphite, sulphate, fly ash, and unreacted lime calcium is formed, but calcium sulphite hemihydrate ($CaSO_3 \cdot ½H_2O$) is the main product:

$$Ca(OH)_2 + SO_2 = CaSO_3 \cdot ½H_2O + ½H_2O \quad (20)$$

$$CaSO_3 \cdot ½H_2O + ½O_2 = CaSO_4 \cdot ½H_2O \quad (21)$$

The average degree of sulphur dioxide removal in semi-dry (spray-dry) processes is 85-95 %.

2.3. Technologies of dry desulphurization

As noted above, dry methods of the flue gas desulphurization are based on adsorption processes of sulphur dioxide on the solid surfaces (Zevenhoven and Kilpinen, 2004; Tumanovskyy, 2005; European Commission, 2016). Substances with a porous structure and relatively large specific surface are usually used as sorbents. For example, the specific surface area of CaO is 90 m^2/g. To absorb sulphur dioxide, the oxides and carbonates of alkaline earth and alkali metals are used.

Depending on the sorbent feed zone, the dry processes can be conventionally divided into furnace sorbent injection (the sorbent is fed directly into the combustion zone, the temperature is about 1000 ^0C), economizer sorbent injection (before/after air heater, about 540 ^0C), duct sorbent injection (in the flue gas flow, about 150 ^0C). There are also hybrid sorbent injection and circulating fluid bed (CFB) dry scrubber (the temperatures from 800 to 900 °C).

The main sorbent for a dry high-temperature desulphurization is the limestone (Tumanovskyy, 2005; European Commission, 2016). While introducing limestone particles together with coal into a fluidised bed boiler chamber, they are burned (calcinated) to form particles of quicklime (CaO) and carbon dioxide:

$$CaCO_3 = CaO + CO_2 \qquad (22)$$

The rate of reaction (22) is high at temperatures over 750 °C. Quicklime CaO particles are covered with a layer of calcium sulphate, which is formed as a result of the reaction between calcium oxide and molecules of sulphur dioxide and oxygen:

$$CaO + SO_2 + \frac{1}{2} O_2 = CaSO_4 \qquad (23)$$

If the amount of oxygen in the flue gases is insufficient, then a significant amount of calcium sulphate may be formed. Purification products are mixed with fly ash and directed to the dump or used as a low-grade building material. Slacked lime, quicklime and sodium hydrocarbonate (carbonate) are used for other types of dry desulphurization. The efficiency of the high-temperature dry desulphurization method depends, first of all, on specific area of the adsorbent surface and residence time of sorbent particles in the reaction zone. Therefore, to achieve high-efficiency values the sorbent is used with an excess: Ca/S molar ratio is 2-3. Further growth of limestone consumption results in the increased content of nitrogen oxides in flue gases because calcium oxide catalyses nitric oxide formation at the temperatures below 900 °C (Peltier, 2004; European Commission, 2016).

Using furnace sorbent injection, the efficiency of sulphur dioxide removal is 30-50 % (in the case of recirculation gases 70-80 % can be achieved), economiser and duct sorbent injection – 50-80 %, hybrid sorbent injection – 50-90 % and CFB processes – 90-99 %.

2.4. **Regenerable processes**

In regenerable processes (dry and wet), the sorbent is regenerated chemically or thermally and reused. As a result, gases with a relatively high concentration of SO_2 are obtained which are the basis for liquefied sulphur dioxide, sulphur or sulphuric acid production using known methods (Rameshni and Santo, 2005; Javorskyj, 2010; Dzhonova-Atanasova et al., 2013).

In the wet regenerable processes, sodium sulphite/bisulphite (Wellman-Lord process), ammonia water (Walther process), magnesium hydroxide/magnesium oxide and amine are used (Department of Trade and Industry, 2000; European Commission, 2006; Dzhonova-Atanasova et al., 2013; Mehrara et al., 2013). The most popular is the Wellman-Lord process, which consists of the adsorption stage:

$$Na_2SO_3 + SO_2 + H_2O = 2NaHSO_3 \quad (24)$$

and the desorption stage (regeneration):

$$2NaHSO_3 = Na_2SO_3 + SO_2 + H_2O \quad (25)$$

During the process nonregenerable byproducts are formed (the main products are sodium sulphate and thiosulphate):

$$2Na_2SO_3 + O_2 = 2Na_2SO_4 \quad (26)$$

$$2Na_2SO_3 + 2NaHSO_3 = 2Na_2SO_4 + Na_2S_2O_3 + H_2O \quad (27)$$

SO_2 removal efficiency of all regenerative processes is almost the same (about 90-98 %).

