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# PRINCIPALS FOR THE CREATION OF EFFECTIVE AND ECONOMICALLY SOUND TREATING PROCESSES OF INDUSTRIAL EMISSIONS WITH SULFUR OXIDE LOW CONTENT

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Abstract. In the present work the sulfur cycle in nature is analyzed. The role of sulfur(IV) oxide, sources and volumes of its production, the dynamics of emissions and forecast for the future have been described. The main part (more than 80 %) of emissions are poor waste gases (<0.5 SO<sub>2</sub>), which are treated with great difficulties. Economically sound and technologically simple methods for gases treating, as well as equipment mostly corresponding to the physico-chemical essence of the processes limiting the general intensity of treating have been suggested.

Keywords: waste gases, sulfur(IV) oxide.

## 1. Introduction

Side by side with the global problems of food, energy and water supply for the growing population in the whole world the changes in the environment caused by the increasing amount of pollutant emissions pose a threat for the humanity. Sulfuric compounds constitute a great part of such pollutions.

Sulfur as chemical element and its chemical compounds are characterized by a series of unique and specific properties due to which sulfuric compounds play a great role in nature, humanity evolution and human life. Therefore they are produced in a great amount. On the other hand the mentioned compounds create a lot of problems because they are present as detrimental impurities almost in all kinds of mineral and organic raw materials. During the technological treating sulfuric compounds convert into sulfur(IV) oxide (SO<sub>2</sub>) and sometimes into hydrogen sulfide (H<sub>2</sub>S).

Sulfuric compounds participate in different physical, physico-chemical, chemical, and biological processes important for nature. Sulfur is a vivifying element for plants and animals. Plants assimilate it as sulfate-ion  $(SO_4^{2-})$  from soil resulting in the synthesis of sulfurcontaining organic compounds. Animals and people obtain sulfuric compounds in assimilated form from plants. Indigested by plants compounds are processed by microorganisms, partially deposited with sediments or washed out by water into seas and oceans [1]. Thus continuous cycle of sulfur takes place in the balanced for thousands years natural environment ensuring its stable content at the definite level in the different components of the Earth's crust. In this eternal cycle gaseous sulfuric compounds,  $SO_2$  namely, play a great role. There is a definite equilibrium of sulfuric compounds in the biosphere and  $SO_2$  presence in the Earth's atmosphere is a natural necessity.

Due to the different natural (biogenic) processes and man's industrial activity (anthropogenic factor) sulfuric dioxide gets in the atmosphere. Quantitatively  $SO_2$ emissions take second place after carbonic acid. Today the world emissions of this compound are 350 million tons per year. Approximately half of this quantity is produced due to biogenic processes and the other half – due to anthropogenic factor [2]. Thus, human's activity distorts the secular balance of  $SO_2$  content in the atmosphere, which may lead to unforeseeable consequences.

## 2. Theoretical Part

The structure of anthropogenic global emissions of sulfur(IV) oxides looks as follows (mas %) [3]: stationary sources of pollutions 95.8–97.1 (including electric power and heat production 68.6-70.2); transport 2.5-4.0 (including vehicles 0.2-0.7); others 0.2-0.4. So, the greatest volume of SO<sub>2</sub> emissions are due to the numeral systems of organic matters burning. The world use of fuel and energy resources (FER) increases from year to year. The rate of change is represented in Table 1 [4].

Table 1

Years	1900	1950	1970	1990	2000	
Total energy consumption, billion tons of standard fuel	0.95	2.86	7.3	17.0	30.0	
Population, billion persons	1.62	2.5	3.6	4.6	6.0	
Energy intensity (tons of standard fuel per 1 person per year)	0.59	1.16	2.03	3.7	5.0	

FER world use

Development of energy consumption is conditioned by two tendencies: the growth of population and power consumption per 1 person. Whereas in the middle of the XX century the population was 2.5 billion, in the end of the century it exceeded six billion. Every year the world's population is growing by over 80 million people, and in 2012 we have 7 billion. It is expected that by the middle of the XXI century about 10 billion people will live on the Earth. Under current climatic conditions and the achieved level of agricultural production the problem of human food is becoming more topical. It is clear that only through science-based application of organic and mineral fertilizers, including sulfur-containing ones, growth promoters, *etc.* we can solve the mentioned problem.

