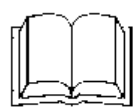


Research Group



InfoMine 

Association of Independent Consultants and Experts
in the Field of Mineral Resources, Metallurgy and Chemical Industry

Sulfur in CIS

Sample PDF

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SUMMARY

Sulfur is a chemical element rather common in nature, the average mass content of which in the earth's crust being 0.05%, and 0.09% in the sea and ocean water. Sulfur and its combinations usually occur in solid, liquid and gaseous states. Solid sulfur (brimstone) is the most common type, as well as its minerals, such as pyrite (FeS_2), chalcopyrite (CuFeS_2), galena (PbS), black jack (ZnS), and the sulfate rock, such as barite (BaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Besides, sulfur makes a part of natural coal and albumens.

Over a half of sulfur obtained in the world is used for producing sulfuric acid, while 25% of the substance obtained is used at production of sulfuric salts (mainly sulfites). The rest of the product is used in rubber-processing industry (as curing agent), in agriculture (for coping with diseases of plants, mainly of vine and cotton-plant), at production of colorants and luminous compounds, artificial fiber, matches and explosives.

Sulfur plays a special role in medicine, where the ability of sulfur is used of interaction with organic substances of human body forming sulfides and pentacarbothionic acid, the presence of which influence antimicrobial and antiparasitic effects.

Sulfur combinations are one of the major polluting agents for environment. The principal source of their formation is burning of coal and oil products. At that, 96% of sulfur goes to air in the form of SO_2 , and the rest are sulfates, H_2S , CS_2 , COS , and other combinations. Besides the negative ecological effect, elemental sulfur, in powder form, brings irritation to respiratory apparatus, mucous membrane, and leads to eczema. MPC in air is 0.07 mg/m^3 .

Sulfur belongs to a category of large-volume products of basic chemistry – in the period of 1997-2005, manufacturing of the product in six out of twelve CIS countries varied within the range from 4.2 to 8.2 million tons per year; at that, the largest production was observed in the last year of the said period.

Existing methods of production of sulfur comprise its extraction from virgin ore by open (open-pit) or mining-technological method, obtaining sulfur from hydrogen sulfide of industrial and natural gases, as well from sulfur dioxide evolving at metallurgical processing of concentrates of sulfide minerals.

The total potential of industrial enterprises producing sulfur on the territory of CIS is 11.42 million tons per year; in 2005, only 73.2% were used, and, at that, 6.30 million tons of the product were manufactured in Russia, which was 75.3% of the total production in CIS.

In the pattern of foreign trade operations with sulfur in RF, export operations dominate, the annual volume of which ten-fold exceeds the import of the product. In 2005, domestic companies exported abroad 3.92 million tons of sulfur, which was 10.6% less than the corresponding index of the previous year, while the amount of the product imported in the country reached 162.5 kt, 1.2 fold exceeding the analogous index of 2004.

In 2005, three Russian manufacturers exported sulfur abroad, so did some

trading companies, the share of which being only 0.5% of the total exports volume in the country.

In the middle of 2006, average wholesale price for a ton of sulfur increased by 2.4% in Russia, as compared with corresponding index of the previous year, and grew up to 384 (not adjusted for VAT). The average export price for sulfur in 2005 was on the level of \$19.4 per ton, the import price was \$21.2 per ton.

In 2005, “apparent” consumption of sulfur in Russia rose by 45.5% as compared with the analogous index of the previous year, thus reaching a level of 2.54 million tons. At that, the index of actual usage of the product in the country is evaluated as 2.00 million tons: the difference observed can be explained by formation of the unrealized rest over 0.5 million tons. Most of the product was used in chemical and petrochemical industries, which consumed 1.80 million tons of the product in 2005, i. e. 90.1% of the total Russian consumption. Production of chemical fertilizers (1.18 million tons) is the main direction of usage of sulfur in this sector of Russian economy, as well as production of sulfuric acid (0.49 million tons).