In the dry regenerable processes, the activated charcoal and various types of coke and semi-coke are used. ReACT technology (regenerative desulphurization technology with activated coke) is considered to be a leader (Peters, 2010). According to this method, at the first stage sulphur dioxide is adsorbed on activated coke grains in the presence of ammonia in the flue gases, which forms ammonium sulphate and bounds nitrogen oxides. Activated coke grains slowly move in the absorber to ensure the uniform surface of adsorption. Activated coke efficiently captures dust particles after ash collector. At the second stage, the contaminated activated coke is regenerated by the hot air within 400-500 °C. Sulphuric acid, and ammonium salts are decomposed into N_2, SO_2 and water. After cooling the grains of activated coke are cleared from dust and returned to the adsorber. The efficiency of ReACT technology exceeds 98 %. Most of all, the process is proposed to be used for cleaning the flue gas with an SO_2 concentration of 200-400 mg/nm^3 (160-320 ppm) to reduce its level to 5-10 ppm.

3. Technologies of coal preventive desulphurization

All methods of sulphur removal from coal before its usage may be divided into four main groups: physical; biological; physico-chemical; chemical. Typically, to characterise the efficiency of FGD technologies the terms “degree of removal”, “efficiency of sulphur dioxide removal” or “process reliability” are used. These parameters characterise the reduction of environmental pollution by SO_2.

If one describes the coal preventive desulphurisation, the term “degree of sulphur removal” is used. The sulphur content in the desulphurized coal depends on the ratio between the coal and sulphur conversion rates. Hence, the removal degree of sulphur (RDS) is calculated in accordance with the formula (28) and indicates the ratio between the rate of sulphur conversion followed by the production of gaseous products and the rate of organic matter reaction, i.e. process selectivity:

$$RDS = \frac{S_0^d - S^d}{S_0^d} \cdot 100 \tag{28}$$

where S_0^d – the content of sulphur relative to the dry sample, mass %; S^d – the content of sulphur in the desulphurized coal relative to the dry sample, mass %.

Considering that during preventive desulphurization the coal yield usually decreases, the removal degree of sulphur is lower than the resulting level of environmental pollution decrease (Pysh'yev et al., 2012; Pysh'yev et al., 2014). For correct comparison of preventive desulphurisation and FGD efficiency the term “sulphur conversion (SC)” should be used. This value indicates the amount of sulphur converted into sulphur-containing products that will not be in the atmosphere while the further burning of desulphurized coal (the level of environmental pollution decrease). It is calculated in accordance with the formula (29), %:

$$SC=\frac{S_0^a\times 100-S^a\times x_C}{S_0^a} \qquad (29)$$

where S_0^a – the content of sulphur in the initial coal relative to the analytical sample, mass %; S^a – the content of sulphur in the desulphurized coal relative to the analytical sample, mass %; x_C – the yield of desulphurized coal, mass %.

While describing technologies of coal preventive desulphurization (Section 3), the authors used the RDS term, because in the majority of the analysed works only this index is used and there are no data about coal yield. While comparing the efficiency of desulphurization technologies and SO_2 removal from flue gases (Section 4), the term SC was used.

3.1. Physical methods

Coal enrichment can be regarded as the physical desulphurization method, the main purpose of which is mineral components removal from coal. It is based on different physical properties (electromagnetic, density, the ability to wetting) of organic and mineral matters of coal. Since inorganic sulphur (primarily pyrite sulphur) is the basis of total sulphur in high-sulphur coal (Yurovskyy, 1960; Pysh'yev, S. et al., 2004; Pysh'yev, Gunka et al., 2012), then using enrichment we can obtain low-sulphur coal. The physical methods include the following enrichment technologies: flotation, gravity methods, magnetic and electrical separation (Kawatra and Timothy, 2001; Smirnov and Biletsky, 2011).

By electrostatic desulphurization, only 40 % of pyrite sulphur may be removed (Gidaspow et al., 1986), by gravity methods – 70-90 % (Kulik, 1987; Uslu et al., 2012), by flotation process using different media – from 60 to 90 % (Bekir, 1984; Ayhan et al., 2005).

For the certain type of flotation (Chi et al., 1989; Pawlak et al., 1990) or combination of gravity separation with semi coking (Çelik and Yildirim, 2000) the values of RDS (pyrite) vary depending on coal type within 28-98 (Pawlak et al., 1990; Chi et al., 1989; Çelik and Yildirim, 2000).

To increase the difference between the physical properties of inorganic parts, including pyrite, and coal organic matrix, i.e. to increase the removal degree of sulphur, it is proposed to carry out agglomeration or electrolytic recovery, to treat coal by ultrasound, sonoelectrochemical or higher acids glycerides (Pawlak, 1989; Zhua, 2003; Zhang, 2012). The method of flotation desulphurization based on coal treatment by bacteria is developed (Amini et al., 2009). Bacterial cells with excellent hydrophilic properties are introduced into pyrite. Pyrite hydrophilicity increases and the degree of pyrite separation from coal increases as well. Application of the aforementioned additional treatments before coal enrichment allows to increase RDS (pyrite) on average by 15-30 %.