Assuming that till the end of the XXI century the population will be 20 billion people and the average energy consumption per person will reach the current U.S. level (16 tons of standard fuel per year), until 2100 the volume of consumed energy in the world will be 10 times higher than in the late twentieth century [1, 6].

According to the International Energy Agency, for the current rate of energy consumption, the proven profitable oil reserves will be sufficient for only 30–40 years; gas reserves – by mid-century; coal – for 300–400 years; nuclear power plants fuel: 25–120 years (for the plants on slow neutrons) and 800–1000 years (for the plants on fast neutrons). Since the volume growth of alternative (renewable) energy sources is slow the hydrocarbons remain the main sources of energy in the near future.

In the general energy balance the world proven reserves of coal are 87 % of all fossil energy sources on the planet. Due to the rapid decrease in oil and natural gas global reserves the volumes of coal, shale oils and other materials used in power engineering will undoubtedly increase. The sulfur content in the mentioned fuels is significant and increases with the increase of their occurrence depth [1]. As mankind is forced to extract raw materials from deeper and deeper deposits, there is a reason to believe that annual global emissions of  $SO_2$  into the atmosphere will continuously increase, causing serious concern. Today the world reserves of coal are 1083 billion tons. Moreover, almost 25 % of the total volume is concentrated in USA, the former Soviet countries -23 % (Ukraine 3.5 %) and China -12 %. Another 30 % of world deposits account for Australia, India, Germany, and South Africa. At present, the world annual coal production is about 5 billion tons [5, 6].

In 2010, in the energy balance of Ukraine the share of natural gas was 42.6% (23.3% – domestic production and 76.7% – import) and coal 28% (98.1%– domestic production and 1.9% – import). Significant volumes of import, rising prices of natural gas together with the absence of its alternative sources of supply, and the lack of a closed nuclear fuel cycle change the problem of coal share increase in the energy sector of Ukraine from economical one to the problem of energy independence [4, 7].

Estimated coal reserves in Ukraine are 117.5 billion tons, including proven reserves of 56 billion tons. Among them are coking coal – 16.7 (29.8 %) and anthracite – 8.4 (15 %). They are concentrated in such regions of Ukraine as: Donetsk basin (operating mines 261); Lviv-Volyn basin (operating mines 17); Dnipro basin (operating mines 6, profiles 7). This is sufficient to maintain the production at current levels for more than 400 years, and with the prospect of increasing production – for 250–300 years [4, 5]. Over the past 15 years the production remained actually unchanged in the range of 72–83 million tons of saleable coal per year. In 2010 (the base year) the coal output was 75.2 million tons per year.

According to the "Revised Energy Strategy of Ukraine till 2030" and the baseline scenario, the annual GDP growth in 2030 will be about 5 %. It also provides a modest annual increase in gas prices. Taking all these factors into account it is estimated that the total gas consumption in 2030 will be about 49 billion  $m^3$ . It is almost 15 % less than in 2010.

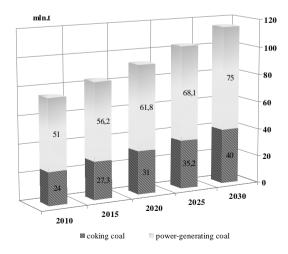


Fig. 1. Predicted growth of coal production in Ukraine for 2015-2030 years (basic scenario)

The expected increase of coal production in 2030 is 115 million tons per year (Fig. 1). The power-generating coal production is approximately 75 million tons per year (50 % if compared with 2010), which is enough to fully meet the domestic demand of power industry and other consumers.

Taking into account the above-mentioned trend of sulfur content growth, we may assert that SO<sub>2</sub> emissions will increase approximately in the same proportions. As a matter of fact, despite a number of different precautions the permanent increase of SO<sub>2</sub> emissions is observed in the world. The amount of anthropogenic SO<sub>2</sub> emissions increased in the recent years about five times, compared with 1900 (35 million tons per year). Thus, in 1950 70 million tons of SO<sub>2</sub> anthropogenic emissions were ejected into atmosphere, in 1975 – 120, in 1980 – 151, in 2010 – more than 180. It should be noted that more than 90 % of global anthropogenic SO<sub>2</sub> emissions are ejected in the northern hemisphere. The main pollutants of the environment are such industrially developed countries as USA, Japan, Great Britain, CIS countries, *et al.* [1, 6].

