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CURRENT PROBLEMS

PRODUCTION OF SULFUR-CONTAINING REAGENTS FROM PETROLEUM FOR USE IN HYDROMETALLURGY

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The recovery of sulfur compounds from petroleum and their use in hydrometallurgy began to attract attention only in the last 10-15 years. Russia is a pioneer in this important field. Scientific and technical principles have already been established for setting up commercial production of concentrates of sulfides, sulfoxides, and sulfones from petroleum raw materials. Specifications for petroleum sulfoxides have been developed and approved. Three schemes have been developed for the commercial production of sulfoxides as hydrometallurgical reagents, the choice depending on how the process is tied into the existing schemes for petroleum refining.

Petroleum sulfoxides provide a qualitative leap in the technology of concentration of many rare and noble metals. These sulfoxides are finding extensive applications as extraction agents in the recovery and separation of radioactive and rare metals such as uranium, thorium, zirconium, hafnium, niobium, tantalum, rare-earth elements (lanthanides), tellurium, rhenium, gold, and palladium, i.e., in almost all of the processes where tributyl phosphate or similar extraction agents are now used for this purpose.

Petroleum sulfoxides are more effective than tributyl phosphate and are also more effective than individual sulfoxides. The respective extraction constants for the recovery of uranyl nitrate by petroleum sulfoxides, a dialkyl sulfoxide, and tributyl phosphate are 4000, 1200, and 100 [1].

The extraction of niobium and tantalum from sulfate-fluoride media by petroleum sulfoxides has been studied quite thoroughly [2]. The recovery of these metals from aqueous solutions is greater than 99%, and the metal pentoxides obtained by this method contain less than 0.01% of each impurity. A commercial scheme has been developed for the separation of niobium and tantalum by petroleum sulfoxides.

Petroleum sulfoxides are also far more effective than tributyl phosphate in the recovery of molybdenum and tungsten from hydrochloric acid solutions [3]. The petroleum sulfoxides also extract palladium and gold from analogous solutions. The recovery of gold is quantitative. The zinc and copper that usually accompany gold are extracted to a slight degree by petroleum sulfoxides, but these metals can be removed readily by washing the organic phase with dilute sulfuric acid [4]. Along with gold, palladium, and platinum, the petroleum sulfoxides extract mercury from hydrochloric acid media [5].

Another promising field for the application of petroleum sulfoxides is in the extraction of thallium from sulfate-chloride solutions, which are often obtained in processing sulfide ores of nonferrous metals. For example, from a sulfate solution con-

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TABLE 1

Sulfide fraction, °C	Yield, wt. % on sulfide concentrate	Quality indexes of sulfoxides			
		content of sulfoxide sulfur, wt. %	solubility in water, g/liter	maximum capacity of 50% solution of sulfoxides in *m*-xylene in extracting neodymium nitrate, g/liter	ratio of maximum capacity to content of sulfoxide sulfur
180—200	2,7	14,3	142,1	123,0	8,6
200—220	3,3	13,5	100,4	109,4	8,1
220—240	7,3	11,2	44,5	90,6	8,1
260—280	15,5	9,6	14,1	77,4	8,0
300—320	13,6	6,5	5,0	55,5	8,6
340—360	7,2	5,9	2,0	46,7	7,9
240—340	64,5	8,5	10,6	71,4	8,4
260—340	55,2	7,6	10,2	60,9	8,0
280—340	39,7	7,2	4,8	64,7	8,3
240—360	71,4	8,0	11,8	70,6	8,5
260—360	62,4	7,3	7,6	64,0	8,1

TABLE 2

Sulfide fraction, °C	Quality indexes of sulfoxides				
	content of sulfoxide sulfur, wt. %	solubility in water, g/liter	viscosity at 20°C, mm^2/sec	maximum capacity of 50% solution of sulfoxides in *m*-xylene in extracting neodymium nitrate, g/liter	ratio of maximum capacity to content of sulfoxide sulfur
211—360	10,77	10,44	71,94	86,9	8,1
300— EP	9,94	5,67	158,8	77,6	7,8
275—350	10,00	7,15	109,9	80,1	8,0
265—360	10,72	7,70	90,4	85,6	8,0
258—360	11,11	7,86	88,3	84,4	7,6
258—360	8,6*	7,62	79,9	67,9	7,9

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*This sulfoxide concentrate was recovered by extraction with acetone; the other concentrates were recovered extraction with sulfuric acid.

taining thallium, zinc, cadmium, and other metals, petroleum sulfoxides in a polyalkylbenzene diluent will recover 95.5% of the thallium. The elements associated with the thallium remain virtually unextracted. Under analogous conditions, tributyl phosphate recovers only 85% of the thallium [5].