3.2. Biological methods

The essence of these methods is the selective oxidation of coal sulphur as a result of biologically active components introduction or creation of conditions for the intense activity of the bacteria present in coal. Thus coal sulphur turns into incombustible and / or soluble forms:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \quad (30)$$

$$2FeSO_4 + \tfrac{1}{2}O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (31)$$

$$2FeS_2 + 7\tfrac{1}{2}O_2 + H_2O \rightarrow Fe_2(SO_4)_3 + H_2SO_4 \quad (32)$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (33)$$

Bacteria help to remove 40-100% of pyrite and 20-100% of organic sulphur (Ju, 1992;

Roffman, 1994; Cara et al., 2003; Aytar, 2011; Marinov, 2011; Fabianska et al., 2012). It should be noted that using biological methods both piryte and organic sulphur may be removed. For example, depending on the content of certain types of sulphur, RDS (pyrite) and RDS (organic) were, respectively: 55 and 38% (Aytar et al., 2014); 29 and 45 % (Mishra et al., 2014). Coal treatment (desulphurization) by bacteria is usually proposed to be realised on the suitable enterprises. The methods of introducing bacteria directly into the coal banks have been developed (Ramana, 1995; Kulkarni, 2016).

3.3. Physico-chemical methods

The essence of this method is relatively selective dissolution (extraction) of sulphur by various chemical reagents at elevated temperatures and pressures (in most cases, extractants are in a supercritical state). These reagents are alcohols, hydrogen peroxide, perchlorethylene, carbon monoxide. "Pure" extraction allows, on average, to reach RDS (pyrite/organic) up to 20-60 % and RDS (total) – up to 20-50 %. (Ali et al., 1992; Lee and Fullerton, 1992; Ehsani, 2006). This group of methods includes extraction of coal sulphur when it is previously converted into soluble (primarily in water) form. Under the action of acids (nitric preferred), sulphur (primarily, pyrite sulphur) is converted into sulphuric soluble form:

$$FeS_2+5NO_3^- +4H^+=Fe^{3+}+2SO_4^{2-}+ 5NO+2H_2O \qquad (34)$$

It is possible to remove 80% of sulphur (Riley and Ruba, 1989). It is proposed to "strengthen" the action of acids on coal sulphur using a microwave radiation and/or a catalyst/solvent (H_2O_2). The degree of sulphur removal was found to be about 90-100% (Ambedkar et al., 2011; Nomvano, 2016). It is possible to use alkali, which reacts with pyrite in accordance with the equation:

$$8FeS_2 + 30NaOH \rightarrow 4Fe_2O_3 + 14Na_2S + Na_2S_2O_3 + 15H_2O \qquad (35)$$

$$2NaOH + R\text{-}SH \rightarrow Na_2S + R\text{-}OH + H_2O \qquad (36)$$

These processes are conducted at 200-350 ^{0}C and pressures up to 17.5 MPa. Removal degree of pyrite and sulphuric sulphur exceeds 90%, and organic sulphur – 50-70% (Franco et al., 1992). Sodium phenoxide or butoxide react with sulphur coal similar to alkalis or KOH/CH_3OH mixture, providing the opportunity to reach RDS (pyrite) on the 50-70 % level and RDS (total) – 30-60 % (Prasassarakich and Thaweesri, 1996; Ratanakandilok et al., 2001). Under the influence of divalent copper sulphur is oxidised to sulphuric acid according to the equation:

$$FeS_2 + 14CuCl_2 + 8H_2O \rightarrow 14CuCl + FeCl_2 + 2H_2SO_4 + 12HCl \quad (37)$$

and organic sulphur is converted into aldehydes and sulphuric acid due to C-S bond opening. Using copper chloride, it is possible to remove total sulphur in the amount of 17 - 53 %, pyrite – 21-100 %, organic – 7-30 % (Oguz and Oleay, 1992). In some cases, only 36 % of total sulphur is removed (Meyers et al., 1991).

3.4 Chemical methods

The essence of these methods is the oxidation or reduction of coal sulphur to form gaseous products. The exception is the oxidation of lignite sulphur by potassium permanganate. Sulphur before coal burning is converted into non-combustible (sulphuric) form. The degree of conversion is 47 % (Jürü, 2008). When sulphur (organic and inorganic) reacts with hydrogen, it converts into hydrogen sulphide, for example:

$$FeS_2 + 2H_2 \rightarrow Fe + 2H_2S \quad (38)$$

$$R\text{-}SH + H_2 \rightarrow R\text{-}H + H_2S \quad (39)$$

To reduce the coal sulphur and form hydrogen sulphide it was proposed to use hydrogenation in resorcinol solution under hydrogen influence at temperatures over 900 °C (Kumaz and Srivastava, 1992); hydrogenation at low temperatures in a stream of organic compounds that can generate hydrogen (low molecular alcohols and hydrocarbons), and atomize hydrogen (O_2, NO) (Garcia and Schobert, 1991); shallow and deep hydropyrolysis of coal at the temperatures from 450 to 900 °C in the presence of catalysts and without them (Klimpel and Hansen, 1989; Garcia and Schobert, 1990; Zhang et al., 2006; Ali et al., 2009); pyrolysis with fractional selection of gases that do not contain sulphur compounds and do not require treatment (at 200-400 °C and 525-800 °C) (Shiley et al., 1989); pyrolysis with simultaneous recovery of hydrogen sulphide by calcium compounds (Sutcu, 2004). The degree of total sulphur removal in these processes sometimes was 90 %.