One of the most important environmental problems in Ukraine is the need of considerable restriction of emissions. According to the Energy Strategy 2030 (ES 2030), the main task of heat-and-power engineering is to reduce pollutant emissions (solid particles, sulfur(IV) oxide, nitrogen oxides) and greenhouse gases into the atmosphere. That heat power and cogeneration plants are the major air pollutants in Ukraine (Table 2). Almost 80 % of total SO<sub>2</sub> emissions and 25 % of NO<sub>x</sub> account for this branch of industry. "Environmental perfection" of power plants in Ukraine is lamentable: total emissions of power plants are 15–35 times higher than requirements of EU standards (Table 3). Ecological, technical and economic perfection of electric power plants is characterized by a specific index of air pollution – amount of emissions formed per unit of energy produced (g/kW·h). Average emissions of large heat power plants in Ukraine in 2009 (g/kW·h) are: SO<sub>2</sub> – 17.3 (EU standard 0.2); NO<sub>x</sub> – 2.3 (EU standard 0.3); dust – 4.4 (EU standard 0.1) [8, 9].

Despite the fact that the Ukrainian environmental standards approached the EU requirements, the total emissions of heat energy companies hardly reduced (Table 2). Moreover, according to the estimates, the predicted emissions of heat power plants by 2030 would exceed the maximum permissible level [5, 9].

Thus, the reduction of energy harmful effects on the environment will not only contribute to the fulfillment of obligations taken by Ukraine, but also will be the foundation for sustainable development of the country as well as health and life safety of its population.

In the Earth atmosphere  $SO_2$  is changeable. Under the influence of many meteorological factors (solar radiation, the presence of ozone, nitrogen oxides, ammonia, aerosols of catalytically active metals in the air, *etc.*)  $SO_2$  is arbitrarily and slowly oxidized to sulfur(VI) oxide ( $SO_3$ ). The latter one together with water vapor forms stable aerosols of sulfuric acid. Then together with rain and snow they fall on the Earth surface (acid rains).

Table 2

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			0	·		
	2005		2006		2007	
Pollutants	Emissions, thousand tons	% from the total volume of emissions	Emissions, thousand tons	% from the total volume of emissions	Emissions, thousand tons	% from the total volume of emissions
$SO_2$	876.1	73.0	1114.6	77.0	1069.2	79.0
NO <sub>x</sub>	154.1	30.0	158.2	32.0	172.3	24.0
Dust	327.7	42.0	347.6	44.0	306.2	41.0

Volumes of pollutants into the air from the activities of heat-and-power industry in Ukraine during 2005–2007 years

Table 3

	Present		Exceeding EU				
Substance	emissions,	Directive	Ministry of Nature order	Ministry of Nature order	directive, times		
	mg/m <sup>3</sup>	2001/80/EU	dated 27.06.2006 №309	dated 22.10.2008 №541	difective, times		
$SO_2$	3000-7000	200	500	200	15–35		
002	2000 7000	200		since 01.01.2016	10 00		
NO <sub>x</sub>	700-1800	200	500	200	3.5–9		
1.01	,00 1000	-00	200	since 01.01.2016	0.0 >		
Dist	1000-1700	30	50	30	33–57		
Dist 1000–1700	50	50	since 01.01.2016	55-57			

#### **Emissions level at Ukrainian power plants**

Acid rains damage our planet's flora, destroy metal wares, roofs, etc. The harmful effect of SO<sub>2</sub> is difficult to define and estimate. At the same time it should be stressed that acid rains that fall on soil are useful. In the recent years there is an increasing deficit of sulfate-ion in soil resulting from a sharp decrease of superphosphate containing gypsum introduced into soil. Acid rains are one of the sources to replenish this deficit. The most important mineral fertilizers are known to be nitrogen, potassium and phosphorus because these components are the main nutrients (macronutrients) consumed by plants in the largest quantities. In addition to the mentioned elements for normal development plants need a number of other elements (copper, zinc, ferrum, manganese, nickel, cobalt, magnesium, calcium, chromium, etc.). Since these elements are necessary in much smaller quantities compared to nitrogen, potassium and phosphorus, they are called micronutrients. Sulfur takes intermediate stand between macro-and micronutrients. The soils require sulfur in 10–15 times smaller quantities than macronutrients, but in much larger quantities than micronutrients. Thus, most of all soils need four chemical elements - nitrogen, potassium, phosphorus, and sulfur. Plants consume them only in chemically bound state [1].