Analysis of dynamics of production of sulfur in Russia over the recent years, as well as projects for development of key enterprises of the sub-industry, allow forecasting increasing production volume in RF in the nearest years, which, in 2006, will be 6.40 million tons, in 2008 – 6.60 million tons, and in 2010 will reach 6.92 million tons. Dynamics of production of sulfur in Russia, along with Kazakhstan, the other leading manufacturer, will form a tendency of manufacturing the product over all CIS countries. According to forecast of “InfoMine”, production of sulfur in CIS will be 10.00 million tons in 2008, and in 2010, will exceed this value by 10.7%, reaching 11.07 million tons.

INTRODUCTION

Sulfur is a chemical element rather common in nature, the average mass content of which in the earth's crust being 0.05%, and 0.09% in the sea and ocean water. Sulfur and its combinations usually occur in solid, liquid and gaseous states. Solid sulfur (brimstone) is the most common type, as well as its minerals, such as pyrite (FeS_2), chalcopyrite (CuFeS_2), galena (PbS), black jack (ZnS), and the sulfate rock, such as barite (BaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Besides, sulfur makes a part of natural coal and albumens; in especially large amounts, this substance occurs in keratin of hair, plume and albumens. Sulfur in gaseous state, presented by hydrogen sulfide (H_2S), has rarer occurrence in nature than that in solid state. The least common in nature is liquid sulfur, which occurs in oil in the form of sulfur-organic combinations.

In the earth's geological history, sources of sulfur were mainly volcanic products containing sulfur dioxide and hydrogen sulfide. Now, over 200 sulfuric minerals are known, formed at endogenous processes. Human economic activity speeded up migration of sulfur, thus intensifying oxidation of sulfides: sulfates dominate among over 150 minerals formed in biosphere.

Many processes going in biosphere lead to concentration of sulfur, which accumulates in humus of soil, coal, oil, seas and oceans, as well as in underground water, lakes and salt marshes. Generally, one can speak of a turnover of sulfur in biosphere: it is brought to continents with atmospheric precipitation and comes back to oceans with drainage.

People have known sulfur in virgin state, as well as in the form of sulfuric chemical combinations, since ancient times, probably, since the 4th century B. C. The first mentions of it can be found in Homer's poems, and later, in the Bible. Sulfur always made a part of incense for religious rituals, as it was supposed that the smell of the products of its burning would banish all evil spirits. Skin diseases had been cured with sulfuric compounds long before. Somewhat later, sulfur became a necessary component of fiery mixtures used at war: in particular, it formed a part of "Greek fire", known in Byzantium in the 10th century A. D. Two centuries earlier, people in China learned to use sulfur for pyrotechnic purposes. In the period of Arabic alchemy, a hypothesis emerged, according to which the sulfur ("root of combustibility"), along with mercury ("root of metallic properties"), was supposed to be a constituent part of all metals.

A.Lavoisieur, a French chemist, discovered the elemental nature of sulfur, and included the element into the list of simple non-metallic bodies in 1789. E.Mitscherlich, a German scientist, discovered allotropy of sulfur in 1822. Along with other 62 elements, sulfur was included in the first version of Mendeleev's periodic table published in 1869.

Physically, sulfur is a solid crystalline substance stable in two modifications: rhombic α -S of primrose color with density of 2.07 g/cm^3 (melting point 112.8°C), and monoclinic β -S of honey color with density of 1.97 g/cm^3 (melting point 119.3°C). The both forms are composed of non-planar octatomic cyclic S_8 crown-shaped molecules, the difference between them being in different inter-orientation of

the molecules in crystal lattice.

At melting, sulfur transforms into a thin fluid, which grows brown when exceeding 160°C, and becomes a sticky dark-brown mass at about 190°C. When a thin stream of melted sulfur heated to 250-300°C is poured into cold water, a dark-brown elastic mass is formed, called *plastic sulfur*.

