CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 10, No. 4(s), 2016 Chemical Technology

Victor Yavorskiy, Andriy Slyuzar and Jaroslav Kalymon

SULFUR GAS PRODUCTION IN UKRAINE (REVIEW)

Lviv Polytechnic National University
12, S. Bandera St., 79013 Lviv, Ukraine; savasl2000@yahoo.com

Received: September 20, 2016 / Revised: September 30, 2016 / Accepted: October 12, 2016

Abstract. The state of sulfur gas production in Ukraine has been examined. The major producers and consumers of sulfur, as well as available technologies for gases purification from hydrogen sulfide have been characterized. The necessity of applying new methods of gas cleaning from hydrogen sulfide to form sulfur of special grades has been grounded. The advantages of quinhydrone cleaning method to form fine sulfur have been shown.

Keywords: sulfur production, gas desulphurization, application, special grade.

1. Introduction

Sulfur is one of the main types of chemical raw materials of strategic importance for the economy of any country. This importance of sulfur is almost entirely related to the supplying of humanity with food. The continuous growth of world population and acreage limitations necessitate the agriculture intensification, which is significantly dependent on the introduction of mineral and organic fertilizers and plant protectors into soil. The need in the fertilizers containing sulfur, calcium and magnesium is great because they belong to basic nutrients of plants along with macro-elements, such as nitrogen, phosphorus and potassium [1].

World sulfuric industry is conventionally divided to the sulfur production from natural deposits, pyrite and gases (natural gas, petroleum gas, *etc*.). To date the need for sulfur and sulfur-containing products is covered with sulfur gas by 88–90 %. The reason is that during processing of the raw materials of organic and inorganic nature sulfur compounds, which are often harmful impurities in the raw materials, turn into SO_2 and/or H_2S and form hazardous emissions. Often sulfur emissions utilization is technologically necessary, of great ecological importance and can fully satisfy the needs for sulfur-containing products. It is a tendency that not only sulfur, but other sulfur-containing products (sulfuric acid, sulfates, sulfides, *etc*.) will be received only as by-products in the processes of natural deposits desulfurization.

The increased role of sulfur gas, which is obtained during desulfurization of natural gas, gases from petroleum, gas, coke, metallurgical and other enterprises, is influenced by stringent regulations for H_2S and SO_2 emissions into the atmosphere. As a result, world production of sulfur, sulfuric acid and other sulfur-containing products (62 mln. tons in 2014) is provided by processing of oil and natural gas (about 62 %), cleaning processes of exhaust gases of non-ferrous metallurgy and coke gases (about 29 %), processing of pyrite (7 %) and natural sulfur ore (2 %) [2].

There are sufficient data on market analysis of sulfur and sulfuric acid production, prices, export and import of these products in Ukraine and in worldwide [1-5]. On the whole, the world sulfur market is a surplus one, *i.e.* sulfur supply exceeds its demand by about 6 mln. tons. The reason is the complexity of regulating this market, because sulfur gas is a by-product and its production is totally dependent on the state of oil and gas market. The largest producers of sulfur today are the Middle East (UAE, Saudi Arabia and Iran), CIS (Russia, Kazakhstan), Asia (China, Japan), and North America (USA, Canada). They have developed oil-and-gas producing industry. Such countries as USA, China, Russia, Morocco, Tunisia, India, and Brazil are the main consumers of sulfur (in the form of acid) for the production of fertilizers.

The problems of the global market associated with overproduction of sulfur force manufacturers to look for contribution to problem resolution. In world practice three basic solutions are used: organization of warehousing and long-term storage of sulfur; pumping of sulfur-containing gas back into beds to maintain their pressure; and expanding applications of sulfur. The first way is concerned with the presence of appropriate technology, preserving of product quality, optimization of environmental costs, and so on. Implementation of the second way is also associated with the presence of technology and irreversible loss of sulfur. Obviously, the most rational and most promising solution is to expand the applications of sulfur.