Fundamentally new is the removal of sulphur compounds from coal using sodium borohydride (degree of total sulphur removal is 30-40 %) (Li et al., 2011) and the electrochemical method in complex suspended catalytic systems in the presence of sodium metaborate or borohydride (RDS (total) reaches 50-60 %, RDS (pyrite) in some cases reaches 100 %) (Shen, Sun et al., 2011; Shen, Yang et al., 2011; Shen et al., 2012). The essence of these processes is that on the anode and cathode in the presence of water and metaborate (borohydride) oxygen and hydrogen radicals, respectively, are formed. They convert sulphur compounds into gaseous (H_2S) or water-soluble (SO_4^{2-}) components, such as:

$$FeS_2 + 2H^{\cdot} \rightarrow Fe + S + H_2S \tag{40}$$

$$2H^{\cdot} + R\text{–}SH \rightarrow R\text{–}H + H_2S \tag{41}$$

$$R_1\text{-}S\text{-}R_2 + 4O^{\cdot} + 2H_2O \rightarrow R_1\text{-}OH + R_2\text{-}OH + H_2SO_4 \tag{42}$$

The essence of oxidative technologies is that sulphur (mainly pyrite sulphur) may convert into gaseous sulphur-containing components at the relatively low consumption of oxidant. In fact, the process may be the first stage of the two-stage coal combustion, when gas with high content of sulphur dioxide is obtained (Hayvanovych and Pysh'yev, 2003). This gas (in contrast to TPS flue gas) may be used to produce a concentrated sulphur dioxide, sulphuric acid or sulphur (Rozenknop, 1952; Rameshni and Santo, 2005; Javorskyj, 2010; Dzhonova-Atanasova et al., 2013). If the SO_2 content in gases exceeds 7 vol. % it can be concentrated by usual stepped compression (Javorskyj, 2010). Hydrogen sulphide, obtained by oxidative desulphurization of lignite can be concentrated by known chemisorption or absorption methods (Grebeniuk et al., 2002; Javorskyj, 2010). However, if the content of hydrogen sulphide in gases is above 5 vol.%, it is advisable to process it directly into sulphur by known methods (Grunvald, 1992; Grebeniuk et al., 2002).). Steam, air or vapor-air mixtures are suggested to be used as oxidants (Sinha and Walker, 1972; Joshi et al., 1983; Hayvanovych and Pysh'yev, 2003).

The authors of this review were involved in a detailed study of desulphurization process of different types of coal: lignite (Pysh'yev et al., 2011; Gunka and Pyshyev, 2014; Gunka and Pyshyev, 2015; Pyshyev and Gunka, 2015); low-metamorphized black coal (Bratychak et al, 2004; Pysh`yev et al., 2004), medium-metamorphized black coal (Pysh`yev et al., 2007; Pysh'yev et al., 2014; Pysh'yev, Prysiazhnyi, et al., 2014), and high-metamorphized black coal, including anthracite (Shevchuk et al., 2007; Pysh'yev et al., 2012).

We also compared the desulphurization efficiency of various types of coal, which differed in the degree of coalification, and studied the impact of coal organic and mineral parts on the process proceeding (Shevchuk et al., 2007; Pysh'yev, Prysiazhnyi et al., 2012; Pysh'yev, Prysiazhnyi et al., 2013).

During coal oxidative desulphurization the content of thermally unstable compounds (volatiles yield) and its ability to sintering decrease, so this process can be used to produce pulverised coal from low- and medium-metamorphized coal with high sulphur content (Pysh'yev et al., 2015).

The sulphur in a black coal was found to be converted into sulphur dioxide and sulphur in lignite – into hydrogen sulphide (due to the interaction with the organic part). Schemes of sulphur conversion in lignite and black coals are shown in Figs. 2 and 3, respectively, depending on the process temperature.

Oxidative desulphurization at 420-445 °C and process time of 10-21.5 min. allows converting 77-90 % of pyrite sulphur (30-75 % of total sulphur) into gaseous compounds. The average content of SO_2 in desulphurization gases of black coal is 2.6-7.0 vol.% and hydrogen sulphide content in desulphurization gases of lignite – 8.0-12.5 vol.% (see Table 4).