Sulfur is a poor conductor of heat and electricity. The substance is practically insoluble in water, poorly soluble in ethanol, hexane and heptane, somewhat better in toluol and benzol. The better solvents of sulfur are liquid ammonia (under pressure), carbon bisulfide (CS₂) and sulfur mono-chloride (S₂Cl₂). The two latter compounds are used in industry (for example, S₂Cl₂ is used at vulcanization of rubber).

Chemical properties of sulfur depend on its variable valence, and, depending on the conditions created, the substance acts as either oxidizer or deoxidizer.

At the same time, sulfur is a chemically active substance able to make compounds practically with all chemical elements, excluding N₂, I₂, Au, Pt and inert gases. Subjected to air with CO₂ at a temperature over 300°C, sulfur forms oxides: SO₂ – sulfurous anhydride, and SO₃ – sulfuric anhydride, which are used for obtaining sulfurous and sulfuric acids, respectively, as well as their salts – sulfites and sulfates. In normal conditions, sulfur combines with F₂, and at heating, also reacts with Cl₂. Sulfur reacts with bromine forming only S₂Br₂; sulfur iodides are not stable.

At rising temperature up to 150-200°C, irreversible reaction starts between sulfur and H₂, the result being sulfurous hydrogen. Besides, sulfur also forms multi-sulfurous hydrogen with general formula of H₂S_x (the so-called sulfanes). Numerous sulfur-organic compounds are also known.

In conditions of rising temperature, sulfur interacts with metals forming corresponding sulfurous compounds (sulfides) and multi-sulfurous metals (polysulfides). At a temperature of 800-900°C, vapor of S reacts with carbon, forming carbon bisulfide CS₂.

Over a half of sulfur obtained in the world is used for producing sulfuric acid, while 25% of the substance obtained is used at production of sulfuric salts (mainly sulfites). The rest of the product is used in rubber-processing industry (as curing agent), in agriculture (for coping with diseases of plants, mainly of vine and cotton-plant), at production of colorants and luminous compounds, artificial fiber, matches and explosives.

Sulfur plays a special role in medicine, where the ability of sulfur is used of interaction with organic substances of human body forming sulfides and penta-carbothionic acid, the presence of which influence antimicrobial and antiparasitic effects.

Sulfur compounds are one of the major polluting agents for environment. The principal source of their formation is burning of coal and oil products. At that, 96% of sulfur goes to air in the form of SO₂, and the rest are sulfates, H₂S, CS₂, COS, and other combinations. Besides the negative ecological effect, elemental sulfur, in powder form, brings irritation to respiratory apparatus, mucous membrane, and leads to eczema. MPC in air is 0.07 mg/m³.

I Production of Sulfur in CIS

I.1 Methods of Obtaining Sulfur in CIS

High geochemical mobility of sulfur in natural geological processes leads to its formation in different natural combinations. Until comparatively recent time, namely the middle of the 19th century, the principal method of obtaining sulfur was a primitive smelting and further purifying through distillation carried out in clay retorts or in special ovens, as well as through sublimation, which allowed obtaining the finest crystals of sulfur due to condensation of vapor of the product, which crystals were used for medical purposes.

There are three principal types of the modern commercial production of sulfur:

1. Extraction from virgin ore;
2. Obtaining sulfur from sulfur dioxide of industrial and natural gas;
3. Obtaining sulfur from sulfur dioxide.

The most industrial enterprises in CIS produce sulfur at processing oil, while the largest potential belongs to enterprises dealing in extraction and processing of natural gas (see Table 1).

I.1.1 Extraction of Sulfur from Virgin Ore

Generally, sulfur ores are mineral formations containing such concentration of virgin sulfur that its extraction is technically possible and economically profitable. As to content of the useful component, sulfur ores are subdivided into *highly rich* (over 25%), *rich* (18-25%), *medium* (12-18%) and *poor* (5-12%) ores.

Types of sulfur ores are defined by composition of surrounding rock, among which carbonate-containing ores take the principal position. Thus, over 90% of the total world extraction is carried out from calcite ores, and much less, from calcite-dolomite, argillaceous, gypsum, quartzite and opal ores.