In the 90's of the twentieth century Ukraine was one of the major producers of sulfur in the world. However, the shutdown of natural sulfur production due to its unprofitability and sharp decrease in the production of phosphate fertilizers, processing of gas, oil and coal in the recent years had a significant impact on sulfur production in Ukraine. New trends in the global sulfur market may increase the country's role in this area. The aim of this work is to analyze the current situation and prospects of sulfur gas production in Ukraine.

2. State of Sulfur Consumption and Production

Till recently the production of sulfur in Ukraine was carried out based on Precarpathian sulfur ore, gases containing hydrogen sulfide from refineries, coke plants, and others. Dynamics of sulfur production in Ukraine for 1995–2012 is presented in Table 1 [1, 4].

As seen from Table 1, for almost two decades the production of sulfur in Ukraine decreased almost more than an order of magnitude. Since 2004 the share of sulfur gas in total sulfur production became dominant. In early 2006 the plant of underground sulfur melting was decommissioned in Yavoriv, Lviv region. Although sulfur ore reserves suitable for the production of natural sulfur are still quite large (more than 200 mln. tons) since that time the extraction and production of natural sulfur in Ukraine were completely stopped. The main burden of sulfur production in Ukraine is assigned to refineries and coking plants.

Ukrainian gas processing industry is represented by the following enterprises: Borislav gas-processing plant (GPP); Glinsko-Rozbyshivskyy GPP; Hnidyntsivskyy GPP; Dolinsky GPP; Kachanivsky GPP; Shebelynka, and Yablunivskiy GPP. Unlike Russia or Kazakhstan, where the basic amount of sulfur gas is obtained during natural gas cleaning, most Ukrainian gas fields do not contain hydrogen sulfide. Therefore, in Ukraine there are no big industrial or ready-for-exploitation gas deposits which are profitable to be purified from hydrogen sulfide in order to convert it into sulfur or sulfuric acid. However, the question of natural gas purification from hydrogen sulfide is relevant. Thus, in addition to operating plants (*e.g.* Lokachi gas field, Volyn region), Ukraine has preserved deposits of natural gas containing hydrogen sulfide, which eventually will be engaged in the processing, and large deposits of oil and gas in the shelf zones of the Black and Azov seas.

Petroleum industry is represented by six companies: JSC "Naftokhimik Prykarpattia"; JSC "NPK-Galychyna"; JSC "Kherson Oil Refinery"; PJSC "Ukrtatnafta"; JSC "Odessa Refinery"; JSC "Lisichansk Petroleum Investment Company". Desulfurization plants are available only at those enterprises, where large volume of oil is processed and, hence, large volume of hydrogen sulfide gas is obtained (Lisichansk, Kremenchuk and Odessa refineries). Gas containing hydrogen sulfide is produced mainly during the hydrofining of diesel fuel. Hydrogen sulfide removal from gas is carried out only *via* ethanolamine methods (MEA MDEA, *etc.*) and its conversion into sulfur – *via* Claus method. A large share (~80 %) of the total capacity of these enterprises, which is more than 50 mln.t of oil per year, stands idle due to imperfect technology and low depth of oil processing (~66 %).

Coke industry of Ukraine is represented by 13 companies. Almost half of all produced coke and coke products were obtained in Donetsk region: JSC "Avdeevka Coke Plant", JSC "Donetskkoks", JSC "Yenakievo Koksohimprom" PJSC "Makiyivkoks" JSC "Yasynivskyi Coke Plant", JSC " Azovstal Metallurgical Plant". Dnipropetrovsk region (~25 % of total coke production) is represented by PJSC "Evraz Yuzhkoks", JSC "Evraz Dniprodzerzhinsk Coke Plant", JSC "ArcelorMittal Kryviy Rih" and OJSC "Dniprokoks." The remaining volume of coke is produced at JSC "Zaporizhkoks", PJSC "Alchevsk Coke Plant" and JSC "Kharkiv Coke Plant." Desulfurization plants are built at 9 enterprises. "Azovstal", "Dniprokoks" and "Zaporizhkoks" use arsenic-soda method of coke oven gas cleaning accompanied with the sulfur production, "Evraz Yuzhkoks" – monoethanolamine method and other enterprises – vacuum-carbonate purification with the method of wet catalysis for the production of sulfuric acid from hydrogen sulfide. Four companies ("Yenakiyevo Koksohimprom", "Makiyivkoks", "Kharkiv Coke Plant" and "Evraz Dniprodzerzhinsk Coke Plant"), whose total share of coke production is ~12 %, do not remove hydrogen sulfide from coke oven gas. They use nonpurified coke oven gas as a fuel, polluting the environment by SO_2.