4. Evaluation of efficiency/economy of different reduction methods of sulphur dioxide emissions

Methods of reducing pollution during coal combustion are the most effective ones among the above-mentioned (they provide removal degree of sulphur dioxide above 85-98 %), so they have found a wide range industrial applications. However, these methods have several disadvantages:

- sorption does not solve the problem of equipment corrosion, including high-temperature corrosion. For example, the use of the ammonia method at coal block with electric power of 191 MW in Germany (Karlsruhe) showed significant problems with the absorber corrosion (Pyshyev and Bratychak, 2015);

- if you do not take into account dividends from the environmental protection, all desulphurization methods while coal combustion or flue gases cleaning, even in the case of by-products sale (gypsum, dry ash, ammonium sulphate, etc.), are loss-making processes (Bazayants, 1999; Pasini and Walker, 2012) and require substantial capital contributions for the modernization of thermal power plants. The average cost of power units reconstruction with the installation of new filters and systems for sulphur(IV) oxide removal from flue gas varies from 60 to 600 dollars per 1 kW power (European Commission, 2006; Hussar, 2010; Nechayeva, 2011);

- flue gas cleaning systems can reduce the efficiency of the power units by 1.5-5 % and require relatively high operating costs (3.3–6.6 $ USA per MWh; it is on average 500-1200 $

USA per 1 ton of removed SO_2), which vary from 3,3 to 9 millions $ USA per year, depending on the unit (Johansson, 2009; Podda, 2009; European Commission, 2016);

- degree of SO_2 removal from the flue gas via all methods depends on its concentration. Therefore, based on the necessity to obtain flue gas with SO_2 content of 200-400 mg/nm^3, the maximum content of sulphur in coal, which is used for energy production, may be 1.5-3.5 wt %., depending on the efficiency of the process. This fact is confirmed by the literature data (EPA, 2001; Marsulex Environmental Technologies, 2009; European Commission, 2016).

However, the greatest disadvantage of the above-mentioned technologies is the problem of using flue gas cleaning products. Among the processes mentioned in Section 2, the wet limestone forced oxidation method with gypsum production seems to be the most promising one. However, due to easy demand for this product (EPA, 2001; Pasini and Walker, 2012), only 30-50% of the product can be used as secondary raw materials (most often – for construction products); other 50-70% are usually in the dump.

Another disadvantage of the wet method is that sea water is used as the absorbent. After usage, it is returned to the sea, but the biochemical oxygen content in water is reduced, resulting in depletion of marine life (Poullikkas, 2015).

Among the processes mentioned in Section 2, only physical ones have found application in industry. Desulphurization is positioned as a side effect that accompanies the removal of the mineral part. However, the removal degree of inorganic sulphur does not only depend on the enrichment technology, but also on the form in which pyrite is present in the organic mass of coal. So, sometimes it is possible to remove almost all pyrite sulphur, sometimes (when pyrite particles in the coal organic mass are small) only small quantities of it. The level of environmental pollution by sulphur dioxide is low or high, respectively (Pawlak et al., 1990; Çelik and Yildirim, 2000; Pyshyev et al., 2013).

With a high content of sulphur in the raw material, biological desulphurization methods require extremely large residence time of carbon in the reaction zone (up to several weeks). It is a significant disadvantage of these processes (Acharya et al., 2005; Cara et al., 2006).

Physico-chemical and chemical desulphurization methods are relatively expensive and technologically complex processes. It is necessary to use the solvents/reagents, which are difficult to be separated from desulphurized coal; selectivity is relatively low – the organic part of coal is extracted/converted together with sulphur compounds. The disadvantages of physical and chemical processes using acids or alkalis are additional costs associated with subsequent neutralisation of these compounds and the formation of nitrogen oxides. But first of all, the non-implementation of physico-chemical and chemical desulphurization methods into the industry is connected with predictable high operating costs (see Table 5).

Oxidative desulphurization processes, which use air or vapor-air mixture, could be the exclusion because they do not require significant costs for reagents and are relatively cheap. They could be the first stage of coal combustion. During this stage, the concentration of sulphur oxide in final flue gases is higher by order than that of TPS flue gases. Therefore, they could be concentrated by known methods. The obtained coal with relatively low sulphur content could be combusted at the second stage.

One more disadvantage of coal oxidative desulphurization is the removal of only inorganic sulphur. The content of the organic part decreases slightly. It means that it is impossible to reduce sulphur dioxide emissions in accordance with the requirements Directive EC (2001). However, application of coal oxidative desulphurization before its combustion is extremely effective in combination with the use of formed flue gases. This approach will provide an opportunity:

- to significantly reduce the amount of flue gas cleaning products that have limited use (gypsum, ammonium sulphate);

- to utilise a part of coal sulphur in the form of liquefied sulphur dioxide or sulphuric acid;

- to reduce high-temperature corrosion of TPS main equipment;

- to improve the economic performance of the flue gas cleaning units by receiving by-products of coal oxidative desulphurization, which are more expensive than coal (bitumen components or fuel oil) (Shved et al., 2016).

Capital and O&M costs for coal oxidative desulphurisation process were not calculated. We can predict a relatively low cost of the process, because one of the existing TPS boilers may be used instead of the reactor, where coal will be "burned" at 400-450 ^{0}C and air deficiency. Main advantages and disadvantages are described after methods in Table 5.