The possibilities of using petroleum sulfoxides as an extractant are by no means restricted to the examples we have cited. In the future, these materials will become less expensive than tributyl phosphate. Their higher extraction power affords such technological advantages as a reduction of the number of extraction stages or the use of milder process conditions with lower acidity or lower concentration of salting-out agents, as well as a higher separation factor in many cases, better resistance of the extractant to radiological and hydrolytic degradation, and so on [6].

Petroleum sulfides are another class of compound finding applications in hydrometallurgy. In terms of their effectiveness and selectivity in the recovery of gold, palladium, and sulfur, they are classed among the best extractants. Thus, in terms of reactivity in processes of extracting noble metals, the petroleum sulfides are better than dialkyl sulfides, as confirmed by results obtained in an x-ray spectroscopic study of the valence state of the sulfur atom in their molecules [7]. They are not at all inferior to individual sulfides in selectivity of extraction of noble metals, and hence they are finding diverse applications in the technology of noble metals, not only in the stage of hydrometallurgical processing of ores and concentrates, but also in the refining stage [8].

RAW MATERIAL SELECTION AND PETROLEUM SULFOXIDE SPECIFICATIONS

The acceptability and efficiency of solvents for use in separation processes based on extraction are determined by the chemical and physical properties of the solvent. The most important solvent properties are its capacity for the metal being extracted and its solubility in water. In accordance with the demands of hydrometallurgy, sulfides used as extractants for rare metals must have the following properties: Capacity for neodymium nitrate not less than 50-55 g/liter; solubility in water not greater than 8 g/liter [9].

The petroleum sulfides that are oxidized to obtain sulfoxides are complex mixtures of compounds with various structures and molecular weights. In selecting the optimal distillation range of the feedstock to obtain sulfoxides meeting consumers' requirements, studies have been made of the properties of sulfoxides obtained by various methods [10].

In Table 1 we have listed the characteristics of sulfoxides obtained by oxidation of 20°C fractions and wide fractions of a sulfide concentrate recovered from a diesel fuel cut from Arlan crude by extraction with sulfuric acid; in Table 2 we have listed the characteristics of sulfoxides obtained by oxidizing fractions of the diesel fuel from the same crude, with subsequent recovery of the sulfoxides by the use of selective solvents.

The maximum capacities (90-123 g/liter) are observed for the sulfoxides obtained from 20°C fractions of the petroleum sulfides in the low-boiling range (180-240°C). The content of sulfoxide sulfur in these products is 11.2-14.3% by weight. As the transition is made to higher-boiling sulfides, the capacity of the sulfoxide products decreases. This trend reflects the fact that as the molecular weight of the oxidized product is increased, its content of sulfoxide sulfur decreases, while the extraction capacity of the sulfoxides is governed by the presence of the S=O group. The same sort of relationship was established for sulfoxides obtained by oxidizing fractions of the diesel fuel.

The solubility of the sulfoxides in water also depends on the distillation range of the raw material. For the sulfoxides obtained from the 20°C fractions, the water solubility varies over a broad range, from 142 g/liter for the 180-200°C fraction to 2 g/liter for the 340-360°C fraction. For the sulfoxides obtained from the wide fractions of the sulfides, the water solubility amounts to 4.8-11.8 g/liter. The lowest values were observed for the 260-360, 260-340, and 280-340°C fractions: 7.6, 10.2, and 4.8 g/liter, respectively.

The same sort of variation is observed in the solubility of sulfoxides obtained by direct oxidation of the diesel fuel fractions (see Table 2). The sulfoxides from the 211-345°C fraction have a solubility of 10.44 g/liter; for the fractions with a higher initial boiling point, for example the 258-360 and 265-360°C fractions, the respective values are 7.86 and 7.7 g/liter.

Thus, in order to obtain highly soluble* sulfoxides, it would be advisable to use the highest-boiling raw material. However, with increasing initial boiling point of the raw material, the content of sulfoxide sulfur in the sulfoxide concentrate decreases, as does the yield of the concentrate. The optimal combination of capacity and solubility is found in the raw material with a distillation range of 260-360°C. The sulfoxide concentrates obtained from this material manifest high extraction capacities, 64.0-84.4 g/liter.

These capacities are somewhat lower than for the concentrates from the low-boiling feed, but the losses of the product during the course of service are incomparably smaller, with a solubility of 8 g/liter in comparison with 100-142 g/liter for the low-boiling products. In order to estimate the possible losses of the new extractant under actual processing conditions, a study was made of the changes in its water solubility and other properties in the course of successive contacts of the organic phase with fresh portions of water [11].

The decreases of the quantity of sulfoxides in the organic phase and of their maximum capacity for neodymium nitrate upon successive contacts with water proceed at identical rates, with a trend towards stabilization. The explanation for this behavior is that the sulfoxide concentrate is a multicomponent mixture. Upon contact with water, the first to dissolve are the low-molecular-weight components of the concentrate, which have the highest water solubilities. The remaining components, sulfoxides with higher molecular weights, are less soluble.