The total capacity of the coke industry of Ukraine is estimated at the level of 28 mln.t of coke per year. The industry is dependent on the supply of raw materials – coking coal, its deficit and on changes in the metal market, which regulates the capacity. The average load of coke enterprises is 60–70 %. The mass ratio of power enterprises by sulfur and sulfuric acid (calculated relative to sulfur) is 1 to 3. The bulk of the resulting sulfuric acid is used by the enterprises for their own needs.

Table 1

Dynamics of sulfur production in Ukraine (thousands of tons)

Indices	Years					
	1995	2000	2004	2007	2010	2012
Total production	237.5	110.0	128.6	43.9	52.6	16.1
Sulfur gas	35.9	22.58	71.2	43.9	52.6	16.1
Share of sulfur gas, %	15	20	55.4	100	100	100

Table 2

Dynamics of main industrial products related to sulfur obtaining and consumption

Industrial products	Years										
	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013
Coke and semi-coke from coal, mln.t [5]	20.8	22.0	18.9	19.2	20.6	19.5	17.4	18.6	19.6	18.9	17.6
Sulfur from coal, thnd.t	178.3	188.6	162.0	164.6	176.6	167.1	149.1	159.4	168.0	162.0	150.9
Diesel oil for motor and rail transport, thnd.t [5]	6325	6265	5290	4270	4147	3659	3903	3709	2664	1372	999
Sulfur from oil, thnd.t	50.6	50.1	42.3	34.2	33.2	29.3	31.2	29.7	21.3	11.0	8.0
Sulfuric acid, thnd.t [5]	1133	1425	1606	1493	1657	1479	890	1295	1639	1454	1218
Sulfur for H_2SO_4, thnd.t	333.0	418.8	472.0	438.8	487.0	434.6	261.6	380.6	481.7	427.3	357.9

Table 3

Sulfur production, import and consumption for 2010–2012 y.y. (thnd. T) [4]

Indices	Years		
	2010	2011	2012
Sulfur production	52.6	46.8	16.1
Sulfur import	431	463	490
Sulfuric acid production	1377	1614	1485

In Ukraine, same as globally, more than 80 % of all sulfur is used for the production of sulfuric acid, which is mainly consumed by the enterprises producing titanium(IV) oxide, fertilizers or by uranium ore concentration plant. The main consumers of sulfur, and therefore manufacturers of sulfuric acid (90 % of the total production) are PJSC "Crimean Titan", JSC "Sumykhimprom", "Konstyantynivskyy Chemical Plant" and "Eastern Mining and Processing Plant". Other companies that use sulfuric acid for the production of phosphate fertilizers actually stop their work due to the absence of phosphate raw materials. The share of sulfuric acid as a by-product reaches 7–10 % of the total. Acid consumption is almost entirely satisfied by domestic production.

Dynamics of main industrial products related to receiving and consumption of sulfur (coke, diesel fuel and sulfuric acid) in Ukraine during 2003–2013 [5], as well as design data on the production and consumption of sulfur, are presented in Table 2.