Mass of natural deposits of sulfur ores, presented by tabular, lenticular and nest-shaped bodies of simple and complex form (with streaks of rock), varies within the range of some dozens of centimeters to dozens of meters. Depending on the reserves of sulfur raw material, the masses are subdivided into *large* (over 50 million tons), *medium* (10-50 million tons) and *small* (less 10 million tons) ones.

For extraction sulfur from virgin ores, two methods are mainly used: *mining-technological* (mainly open), the share of which does not exceed a fifth part of the total world extraction, and *geo-technological* (up to 90% of the world extraction). Selection of the extraction technology largely depends on the depth of ore bed, as well as on the content of useful element. Besides, a great attention is paid to security of the process, because sulfur possesses a property of spontaneous ignition, and deposits of sulfur ores are often accompanied by hydrogen sulfide (H₂S), a poisonous gas.

Table 1: Enterprises in CIS Possessing Capacities for Producing Sulfur, and Technologies Used

Enterprise	Location	Method of production	Capacity, kt per year
RUSSIAN FEDERATION			
LLC “Astrakhangazprom”	Aksaraisky settlement, Astrakhan Region	Gas extraction and processing	
LLC “Orenburggazprom”	Orenburg	Gas extraction and processing	
JSC “GMK “Norilsky Nikel””	Norilsk, Krasnoyarsk Region	Non-ferrous metallurgy	
JSC “Salavatnefteorgsintez” (SNOS)	Salavat, Bashkortostan Republic	Oil processing	
LLC “LUKOIL-Permnefteorgsintez”	Perm	Oil processing	
JSC “Novoil” (“Novo-Ufimsky NPZ”)	Ufa, Bashkortostan Republic	Oil processing	
JSC “Ufimsky Neftepererabatyvayushchy Zavod”	Ufa, Bashkortostan Republic	Oil processing	
JSC “Sibneft – Omsky NPZ”	Omsk	Oil processing	
JSC “Slavneft-Yaroslavnefteorgsintez”	Yaroslavl	Oil processing	
LLC “LUKOIL-Volgogradneftepererabotka”	Volgograd	Oil processing	
JSC “Moskovsky Neftepererabatyvayushchy Zavod”	Moscow	Oil processing	
JSC “Kuibyshevsky Neftepererabatyvayushchy Zavod”	Samara	Oil processing	
CJSC “TAIF-NK”**	Nizhnekamsk, Tatarstan Republic	Oil processing	
LLC “KINEF” (“Kirishinefteorgsintez”)	Kirishi, Leningrad Region	Oil processing	
JSC “Khimprom”	Volgograd	Chemical production	
JSC “Saratovsky Neftepererabatyvayushchy Zavod”	Saratov	Oil processing	
JSC “Achinsky Neftepererabatyvayushchy Zavod”	Achinsk, Krasnoyarsk Region	Oil processing	
JSC “LUKOIL-Ukhtaneftepererabotka”	Ukhta, Komi Republic	Oil processing	
CJSC “Neftegorsky Gazopererabatyvayushchy Zavod”	Neftegorsk, Samara Region	Petroleum gas processing	
CJSC “Otradnensky Gazopererabatyvayushchy	Otradny, Samara Region	Petroleum gas processing	