A study was made of the influence of depth of oxidation of the 260-360°C fraction of Arlan crude on the quality of the sulfoxides extracted from the oxidized product by 62% sulfuric acid or by acetone. Increases in the depth of oxidation of the sulfides had practically no effect on the service properties of the sulfoxides [12]. Extended storage (1.5 years) of the sulfoxide concentrate in a mild steel drum likewise had no effect on the properties of the concentrate. In the presence of water,

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*As in Russian original. If this refers to solubility in water, the text should read "highly insoluble" —Translator.

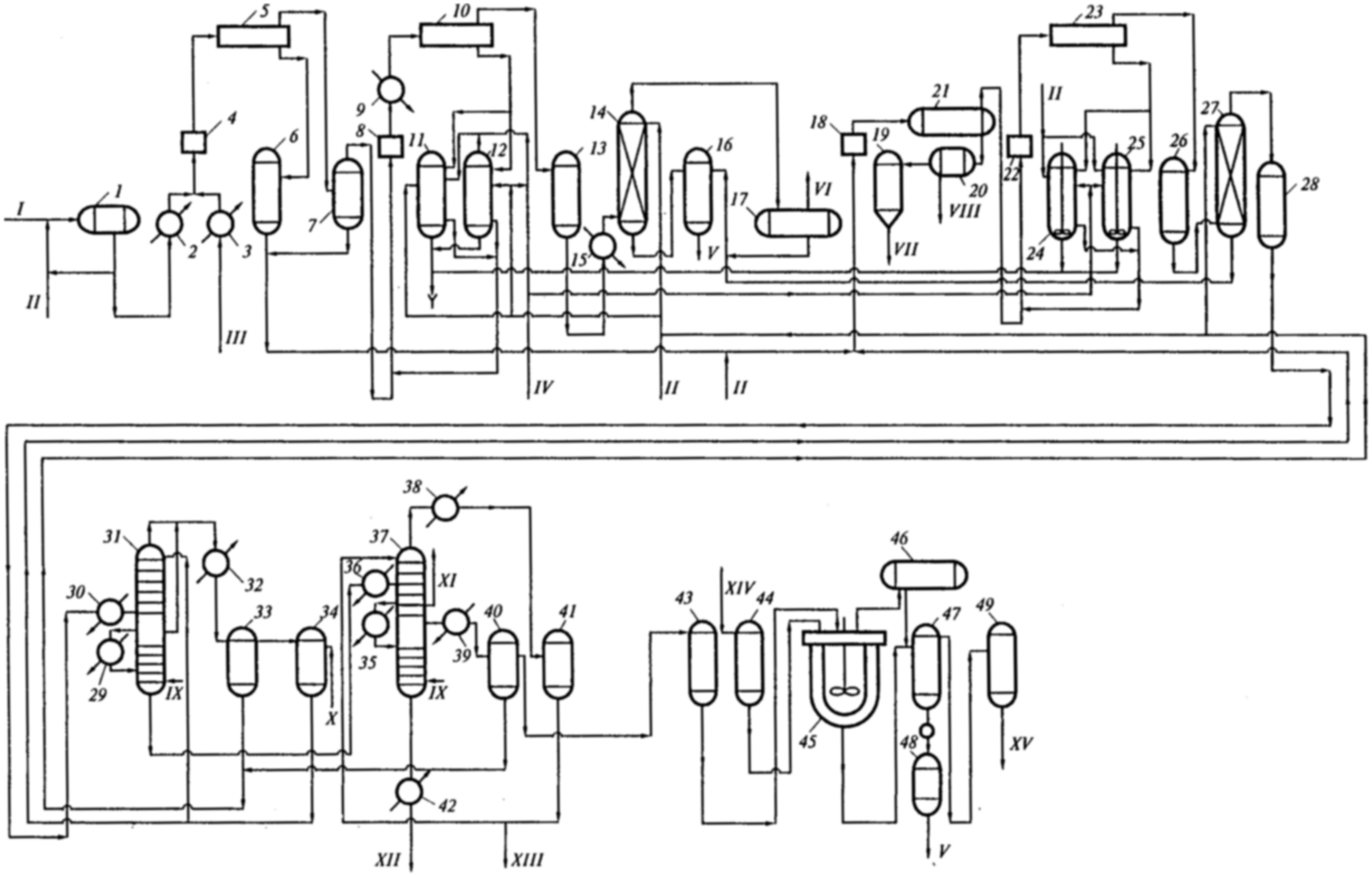

Fig. 1. Process flow plan for the production of sulfoxides by oxidation of sulfides recovered from feed by sulfuric acid extraction: *1,2,7,11-13,16,17,19,24-26,28,33,34,41,43,44,48,49)* Tanks; *2,3,42)* coolers; *4,8,18,22)* mixers; *5,10,20,21,23,40,47)* settlers; *9,15,29,30,35,36,39)* heaters; *14,27)* wash towers; *31)* naphtha stripping tower; *32,38,46)* condenser-cooler; *37)* sulfide distillation tower; *45)* reactor; *I)* spent acid; *II)* water; *III)* feed; *IV)* caustic; *V)* to wastewater treating section; *VI)* raffinate; *VII)* tar; *VIII)* secondary spent acid; *IX)* steam; *X)* naphtha; *XI)* to vacuum system; *XII)* still residue; *XIII)* light sulfides; *XIV)* hydrogen peroxide; *XV)* sulfoxides.

TABLE 3

Product	Yield, wt. % on crude	Sulfur content, wt. %		
		total	sulfide	sulfoxide
Sulfoxides	4,61	11,13	—	at least 7
Raffinate	90,96	1,4—1,6	0,4—0,5	—
Light sulfides	1,25	12	10,5	—
Tar + residue from distillation of sulfides	1,42	—	—	—

however, the sulfoxides become contaminated with corrosion products. Therefore, they should be transported and stored in tightly sealed drums made of carbon steel, with a water content no greater than 5% by weight [13].

The toxicology of sulfide concentrates as influenced by the distillation range of the raw material has been investigated in considerable detail. Sulfides from low-boiling feed are more toxic than those from high-boiling feed, in which bicyclic, tricyclic, and polycyclic sulfides predominate [14]. For the sulfoxides from the 260-360°C fraction, the reference safe level of exposure (GOST 1210076-76) is 2 mg/m^3. An effective method has been developed for treating wastewater in obtaining the sulfoxide concentrate from this fraction [15].

On the basis of the results from these studies, the specification TU 3840221-91 has been developed. According to this specification, petroleum sulfoxides for use in hydrometallurgy must meet the following requirements: Content of sulfoxide sulfur no less than 7% by weight; acidity (calculated as sulfuric acid) no greater than 1.5 g/liter; solubility in water no greater than 8 g/liter; viscosity at 20°C no higher than 170 mm^2/sec; flash point (open cup) no lower than 140°C; water content no greater than 5% by weight.