To calculate the sulfur production at refineries and coking plants, as well as the amount of sulfur necessary to produce sulfuric acid we assumed the following performance measures: diesel oil output during oil processing ~35 %; sulfur content in diesel fuel ~0.8 %; coke output from coal ~70 %; average sulfur content in coal ~2 %; ~30 % of sulfur from coal transfers into hydrogen sulfide of coke gas. We also assumed that 100 % of hydrogen sulfide from gas coke is converted into sulfur; 10 % of resulting sulfuric acid is a by-product; acid output is 100 %.

One can see from Table 2 that in Ukraine there is a steady downward trend of coal and oil processing and thus decrease in sulfur production. Obviously, the total sulfur production at refineries and coking plants of Ukraine (calculated data) can not cover the needs for sulfuric acid production.

The deficit of domestic product is covered by import from Kazakhstan, Russia, and partly from Poland and Germany. Analysis of data on domestic production and import of sulfur and sulfuric acid [4] presented in Table 3, makes it possible to state the obvious tendency to import increase. The average price of imported sulfur at the border of Ukraine in 2012 was 110–120 $/t [3]. However, while during 2000–2002 natural sulfur production covered domestic needs by 30–35 % [1], during 2010–2012 sulfur import from neighboring markets significantly exceeded own production, which was only 3–10 %. There is some correlation between sulfur import and sulfuric acid production allowing to conclude that almost all imported sulfur was used for acid production.

Apart from sulfur consumption for the production of fertilizers, agriculture is also a direct consumer of sulfur. As already mentioned, sulfur is an important nutrient for plants; moreover, sulfuric products are plant protection products. Introducing sulfur into the soil as fertilizer increases the yield of some crops by few times and positively affects protein synthesis. Plants also gain increased drought, frost and disease resistance. Scientifically proved need of sulfur in the soil is 10–20 kg/ha. According to acreage area of Ukraine (~40 mln.ha) this need is at least 400 thnd.t of sulfur per year. Evidently, the minimum needs of agriculture are not satisfied. In 2013 domestic production of sulfur in the fine form (sublimated, precipitated and colloidal sulfur, *i.e.* the form used in agriculture) was only 4.4 thnd. t [5]. Therefore, some of the imported sulfur is used in agriculture, rubber and tire industry.

3. Production Problems

There are three main problems of sulfur gas production in Ukraine: 1) unprofitability of available desulfurization technologies; 2) oversupply of cheap sulfur gas in neighboring markets; 3) small utilization capacity of special types of sulfur in Ukraine.

The cleaning process of any gases containing hydrogen sulfide includes hydrogen sulfide removal from gas and its conversion into sulfur or sulfuric acid. The first stage is carried out by various physical and chemical methods, which differ in absorbent nature, conditions, equipment, *etc*. The removed hydrogen sulfide is converted into sulfur or sulfuric acid by different methods. Each of the cleaning processes has advantages and disadvantages [1, 6, 7].

MEA-Claus technologies complex has the widest application in the global gas and oil industry. However, the use of this complex is difficult for the coke oven gas cleaning and economically unjustified for the purification of natural and petroleum gas low-yield deposits. Claus method has significant technological, economic and environmental drawbacks, which suggest it to be outdated and noncompetitive process. The main disadvantages of Claus method include: partial conversion of hydrogen sulfide to sulfur (till 99 %); the need for additional (mainly catalytic) cleaning of waste gases from sulfur; low level of heat streams recovery; and obtaining of sulfur in a liquid state [1, 6].

Vacuum-carbonate method is most widely used at desulfurization plants of Ukrainian coke enterprises, although it also has some significant drawbacks. The main disadvantages of these systems are: low level of coke gas cleaning (84–92 %), which does not ensure the achievement of residual hydrogen sulfide content in the coke gas at the level of 0.5 g/m^3; high power consumption; the need for Claus installations or wet catalysis to treat the concentrated hydrogen sulfide. However, due to the low cost and availability of soda and potash vacuum-carbonate plants continue to be exploited, developed and modernized [1, 7].