The presence of sulfur(IV) oxide in the air is biologically harmful to flora and fauna. At high SO<sub>2</sub>concentrations in the air chlorophyll quickly disappears in plants, causing necrosis of tissues, *etc.* Most sensitive plants are barley, alfalfa, soybeans, and others which show symptoms of damage already under SO<sub>2</sub> concentration of  $0.3-0.5\cdot10^{-6}$  vol % and action time of not less than 2–3 h [10].

Sulfur(IV) oxide irritates the eyes mucous membrane and respiratory tract of humans and animals. Prolonged exposure of even low SO<sub>2</sub> concentrations causes chronic gastritis, hepatopathy, laryngitis, and other diseases. There is an evidence of the relation between SO<sub>2</sub> content in the air and death-rate from lung cancer. Maximum allowable SO<sub>2</sub> concentration in the air is 20 mg/m<sup>3</sup>, odor threshold is 6 mg/m<sup>3</sup>, SO<sub>2</sub> concentration which causes coughing is 50 mg/m<sup>3</sup>. Lethal SO<sub>2</sub> concentration is 400 mg/m<sup>3</sup> for exposure of 0.5–1.0 h [11].

It should be noted that every country has its own SO<sub>2</sub> emissions and so-called trans-boundary pollutions, *i.e.* carried by the wind from other countries. It is established that volumes of SO<sub>2</sub> moved from Western Europe towards Ukraine are considerably higher than those moved in the counter direction. In the recent years their volume was 600–700 thousand tons per year. Taking into account own emissions at the level of 2.5–2.7 million tons, the pollution density in Ukraine is 5.24 t/km<sup>2</sup>; that is slightly less than the pollution density for the countries with developed coal energetics (*e.g.* Great Britain – 10.2,

the Czech Republic and Slovakia -11.7), but higher if compared to the countries with better ecology (Austria -2.55, Sweden -0.61) [2, 3].

The most promising coal deposits in Ukraine are in the Donetsk basin containing 1.7-3.6% of sulfur and Lviv-Volyn basin containing 2.6-3.1% of sulfur. The combustion of one ton of the mentioned coal forms 34-72 kg of SO<sub>2</sub>, concentration of which in smoke fumes will be 3000-6500 mg/m<sup>3</sup> (0.10-0.22 vol %). Taking into account SO<sub>2</sub> maximum allowable concentration of 0.5 mg/m<sup>3</sup> the required dilution is 6000-13000 times (65-150 million m<sup>3</sup> for 1 ton of coal). If we add the summation effect resulting in the formation of nitrogen oxides during combustion, these values will be even greater. However, the dilution does not solve the problem of environment protection from harmful emissions.

The gases with SO<sub>2</sub> content of more than 7 % are called rich gases; 7–4 % – relatively rich; 4–0.5 – poor and <0.5 – very poor. Rich and relatively rich gases are used for the production of sulfuric acid and sometimes sulfur. In this case the treating of waste gases is accompanied by the production of valuable industrial products, providing the process economy. SO<sub>2</sub> oxidation to SO<sub>3</sub> is well studied and industrially developed [1, 12]. Thus, treating of these gases can be called the technology of sulfur utilization with the production of important product.

In the balance of sulfur(IV) oxide industrial emissions the main part (over 80%) are very poor gases. The multiplicity of waste gases sources, their huge volumes (e.g. gases from heat plants) and, especially, the low concentration of SO<sub>2</sub> are those technological, technical and economic difficulties which do not permit to realize the industrial treating process. It is very difficult and expensive to utilize sulfur from the mentioned gases. Therefore, the problem concerning the atmosphere protection from the increasing volumes of SO<sub>2</sub> emissions may be solved not by means of SO<sub>2</sub> utilization but via its neutralization. Cheap reagents (oxidants or reducing agents) for this purpose should be founded among other harmful industrial emissions. The cheapest SO<sub>2</sub> oxidizing agent is oxygen, which is available in most SO<sub>2</sub>containing gases. It is also possible to involve air oxygen in the process. These principles seem to be most appropriate to solve the treating problems of poor SO<sub>2</sub>containing gases. They give the possibility to minimize the cost of treating (neutralization) and to obtain sulfurcontaining by-products with commercial application in other industries.