Enterprise	Location	Method of production	Capacity, kt per year
Zavod”			
JSC “Sivinit”	Krasnoyarsk, Krasnoyarsk Region	Chemical production	
JSC “Sibvolokno”	Zelenogorsk, Krasnoyarsk Region	Chemical production	
CJSC “Russkaya Metallurgicheskaya Kompaniya”	Magnitogorsk, Chelyabinsk Region	Coke production	
<i>Natural gas extraction and processing</i>			
<i>Oil processing</i>			
<i>Non-ferrous metallurgy</i>			
<i>Chemical production</i>			
<i>Associated petroleum gas processing</i>			
<i>Coke production</i>			
<i>Total over Russian Federation</i>			
MSIE “Sera”	Yavorov, Lvov Region	Sulfur deposits development	
SIE “Sera”	Novy Rozdol, Lvov Region	Sulfur deposits development	
JSC “Lisichansknefteorgsintez” (“Linos”)	Lisichansk, Lugansk Region	Oil processing	
CJSC “Ukratnafta” (“Kremenchugsky NPZ”)	Kremenchug, Poltava Region	Oil processing	
JSC “Zaporozhkoks”	Zaporozhie	Coke production	
CJSC “Markokhim”	Mariupol, Donetsk region	Coke production	
JSC “LUKOIL – Odessky NPZ”	Odessa	Oil processing	
JSC “Dneprokoks”	Dnepropetrovsk	Coke production	
<i>Sulfur deposits development</i>			
<i>Oil processing</i>			
<i>Coke production</i>			
<i>Total over Ukraine</i>			
BYELORUSSIA			
JSC “Mozyrsky Neftepererabatyvayushchy Zavod”	Mozyr, Gomel Region	Oil processing	
<i>Oil processing</i>			
KAZAKHSTAN			
LLP “Tengizshevroil”	Kulsary, Atyraus Region	Petroleum gas processing	
JSC “Zhanazholsky Gazopererabatyvayushchy Zavod”	Aktobe, Aktiubinsk Region	Petroleum gas processing	
CJSC “Pavlodarsky Neftepererabatyvayushchy Zavod”	Pavlodar	Oil processing	
<i>Associated petroleum gas processing</i>			

Enterprise	Location	Method of production	Capacity, kt per year
<i>Oil processing</i>			
<i>Total over Kazakhstan</i>			
UZBEKISTAN			
USE “Mubareksky Gazopererabatyvayushchy Zavod”	Mubarek, Kashkadaria Region	Natural gas processing	
JV “Zaurak-Mill”	Akhunbabayev, Andizhan Region	Natural gas processing	
USE “Shurtanneftegaz”	Shurtan, Kashkadaria Region	Natural gas processing	
<i>Natural gas processing</i>			
TURKMENISTAN			
PA “Turkmenmineral”	Govurdak, Turkmenabad Region	Sulfur deposits development	
<i>Sulfur deposits development</i>			
<i>Total over CIS</i>			
<i>Natural gas extraction and processing</i>			
<i>Associated petroleum gas processing</i>			
<i>Sulfur deposits development</i>			
<i>Oil processing</i>			
<i>Non-ferrous metallurgy</i>			
<i>Coke production</i>			
<i>Chemical production</i>			
TOTAL over CIS			

* – transformed into JSC “Omsky NPZ” after absorbing NK “Sibneft” by “Gazprom” (and creating JSC “Gazpromneft”),

** – formed on the base of “Nizhnekamsky Neftepererabatyvayushchy Zavod” in 2005.

Source: State Statistics Office of Russia, State Statistics Office of Ukraine, State Statistics Office of CIS, data from enterprises, “InfoMine”

A. *Open mining* of sulfur deposits is carried out at shallow production seams (less 100 m). As sulfur ores are rather dense, for their softening, drilling and blasting operations are necessary.

After preliminary softening, the rock is broken off by a bucket excavator and taken off by large dump trucks, which carry it to a dressing factory, where the material is processed using flotation separation method based on the natural hydrophobic property of sulfur and hydrophilic property of rock. Sulfur concentrate, thus obtained, is processed in cauldrons and autoclaves for obtaining raw (“ball”) sulfur, which further is refined to finished product.

At pressure leaching process, the dressed concentrate, usually containing up to 80% S, is supplied by pumps to autoclave, in the form of liquid pulp containing chemical agents. Water vapor is also injected there under pressure. Under the influence of the temperature of 130°C, sulfur contained in the concentrate melts, is

separated from the rock, and, after short settling, poured out. If on the stage of preliminary flotation, concentrate obtained contains 70-85% S (at its extraction of 90-97%), commodity product contains over 99% of sulfur at their total extraction within the range of 75-90%.

It should be noted that, along with sulfur ores, pyrites are a most important source for flotation sulfur and its compounds, as well as tails of dressing of sulfide ores.