Although arsenic-soda method compared to the vacuum-carbonate one enables to achieve a higher degree of gas cleaning and fine sulfur is a resulting product, the design and construction of new plants is stopped due to its drawbacks. The main disadvantages of the method are: low capacity of absorbing solution relative to hydrogen sulfide; intensive side reactions with a lot of wastes needed to be processed; toxicity and high cost of arsenic compounds, their low resistance to the changes in technological regime and organic impurities in gases; bulkiness and complexity of equipment [1, 7].

Other cleaning technologies are also used in Ukraine. To clean natural gas from hydrogen sulfide at Lokachine gas field the adsorption method with zeolites is used. However, the resulting hydrogen sulfide is not utilized; it is burned together with natural gas at the power plant contaminating the environment. At the petrochemical plant JSC "Karpatnaftokhim" pyrolysis gas is cleaned by alkali washing. Hydrogen sulfide is also not utilized and formed sulfide-alkaline wastewaters require neutralization. Thus, the current desulfurization technologies used at the domestic refineries and coke plants do not provide complete cleaning of gases from hydrogen sulfide. Moreover, they are complicated, power-consuming, outdated and require improvements and renovations.

In our opinion, the main option for increasing the production of sulfur gas in Ukraine is to expand the application areas of special grades of sulfur, which will promote the construction and use of new, technologically simple and efficient technologies for gas purification from hydrogen sulfide. Since all cleaning processes, including purification from hydrogen sulfide are expensive, new processes will significantly improve profitability of desulfurization systems, reduce energy consumption, increase environmental protection, *etc*. The production of high-priced products – special grades of sulfur – will significantly improve the economics of the cleaning processes and turn them from expensive to the profitable ones.

4. Commercial and Special Grades of Sulfur and Prospective Areas of its Application

The range of sulfur application is extremely wide. It is known that 80–90 % of sulphur world production is used to obtain sulfuric acid. Approximately 65 % of produced sulfuric acid is used for the production of phosphate and complex fertilizers. Another 11–12 % is used for other sectors of agriculture, *e.g.* for obtaining ammonium sulfate and other sulfur-containing fertilizers, crop protection from pests and various chemicals. The rest is used in the mining industry (leaching of copper, uranium and other ores), chemical industry (production of synthetic rubber and rubber products, dyes, pigments, synthetic fibres), oil industry and refinery (preparation of drilling fluids, alkylation processes), pulp and paper industry (pulping), and others.

Apart from sulphuric acid, sulfur itself is also used in the chemical, pulp and paper, tire and rubber industries, agriculture, construction, medicine, pharmaceutics, and military-industrial complex.

In world practice there are 4 commercial grades of sulfur (liquid, block, granulated, powder) and special grades (medical, semiconductor, colloidal (fine), polymer (insoluble), *etc.*) [1, 8]. The first three commercial grades of sulfur are the main to produce sulfuric acid. ***Liquid sulfur*** is the primary form – in this aggregate state it is prepared by Claus method, and all other commercial forms are derived from it. Since the sulfur crystallization temperature is equal to 392.9–385.8 K, its transportation and storage in liquid form requires constant heating. ***Block sulfur*** is derived from the liquid one *via* crystallization and subsequent grinding. Regarding to the aggregative state the block sulfur is lumps of different shapes with wide range of particles size – from dust to pieces of 200 mm or more. The main advantage of this grade is the ease of preparation. ***Granulated sulfur*** (in the form of granules, flakes, plates with preferred size of 1–10 mm) has a number of advantages compared to previous grades. Despite the need for special granulation technology, this product is technologically easy to be stored, transported and used; during its production, storage and transport there are almost no losses and reduction of quality. Granulated sulfur is one of the most profitable types of sulfur. ***Powder sulfur*** is a product obtained by block sulphur grinding in special mills. The process of grinding requires preparation of raw materials, because block sulfur contains several allotropic modifications, which are characterized by different physico-chemical properties, including ability to grinding. To improve grinding various additives are needed. The process is accompanied by the formation of sulfur dust which is explosive when mixed with oxygen in the amount of over 4 %. That is why grinding is carried out in an inert atmosphere of flue gas containing 11 % of CO_2. Fine-powder (fine) sulfur clogs service lines, forms lumps during storage, is deposited on the apparatus surface, and so on. Fine sulphur assumes that the size of its particles is less than 50–70 μm. In general, the grinding of block sulfur is an expensive, power-consuming and not efficient process, therefore powder sulfur is more expensive than block one by more than an order of magnitude.