Abbreviations

CFB	circulating fluid bed
EEA	European Environment Agency
EPA	Environmental Protection Agency
FGD	flue gas desulphurization
ICCT	International Council on Clean Transportation
ICPS	International Centre for Policy Studies
IEA	International Energy Agency
LCP	large combustion plants
RDS	removal degree of sulphur
SC	sulphur conversion
TPS	thermal power stations

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Table 1

Proven reserves of coal in the end of 2015 (BP Statistical Review, 2015)

Countries	Anthracite and bituminous, million tonnes	Sub-bituminous and lignite, million tonnes	Total, million tonnes	Share of total, million tonnes	Reserves-to-production (R/P) ratio
North America	112835	132253	245088	27.5	276
S. & Cent. America	7282	7359	14641	1.6	150
Europe & Eurasia	92557	217981	310538	34.8	273
Middle East & Africa	32722	214	32936	3.7	123
Asia Pacific	157803	130525	288328	32.3	53
Total World	**403199**	**488332**	**891531**	**100.0**	**114**
of which: European Union	4883	51199	56082	6.3	112

Table 2

The structure of world emissions of sulphur (IV) oxide in the atmosphere, %

Sector	Year			
	2005 (EEA, 2010)	2009 (EEA, 2011)	2010 (EEA, 2012)	2011 (EEA, 2014)
Stationary source	95.0	97.3	96.9	97.3
Energy production and distribution	62.0	70.2	57.4	58.1
Non-road transport	4.8	2.3	2.9	2.6
Road transport	0.9	0.2	0.1	0.1
Other	0.1	0.4	0.2	0.1

Table 3

Comparison of forced and natural oxidation (European Commission, 2006)

Mode	By-product	Size of by-product	Use of by-product	Dewatering
Forced oxidation	Gypsum (90 %) Water (10 %)	0-100 μm	Wallboard, cement	Easy (hydrocyclone and filter)
Natural oxidation	Calcium sulphite/sulphate (50-60 %) Water (40-50 %)	1-5 μm	No use (landfill)	Complicated (thickener and filter)

Table 4

Composition of desulphurization gases of different types of coal (Pyshyev et al., 2013; Pysh'yev et al., 2011; Gunka and Pyshyev, 2014; Gunka and Pyshyev, 2015; Pyshyev and Gunka, 2015; Bratychak et al, 2004; Pysh`yev et al., 2004; Pysh`yev et al., 2007; Pysh'yev et al., 2014; Pysh'yev, Prysiazhnyi, et al., 2014; Shevchuk et al., 2007; Pysh'yev et al., 2012; Shevchuk et al., 2007; Pysh'yev, Prysiazhnyi et al., 2012; Pysh'yev, Prysiazhnyi et al., 2013; Pysh'yev et al., 2015)

Desulphurization gases	Content, vol.%					
	Lignite		Black coal			
	4.5 vol.% of water steam in the oxidant	50 vol.% of water steam in the oxidant	Candle	Fat	Lean	Run-of-mine
SO_2	0.00	0.00	6.96	2.58	3.80	5.60
H_2S	8.01	12.49	0.32	0.05	0.00	0.34
H_2	0.79	1.34	0.21	0.00	0.00	0.29
CH_4	2.68	3.28	2.70	1.48	0.51	3.83
C_2H_4	0.68	0.98	0.36	0.21	0.12	0.40
C_2H_6	0.93	1.56	1.05	0.43	0.14	1.56
C_3	1.23	1.97	0.60	0.18	0.16	0.56
CO	5.51	6.45	3.25	1.81	1.09	3.77
CO_2	23.54	24.99	8.13	9.84	5.07	9.44
O_2	1.23	0.65	3.09	3.89	11.02	1.69
N_2	54.76	45.76	72.49	78.64	77.18	71.69
Ar	0.64	0.53	0.85	0.89	0.91	0.84