 $SO_2$  neutralization may be realized as its conversion to sulfur or metals sulfate, sulfur(+4) reduction or its oxidation, respectively. Reduction requires the attachment of four electrons to  $S^{+4}$  ion; oxidation – detachment of only two electrons. Thus energy costs for reduction will be obviously larger than those for oxidation. Therefore,  $SO_2$  should be neutralized *via* sulfur oxidation to the oxidation degree of +6 by oxygen. The oxidation may proceed both in the gaseous and in the liquid medium.

 $SO_2$  oxidation with oxygen in the gas phase is thermodynamically possible under normal conditions and up to the temperature of 1045 K [1, 12]. Oxygen is characterized by high electronegativity (3.5 regarding Pauling) and significant energy of chemical affinity for electrons (142 kJ/mol), i.e. it has strong oxidative properties. Despite the mentioned fact, gaseous SO<sub>2</sub> and  $O_2$  do not directly react because the reaction  $2SO_2$  (g) + +  $O_2$  (g)  $\Leftrightarrow$  2SO<sub>3</sub> (g) is characterized by high activation energy (210 kJ/mol). It is possible to accelerate this process by the use of catalysts. The existing industrial vanadium catalysts are relatively expensive; their optimum temperature is at least 683 K. Therefore SO<sub>2</sub> utilization via its catalytic oxidation in the gas phase is unacceptable from all points of view and is expensive. Taking into account the above-mentioned, let us analyze  $SO_2$  oxidation by oxygen in the liquid phase.

Electrode potential of sulfur(+4) oxidation to sulfur(+6) is 0.17 V; reduction to sulfur is 0.45 V, *i.e.* 2.5 times higher. In addition, twice more electrons are need for the reduction compared to oxidation. In the first case oxygen of waste SO<sub>2</sub>-containing gases may be the oxidizing agent, *i.e.* the reagent-oxidants, the cost of which largely determines the cost of treating (neutralization), are needless [7, 8]. So, from all points of view SO<sub>2</sub> oxidation in a liquid medium is of great interest. It means that both reagents should be transferred into the solution.

Water is the cheapest and most available SO<sub>2</sub> absorber. Production processes using water as SO<sub>2</sub> absorber exist in Sweden (Boliden process) and Japan [3], where technical or sea water is used. SO<sub>2</sub>, being highly polar compound, is well soluble in water. Thus, under the pressure of 101.3 kPa SO<sub>2</sub> solubility in water is: 273 K – 79.79 l/l or 233.28 g/l; 283 K – 56.65 or 165.62; 293 K – 39.37 or 115.12; 303 K – 27.16 or 79.41; 313 K – 18.77 or 53.61, respectively [1]. Since SO<sub>2</sub> solubility in water is described by Henry's law, at SO<sub>2</sub> concentration in waste gases of about 0.5 vol % its solubility in water is about 200 times smaller, but still relatively high. Thus, at the temperature of 293 K one liter of water can absorb 0.2 l or 0.58 g of SO<sub>2</sub> from such gases, *i.e.* 5-fold excess of water is need compared with SO<sub>2</sub> amount must be absorbed.

All the mentioned above allows to assert that for Ukraine, which has a relatively small reserve of fresh water (about 1000 m<sup>3</sup> of water per person), water can not serve as  $SO_2$  absorber from poor waste gases. Thus aqueous solutions (suspensions) of hydroxides, Ca(OH)<sub>2</sub>

namely, which are available and cheap reagents, should be used as  $SO_2$  absorbers. The formed calcium sulfite may be easily afteroxidized to calcium sulfate, which is widely used as gypsum in the construction industry.

For a long time it was considered that  $SO_2$  forms a sulfite acid (H<sub>2</sub>SO<sub>3</sub>) in aqueous solutions. Hence such name as sulfite anhydride arose and became customary. In fact, SO<sub>2</sub> aqueous solutions are acidic ones, which is explained as follows:

 $SO_{2(a)} + nH_2O \Leftrightarrow [HSO_3(n-1)H_2O]^- + H^+$  (1)

It has been established that sulfite acid does not exist at all, although there are its basic and acid salts. There is a fact that in aqueous solutions the main part of absorbed SO<sub>2</sub> binds in SO<sub>2</sub>·7N<sub>2</sub>O hydrate [1, 12]. There are reasons to believe that the formation of this hydrate results in passivity of dissolved in water SO<sub>2</sub> relative to oxygen, since it is known that sulfite ions in aqueous solutions can relatively be easy oxidized by dissolved oxygen.