Despite the complexity and expensiveness of the process, new properties of fine sulfur outlined the benefits of this form and considerably expanded its area of application. It was established that this sulfur efficiency increases with the decrease in particles size and the increase in grinding fineness to 5 μm sharply increases the wettability. Powder sulfur became the basis for the production of special products: wetting powder for agriculture, fine powder for the tire and rubber industry and fine powder with modifying additives to produce sulphur concrete and sulphur asphalt-concrete.

Fine powder sulfur in the form of suspension is used as a fungicide to control plant diseases. The commercial chemicals for this purpose are “Colloidal sulfur” and “Sulfur – 80 % wetting powder”. Another effective application of fine sulfur in agriculture is sulphur-coated granular fertilizer [9]. Due to the sulfur coating such fertilizers have excellent physical properties, prolonged action and do not become compressed. The sulfur content in the granular fertilizer (nitroamophoska, ammophos) must be 4–8 wt %. Sulfuric capsule on fertilizer granules is not ballast, in contrast to the traditional additives (polyethylene, polyvinyl, *etc.*). Under the action of aerobic bacteria in soil the sulfur is gradually transformed into sulfate ion and so absorbed by plants.

In the construction industry sulfur bitumen binder is a very promising product for road construction and sulfur cement to obtain stable sulfur concrete. Construction materials modified by sulfur have high strength and chemical resistance, improved antiwear and anticorrosive characteristics, low permeability, and high resistance to extreme temperatures. Moreover, they are environmentally friendly. Thus, using modified sulfur instead of Portland cement significantly improves the quality and durability of reinforced concrete and unreinforced products such as paving slabs or curbs. Replacing one third of conventional bitumen (used for sulfur asphalt-concrete production) for modified sulfur allows to avoid expensive additives added to improve the adhesive properties, reduces the product cost and simultaneously improves its quality. Although the fact of using sulfur to obtain construction materials was mentioned in the 80-90th of the XX century, nowadays these materials are actively used only in some countries, such as Japan and South Korea [1, 2]. Production of new road-construction materials containing sulfur will help expand the market for this product and contribute to solving the problem of road surfaces quality.

Fine sulfur is also used as curing agent for the production of tires, but in this case it is better to use another special grade – polymeric sulfur. Polymeric sulfur, in comparison with orthorhombic sulfur, is more evenly distributed in the mass of rubber compositions and do not migrate to the surface of rubber products. This allows to simplify the process and improve the quality of multilayer rubber products [1, 10]. Polymeric sulfur is also used to protect against ionizing radiation; to purify wastewater from heavy metals ions, including mercury; and to obtain above-mentioned sulfur concrete. Thus, the modified sulfur used to produce sulfur concrete should contain 8–15 % of polymeric (insoluble) sulfur.

Traditional technologies of polymeric (copolymeric) sulfur are based on sharp cooling of its melt or vapors. In both cases a mixture of sulfur modifications (orthorhombic and polymeric) is formed. Polymeric sulfur content in the mixture is 40–60 %, which necessitates cleaning product from orthorhombic sulfur *via* its extraction. Carbon disulfide, tri- and tetrachlorethylene are used as extractants of orthorhombic sulfur. They are very toxic, inflammable, explosive and highly volatile compounds [1, 10]. The need for extraction operations and losses of extractant complicate the production of polymeric sulfur and make it imperfect from environmental standpoint. Therefore, the cost of polymeric sulfur produced by the traditional method is high. All the mentioned facts are the reason for the absence of polymeric sulfur production in Ukraine, although the need for it is significant. The main Ukrainian producers of tires (PJSC “Rosava” and JSC “Dniproshina”) meet their demand in polymeric sulfur by importing such popular brands as Crystex, Polsinex and others. Polsinex sulfur is produced in Poland since 2012 by “Grupa Azoty Siarkopol” (capacity of 5,000 tons per year).