B. Geo-technological method of obtaining sulfur was developed at the end of the 19th century by G.Frash, an American scientist, now bears his name; the method supposes underground smelting from deposits over 100 m of depth. The main principle of the method is smelting of sulfur in the depth with overheated water (up to 160°C). Due to density twice as large as that of water, molten sulfur sinks to the lower part of the sulfur-ore deposit, whence is pumped out to surface. Supplying water and pumping out the sulfur are carried out through special holes equipped with strings of piping located somewhat coaxial. Forced hot water is filtrated through ore body giving out heat and, therefore, melting the sulfur, and then goes to the surface through water-discharge holes and natural sources.

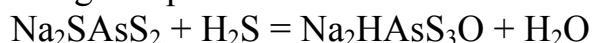
Technological aspects of the method of Frash first suggested the usage of annular tube construction, the space between the tubes being supplied with overheated water, while the inner tube, heated from all sides, served for lifting of molten sulfur. Modern variant comprises a third, more narrow tube. It is the tube through which compressed air is supplied for lifting the sulfur to surface.

One of unquestionable advantage of the method of Frash, the most effective for dressing rich sulfur ores, is obtaining the pure sulfur, containing up to 99.5% of the element, just at the first stage of processing.

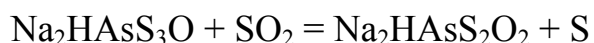
I.1.2 Obtaining Sulfur from Hydrogen Sulfide and Natural Gas

Extraction sulfur from hydrogen sulfide contained in deposits of oil and natural gas pursues primarily an ecological purpose, as utilization of sulfur, of neutralization of its compounds, is compulsory at production of the main hydrocarbon products. In this connection, oil, gas and coal are considered as accompanying sources for obtaining sulfur.

All existing methods of sulfur utilization during processing hydrogen-sulfide containing gases are based on separation of acid gases (H₂S and CO₂) from hydrocarbon phase using various chemical agents (mainly di-ethanolamine or solution of sodium mono-hydro-arsenate) with further oxidation of H₂S to elemental sulfur. On the first stage of the process, formation occurs of a complex arsenic-containing compound:



Then, due to blasting the air through the solution, sulfur precipitates in pure form:

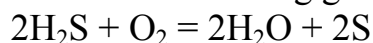


At most oil-processing plants, hydrogen sulfide is obtained during the process of purifying accompanying products from sulfur, which exit from gas fractionation unit (GFU) together with liquefied gas. In its turn, input product supplied to GFU is

gaseous fractions formed at the primary processing of oil. It should be noted that, in spite of the fact that sulfur cleaning is compulsory, far from all NPZ produce sulfur in commercial scale (or sulfuric acid, which, as a rule, is an alternative to sulfur).

The principal methods of obtaining sulfur from oil fractions (benzine, kerosene, ligroin etc.) are heat treatment for decomposing sulfurous compounds, further utilization of gaseous forms, and treatment with sulfuric acid, in which they dissolve. However, obtaining of sulfur at processing sulfurous oil requires a considerable consumption of power, which somewhat restrains expanding these processes on all oil fractions obtained during distillation (including black oil).

Along with gas- and oil-processing enterprises, some coke-producing works in CIS also obtain sulfur through desulphurization of the products of gasification (water, air-blast and illuminating gases).



A similar reaction takes place under the influence of air and activated carbon as catalyst.

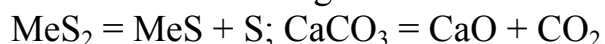
I.1.3 Obtaining Sulfur from Sulfur Dioxide

In metallurgy, separation of sulfur occurs during processing concentrates of non-ferrous metals. At that, sulfur concentrates in waste gases in the form of sulfur dioxide (SO_2), in the amount of 0.1-3.0%. Further processing of the product requires additional dressing, most often realized by burning extra elemental sulfur.