To increase the water absorption relative to  $SO_2$  the substances capable to oxidize sulfur(+4) to sulfur(+6) are introduced into absorbing solutions. From this aspect iron sulfates are of considerable interest.

It is known [13-17] that in aqueous solution oxygen can oxidize  $Fe^{2+}$  to  $Fe^{3+}$ . The process is accelerated by passing SO<sub>2</sub> and O<sub>2</sub> gases through a solution in the presence of H<sub>2</sub>SO<sub>4</sub> system. The occurred reactions can be expressed as stoichiometric equations:

$$2\text{FeSO}_4 + \text{O}_2 + \text{SO}_2 \Leftrightarrow \text{Fe}_2(\text{SO}_4)_3 \tag{2}$$

Simultaneously, formed iron(III) sulfate is reduced by dissolved  $SO_2$  to  $FeSO_4$ :

 $Fe_2(SO_4)_3 + SO_2 + H_2O \Leftrightarrow 2FeSO_4 + 2H_2SO_4$  (3)

In total, this process can be expressed by the following reaction:

$$2SO_2 + O_2 + 2H_2O \Leftrightarrow 2H_2SO_4 \tag{4}$$

Thus, iron ions  $(Fe^{2+}, Fe^{3+})$  play the role of oxygen transmitter to SO<sub>2</sub>, meaning they can be homogeneous catalyst for the oxidation of sulfite ions to sulfate ions. These processes are equilibrium. Hence, changing the conditions we can turn the process in the desired direction. Sulfuric acid is the end product, the accumulation of which will move the equilibrium to the left. It means that the acidity of the absorbent solution must be limited. The acidity of absorbing solution can be controlled by lime milk. Precipitated gypsum will be a valuable by-product for the building industry.

Standard electrode potential of  $\text{Fe}^{3+} \Leftrightarrow \text{Fe}^{2+}$  system is equal to 0.77 V, and of  $O_2 + 4\text{H}^+ + 2e \Leftrightarrow 2\text{H}_2\text{O}$  system – 1.23 V. Since oxidant electrode potential is greater than that of reducer, the reaction proceeds, and the driving force of the process is 0.46 V (1.23-0.77). Thus, liquidphase oxidation of SO<sub>2</sub> by oxygen in the presence of Fe<sup>2+</sup> and  $\text{Fe}^{3+}$  ions is theoretically possible and characterized by a significant driving force. Obtaining of valuable byproduct (gypsum) would reduce the treating cost.

When treating the waste gases by hydroxide aqueous solution (*e.g.*  $Ca(OH)_2$ ) sulfites are formed, which are relatively unstable. The area of their practical application is very limited. At the same time it is known [10] that sulfite ions can be oxidized by dissolved oxygen to sulfate ions. When using Ca(OH)<sub>2</sub> suspension, gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) precipitates from the solution, the same as in the previous case. Gypsum has a wide range of consumers.

The process of CaSO<sub>3</sub> oxidation by oxygen in the liquid phase is thermodynamically possible, since the enthalpy of gypsum formation is large enough ( $\Delta H^0 = 2024.8 \text{ kJ/mol}$ ). The heat of gypsum formation certainly recovers energy costs of the earlier stages of oxidation, in particular oxygen activation.

Oxygen belongs to the gases which are poorly soluble in water. At the air total pressure of 101.3 kPa oxygen solubility in water is:  $273 \text{ K} - 10.19 \text{ dm}^3/\text{m}^3$  or 14.55 g/m<sup>3</sup>; 283 K - 7.9 or 11.28; 293 K - 6.40 or 9.14; 303 K - 5.30 or 7.57, respectively. In an aqueous solution of calcium sulfite this solubility is less, because the presence of electrolytes in the water reduces the gases solubility. According to the literature data the total oxidation rate of sulfite ions to sulfate ions is determined by the concentration of dissolved oxygen. Hence, the process of sulfites afteroxidation to sulfates should be implemented in devices providing high intensity of oxygen absorption by aqueous sulfite, *i.e.* it is necessary to create a large and highly active contact surface in the gas-liquid system.