A new promising technology of polymeric sulfur production has been developed at the Department of Chemistry and Technology of Inorganic Substances of Lviv Polytechnic National University. The technology has several significant advantages over the industrial ones and is based on sodium thiosulfate, as a raw material, which is the waste of many productions, especially in the coking industry [1, 11]. The essence of the method is decomposition of sodium thiosulfate concentrated solutions by nitric acid, resulting in a product containing insoluble sulfur modification of at least 90 %, that meets the requirements. The resulting polymeric sulfur is thermostable, suited for milling or grinding to a specified size and for the preparation of oil-filled compositions. An important advantage of the developed technology is absence of extraction, because the formed product has necessary chemical composition [1].

The above-mentioned promising applications require sulfur in the form of fine and polymeric modifications. To obtain fine powder sulfur it is necessary to implement complicated series of technological stages: purification of gases from hydrogen sulfide; conversion of hydrogen sulfide into liquid sulfur *via* Claus method; block sulfur obtaining and its grinding. The technologies available at Ukrainian desulfurization plants are power-consuming, complicated, outdated and can not satisfy the requirements for special grades of sulfur.

However, fine sulfur may be directly produced during purification of gases from hydrogen sulfide. These technologies include such industrial liquid-oxidation methods as arsenic-soda method, Takahaks, Stredford, *etc.* [1, 7], as well as quinhydrone method, which meets all the requirements for new methods of gases desulfurization. The method has several advantages compared to existing technologies, such as simplicity, high efficiency, mild technological regime, low capital and operating costs and allows to utilize sulfur of hydrogen sulfide in the form of fine powder (3 –5 μm). Quinhydrone method can be used for cleaning various types of natural and technological gas (petroleum, coke, pyrolysis, ventilation, biogas, *etc*.). The method was implemented at “Sirka” enterprise (Lviv region, Ukraine) for industrial cleaning of ventilation gases containing hydrogen sulfide [1, 8].

Combining of quinhydrone method with polymeric sulfur production based on waste thiosulfate solutions makes the method more flexible and, depending on market changes, allows to vary technical parameters and profile of desulfurization plants to produce two products with different outputs – fine sulfur and sodium thiosulfate solution, which will be directed to the production of polymeric sulfur.

5. Future Production

There is every reason to expect an increase in the production and processing of natural gas and oil with high content of hydrogen sulfide, primarily from the fields in the shelf zone of the Black and Azov Seas, since the depth of their occurrence is quite large. An increase in oil and natural gas import and processing is also predicted. The implementation of modern technologies (processes of coking, catalytic cracking, hydrocracking, visbreaking) in order to increase the depth of oil processing at Ukrainian refineries (from 66 to required 85 %) will increase the output of petroleum products satisfying world standards and hydrocarbon gases containing hydrogen sulfide. As a result, new desulfurization plants will be required.

Change of priorities in the fuel balance of the metallurgical industry of Ukraine, as a major consumer of coking enterprises products, promotes rejection of natural gas and transition to coke and coke oven gas. Wider use of coke oven gas in the metallurgy states new problems of cleaning gases from hydrogen sulfide.

Obviously, the need to solve environmental problems on desulfurization of gases from low-yield sources (oil and gas fields, biogas and pyrolysis plants of waste tire recycling, *etc*.) will also be an important factor that will determine the economic feasibility and potential application of new methods (including quinhydrone method) of cleaning gases from hydrogen sulfide with sulfur obtaining.