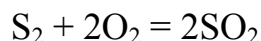
Just before smelting, sulfide concentrates of non-ferrous metals are subjected to a set of preparatory operations including drying, burning and agglomeration. At that, burning is applied for eliminating a part of sulfur for obtaining matte of the set composition.

Practice of most complexes of the former USSR comprised drying the concentrate, its balling on pan granulators and further partial burning at agglomeration machine. Burning for eliminating excessive sulfur is traditionally carried out in boiling-bed ovens, where the charge comes with 15-35% S. At heating, first water evaporates, the process taking fractions of a second. In the mass of material being burnt, the following reactions occur at a temperature of 700-900°C:

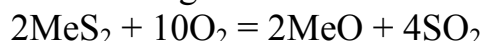
1. Dissociation of higher sulfides and calcium carbonate:



2. Combustion of sulfur vapor:



3. Oxidizing of sulfides:



Further, sulfur dioxide (SO_2) obtained at the burning can be reduced by coke for obtaining elemental sulfur.

As to temperature condition, it has been defined by now that the temperature in boiling-bed ovens should be about 900°C. In these conditions, no metal sulfates are formed, the charge becomes somewhat coarser and there is no dust. The necessary degree of desulphurization is provided by supplying strictly defined amount of air, about 0.7-0.9 m³/kg of concentrate. Generally, during burning, up to 40% of the total sulfur can be eliminated.

Most non-ferrous metallurgy enterprises in CIS mainly utilize the sulfurous gases in the form of sulfuric acid, however, one of them, namely trans-polar affiliated enterprise of JSC “GMK “Norilsky Nickel”” (Norilsk), uses exhaust gases of metallurgical processes for commercial production of elemental sulfur.

I.2 Technology of Production of Sulfur and Raw Materials Used by the Largest Manufacturers

I.2.1 Principal Types of Sulfur Ores and Methods of Their Development

Balance reserves of virgin sulfur in CIS reach about 0.8 billion tons (A+B+C₁ category), and are accounted over 16 deposits located on the territories of Russia, Ukraine and Turkmenistan. All these deposits are of two genetic types: exogenous infiltration-metasomatic and volcanogenic hydrothermal-metasomatic, the former being of more practical importance.

Sulfur from exogenous deposits nearly always accompanies sulfate-carbonate rock forming tabular and lenticular deposits. Depending on predominating accompanying rock and minerals, there can be distinguished proper limestone, as well as limestone-dolomite and limestone-gypsum types.

Limestone ores are characterized by high content of sulfur, which, at different deposits, is on the average 25% or something like that. Texture and structure peculiarities divide the ores into vein and ingrained. The former ores contain large amount of large-crystalline calcite, and are characterized by good dressability and melting properties. Fine-ingrained ores are accompanying rock saturated with sulfur; so, even fine grinding of them does not provide isolation of junctions, which leads to poor characteristics of flotation dressing. Some deposits in Prikarpatzkaya group in Ukraine – *Yazovskoye*, *Nemirovskoye* and *Rozdolskoye*, possess the ore of such category.

Yazovskoye deposit (Lvov Region), possessing the largest reserves of sulfur in CIS, is located on comparatively elevated block of south-west slope of Russkaya platform. Its industrial content of sulfur is related to limestone of Upper Tortonian sub-stage, which passes downward along the crosscut and lateral into gypsum-anhydrite rock. Thickness of ore mass varies within the range of 1-25 m; average content of sulfur is 23% (sometimes reaches 28%). Ores are of nest-vein and ingrained character, sulfur is of cryptocrystalline nature.

Other deposit of sulfur ores of limestone type – *Rozdolskoye* (Lvov Region), was the largest in the USSR, and by the beginning of the 90s of the 20th century was at the completion of its development. In 1990, its balance reserves of A+B+C₁ category were 28 kt. Limestone forming the deposit is dense, often cavernous and fissured layers of cryptocrystalline structure. Sulfur mainly occurs in these deposits in the form of inclusions of 0.02 to 6 mm. Rock-forming minerals are mainly calcite and, in small amounts, feldspar, quartz, zircon, rutile and tourmaline.