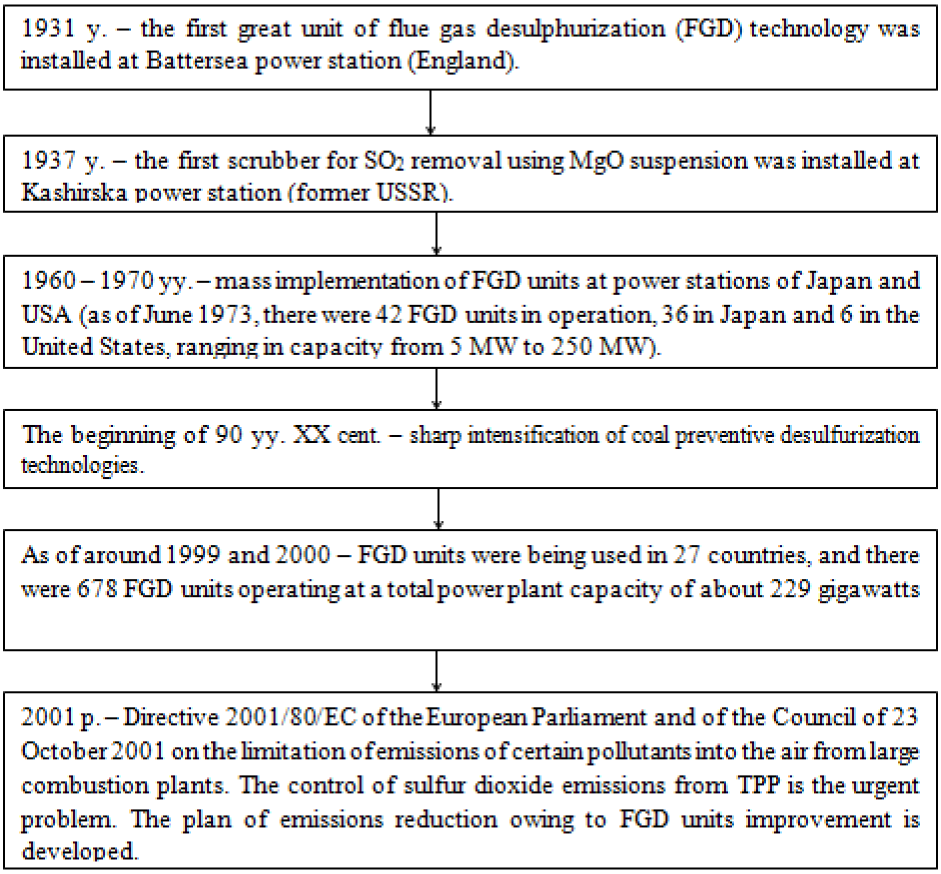
Table 5

Advantages and disadvantages of different reduction methods of sulphur dioxide emissions produced while coal combustion

Method	Main advantages	Main disadvantages	Level (%) of environmental pollution decrease (SO_2 reduction rate or SC (total))	Cost[1]	
				Capital, ($/kW)	O&M ($/ton removal (decrease) of SO_2)
1	**2**	**3**	**4**	**5**	**6**
Methods of reducing pollutions while coal combustion					
Wet	1. High purification degree of SO_2 emissions from flue gas. 2. Technological simplicity. 3. Prevalence in industry.	1. High-temperature corrosion of the equipment (primarily, wet method). 2. High capital investments for TPS modernization. 3. High O&M costs for the flue gas desulphurization. 4. Limited usage of obtained products.	85-100	65-310	750-1265
Semi-dry			85-95	40-205	660-880
Dry	1. Relatively high cost. 2. Minimization of high-temperature corrosion of the equipment.	1. Low degree of SO_2 removal (except CFB processes). 2. Limited usage of obtained products.	30-100	~ 170	~ 490
Regenerable	1. The possibility of sulphur coal recycling in the form of liquefied SO_2, sulphuric acid or sulphur. 2. The obtaining of flue gases with SO_2 content of 5-10 ppm	1. Very high capital costs. 2. The efficiency significantly depends on SO_2 concentration in flue gases.	90-100	380–650	1500-2530
Technologies of coal preventive desulphurization					
Physical	1. Prevalence in industry. 2. May be realized during coal beneficiation.	1. Dependence of sulphur removal degree on pyrite size. 2. Only inorganic sulphur removal.	10-90	–[4]	275-325[2]
Biological	1. High removal degree of sulphur. 2. Absence of reagents.	1. Great time of coal staying in the reaction zone. 2. Low efficiency.	50-100	–[4]	450-900[2]

1	2	3	4	5	6
Physico-chemical	1. Possibility of removing all types of sulphur. 2. High removal degree of sulphur.	1. Expensiveness and technological complexity. 2. To remove all types of sulphur it is necessary to use several methods.	> 30 (only extraction); up to 100 (conversion and extraction)	–[4]	960-2700[2]
Chemical (reducing)	1. Coal sulphur utilization in H_2S form. 2. High removal degree of sulphur	1. Technological complexity. 2. Low selectivity: significant destruction of coal matrix and formation of great amount of by-products.	> 60-90	–[4]	–[4]
Chemical (oxidative)	1. Coal sulphur utilization in H_2S or SO_2 form. 2. Simplicity (may be applied as the first stage of coal combustion). 3. While combining with flue gas desulphurization the amount of products with limited application (gypsum, ammonium sulphate) would be reduced. 4. Cheap reagents (air, water steam).	1. Only inorganic sulphur removal. 2. It can't be used for coal with the abnormally high content of organic sulphur.	~ 55 (lignite); 70-77 (hard coal)	–[3]	–[4]

Remarks: [1]According to (Ozbayoglu, 1998; Nolan, 2000; EPA, 2001; Ratanakandilok, 2001; European Commission, 2016; Poullikkas, 2015). [2]Calculation based on data about the value attributed to 1 ton of coal; during the calculations the average sulphur content in coal was accepted as 1.2 wt.%. [3]As the reactor one of the existing TPS boilers can be used. [4] Data are not available.



1931 y. – the first great unit of flue gas desulphurization (FGD) technology was installed at Battersea power station (England).