The consumer's activity for sulfur in the future will increase, above all, due to its need for agriculture. There is every reason to hope for rapid development of road construction in Ukraine, because of its convenient transit location. Road construction may be one of the largest consumers of sulfur (the level of consumption may be hundreds of thousands of tons per year). Putting into operation new desulfurization plants to meet the growing demand for the sulfur of special grades in road construction and rubber industry, agriculture, *etc*. is the most appropriate solution.

Gradual raising of mineral phosphate fertilizers production, which can occur due to the changes in market conditions, will not create the problem of providing fertilizer companies by sulfuric acid, because in our country there is a reserve of H_2SO_4 production. The growing demand for sulfur for this purpose will be further supplied by gas sulfur from Kazakhstan or Russia. Excessive supply of sulfur in the markets close to Ukraine ensures favorable prices for the purchase of this product.

6. Conclusions

The current state of sulfur production in Ukraine is characterized by complete dependence on technology and outputs of coal, oil and gas processing, setback in production of phosphate fertilizers, and excessive supply of usual commercial grades of sulfur in the neighboring markets. All these facts allow to reservedly predict the growth of sulfur gas production in Ukraine. However, involving high-sulfur oil and gas in processing and the need for their cleaning, insufficient production of special grades of sulfur by domestic manufactures, and the development of promising application areas indicates that putting into operation new desulfurization plants at refineries and coke enterprises of Ukraine to obtain valuable special grades of sulfur gas is the most appropriate solution having great economic importance. When choosing a cleaning technology, the methods for obtaining sulfur in polymeric or fine form should be preferred. In this respect the improved quinohydrone method is of special interest. It has several technological, economic and environmental advantages, as well as allows to obtain fine sulfur during desulfurization process and polymeric sulfur during the processing of waste thiosulfate solutions.

References

[1] Yavorskiy V.: Technologia Sirky i Sulfatnoi Kysloty. Vyd-vo Nats. Univ. Lviv Polytechnic, Lviv 2010.
[2] http://ukrchem.dp.ua/2013/06/17/mirovoj-i-rossijskij-rynki-sery-2010-2012-gody.html
[3] www.expert.kiev.ua/images/news/Digest 24A4.pdf
[4] http://www.chemico-group.com/ru/images/stories/conf_sulf/sulp_ukr.pdf
[5] www.ukrstat.gov.ua
[6] Wienckowska Ya., Bratyhak M. and Topilnytskyy P.: Catalitychno-Adsorbcijne Znesirchennia Gaziv. Wroclaw-Lviv 2000.
[7] Hrebeniuk A., Korobchanskiy V., Vlasov G. and Kaufman S.: Ulavlivanie Khimicheskykh Produktov Koksovania. Vostochnyi izdat. dom, Dnipropetrovsk 2002.
[8] Yavorskiy V., Kalymon Y., Chaiko N. and Znak Z.: Visnyk Nats. Univ. Lviv Polytechnic, 2001, **426**, 180.
[9] Yavorskiy V., Kalymon Y., Tryguba O. and Chaiko N.: Pat. UA68158A, Publ. Jul. 15, 2004.
[10] Znak Z. and Yavorskiy V.: Nauk.-Techn. Inform., 2005, **3**, 25.
[11] Kalymon Y., Znak Z. and Pozniak I.: Vopr. Khimii i Khim. Technol., 2005, **5**, 53.

ВИРОБНИЦТВО ГАЗОВОЇ СІРКИ В УКРАЇНІ

Анотація. *Розглянуто стан виробництва газової сірки в Україні. Охарактеризовано головних виробників і споживачів сірки та наявні технології очищення газів від сірководню. Обґрунтовано необхідність застосування нових методів очищення газів від сірководню з одержанням сірки спеціальних сортів. Показано переваги хінгідронного методу очищення газів з одержанням дрібнодисперсної сірки.*

Ключові слова: *сірка, виробництво, сіркоочищення газів, застосування, спеціальні сорти.*