All the above-mentioned allows to suggest the technological principles of effective and low-cost treating processes for the industrial waste emissions with low  $SO_2$  content. Two options emerge, which are liquid-oxidative ones by their essence.

Under the first option  $SO_2$  is absorbed by water solutions (suspensions) of cheap and available hydroxides.  $Ca(OH)_2$  is of greatest interest. A high degree of  $SO_2$ chemisorption and high process intensity is ensured. The obtained aqueous solutions of sulfite are afteroxidized by air oxygen in the mass transfer apparatus, which creates a large and effective contact area in gas-liquid system. The latter is necessary to ensure a high concentration of oxygen in solution, since this parameter determines the process rate on the whole. Horizontal absorbers with bucket dispersant creating a large, uniform and effective contact surface may be such apparatus with a number of other very important positive characteristics [18-23].

The second option is  $SO_2$  and  $O_2$  chemisorption by iron sulphate aqueous solution in horizontal absorbers with bucket dispersant. They meet the physical and chemical nature of the chemical reactions taking place in the multistage process of gases with low  $SO_2$  content treating by aqueous solutions of iron sulfate. The source of iron sulfates may be wastes of pigmental titanium(IV) oxide (FeSO<sub>4</sub>·7H<sub>2</sub>O) production.

## 3. Conclusions

1. In the eternal cycle of sulfur, which has ensured its contents in different components of the Earth crust at a certain level, sulfur(IV) oxide, whose presence in the atmosphere is a natural necessity, plays a great role.

2. Over the past 50–70 years the volumes of  $SO_2$  anthropogenic emissions into the atmosphere distorted its equilibrium content, which may lead to the emergence of environmental crisis situations and have unpredictable consequences.

3. The majority (over 80 %) of  $SO_2$  industrial emissions are in poor (up to 0.5 %  $SO_2$ ) gases. The total volume of waste gases is 350 million tons per year. Mass character of sources, huge volume and low concentration of  $SO_2$  are the reasons of technological and technical complexity of sulfur utilization and its high cost.

4. The world problems of the atmosphere protection from ever-increasing volume of  $SO_2$  industrial emissions can be solved only on the basis of sulfur removal by cheap oxidants in the liquid phase, oxygen in particular, which is always present in the waste gases.

5. In comparison with  $SO_2$ , sulfite ion is oxidized by oxygen in the liquid phase more intensively. Therefore, the effective direction of  $SO_2$  emissions neutralization is its absorption by lime milk, followed by oxidation of sulfite ion to sulfate ion.

6. Iron sulfates are effective transmitters of oxygen to  $SO_2$  in the liquid phase. Ensuring adequate oxygen concentration in the liquid phase by means of mass transfer apparatus, we can achieve an effective, complete and low cost treating of waste gases from  $SO_2$ .

7. Horizontal absorber with a bucket dispersant is the most appropriate device for mass transfer processes mentioned under points 5 and 6. Such apparatus fully corresponds to the processes nature and has a number of other positive characteristics that provide relatively low cost of treating.

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#### ЗАСАДИ СТВОРЕННЯ ЕФЕКТИВНИХ І ЕКОНОМІЧНО ДОЦІЛЬНИХ ТЕХНОЛОГІЧНИХ ПРОЦЕСІВ ОЧИЩЕННЯ ПРОМИСЛОВИХ ВИКИДІВ З НИЗЬКИМ ВМІСТОМ СУЛЬФУРУ(IV) ОКСИДУ

Анотація. У наведеній статті проаналізовано колообіг Сульфуру в природі. Висвітлена роль у ньому сульфуру(IV) оксиду, джерела і обсяги його утворення, динаміка викидів в атмосферу, прогнози на майбутнє. Показано, що в балансі викидів основна маса (понад 80%) приходиться на бідні (< 0,5% SO<sub>2</sub>) відхідні гази. Обгрунтовано, що зазначені викиди є надзвичайно складними в аспекті їх очищення. Запропоновано економічно доцільні і технологічно прості засади очищення таких газів та апаратурне оформлення, що найбільш відповідає фізико-хімічній сутності процесів, які лімітують загальну інтенсивність очищення.

Ключові слова: відхідні гази, Сульфуру(IV) оксид.