1937 y. – the first scrubber for SO_2 removal using MgO suspension was installed at Kashirska power station (former USSR).

1960 – 1970 yy. – mass implementation of FGD units at power stations of Japan and USA (as of June 1973, there were 42 FGD units in operation, 36 in Japan and 6 in the United States, ranging in capacity from 5 MW to 250 MW).

The beginning of 90 yy. XX cent. – sharp intensification of coal preventive desulfurization technologies.

As of around 1999 and 2000 – FGD units were being used in 27 countries, and there were 678 FGD units operating at a total power plant capacity of about 229 gigawatts

2001 p. – Directive 2001/80/EC of the European Parliament and of the Council of 23 October 2001 on the limitation of emissions of certain pollutants into the air from large combustion plants. The control of sulfur dioxide emissions from TPP is the urgent problem. The plan of emissions reduction owing to FGD units improvement is developed.

Figure. 1 Development stages of technologies allowing to reduce the amount of sulfur dioxide emissions produced while coal combustion

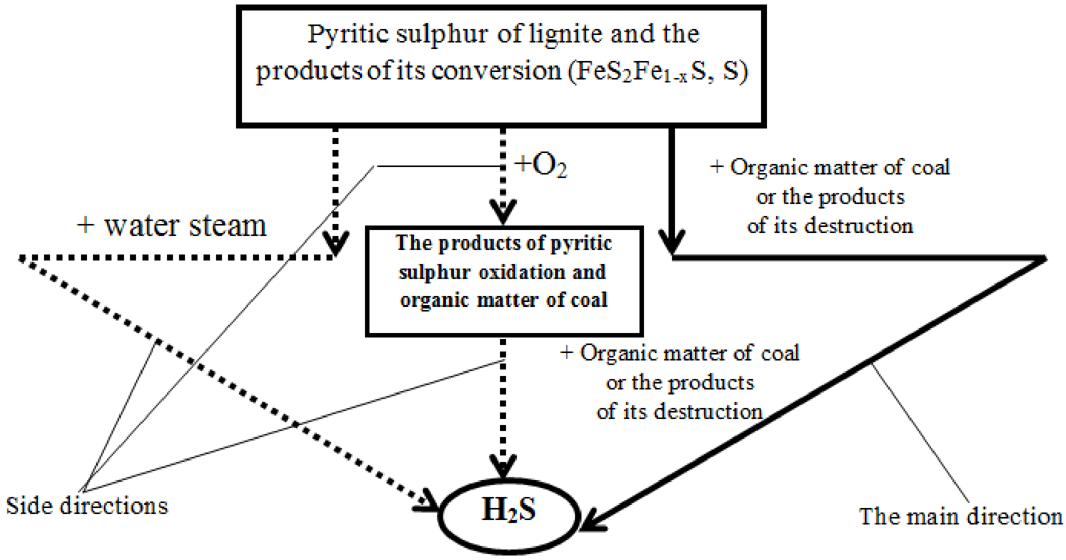


Fig.2. The scheme of the directions of conversion of lignite pyrite during the process of its oxidative desulphurization

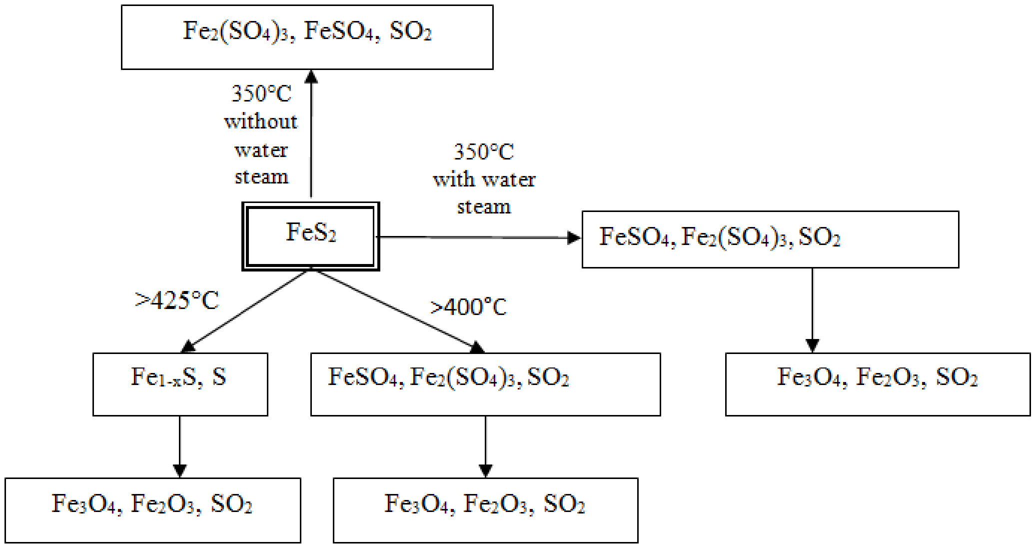


Fig.3. The scheme of chemism of the conversion of black coal pyrite during the process of its oxidative desulphurization