It was established that the capacity of the sulfoxides is directly proportional to their content of sulfoxide sulfur. This relationship was investigated for a group of sulfoxides obtained from different starting materials by the use of different technologies. In all cases, the ratio of capacity to the content of sulfoxide sulfur was very close to 8 (see Tables 1 and 2). The range of variation, from 7.4 to 8.6, is commensurate with the error in determining the maximum capacity and the content of sulfide sulfur. Therefore, the capacity of the extractant for commercial use is not specified, rather being replaced by an index that is simpler to determine, i.e., the content of sulfoxide sulfur.

The other properties that are specified are the viscosity, acidity, flash point, and water content.

The viscosity of the sulfoxides, as required by consumers, must not exceed 200 mm^2/sec at 20°C. The sulfoxide viscosity increases with increasing initial boiling point of the feed that is oxidized (see Table 2). In view of the possible variations of distillation range of the feed, the viscosity limit for the sulfoxides was set at a maximum of 170 mm^2/sec at 20°C.

The acidity is due to the presence of organic and sulfonic acids that are formed in the oxidation of the feed. The presence of acids is undesirable in certain processes of the hydrometallurgical industry, and also in storage and transportation, as it may cause corrosion of equipment. The acidity can be reduced by neutralizing and washing the sulfoxides. However, it is generally impossible to guarantee zero acidity. For commercial processing conditions, the standard for acidity has been set at a maximum of 1.5 g/liter (as sulfuric acid).

The closed-cup* flash point of the sulfoxides, which characterizes the fire hazard, must be no lower than 140°C. Actually, the sulfoxides have higher flash points, generally 170°C and up.

In determining the conditions for service of petroleum sulfoxides, a study has been made of their thermal stability. Thermal breakdown occurs at higher temperatures with longer heating times. At temperatures above 130°C, sulfur dioxide and hydrogen sulfide are evolved, and the capacity of the sulfoxides for neodymium nitrate drops off sharply [16].

COMMERCIAL SCHEMES FOR THE PRODUCTION OF SULFIDE AND SULFOXIDE CONCENTRATES FROM PETROLEUM RAW MATERIAL

Sulfoxide concentrates can be obtained by two methods [17]. The first method consists of extracting the sulfides from the feed by selective solvents in the first stage, followed by oxidation of the resulting concentrate to sulfoxides in the second

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*As in Russian original; previously stated as open-cup flash point—Translator.

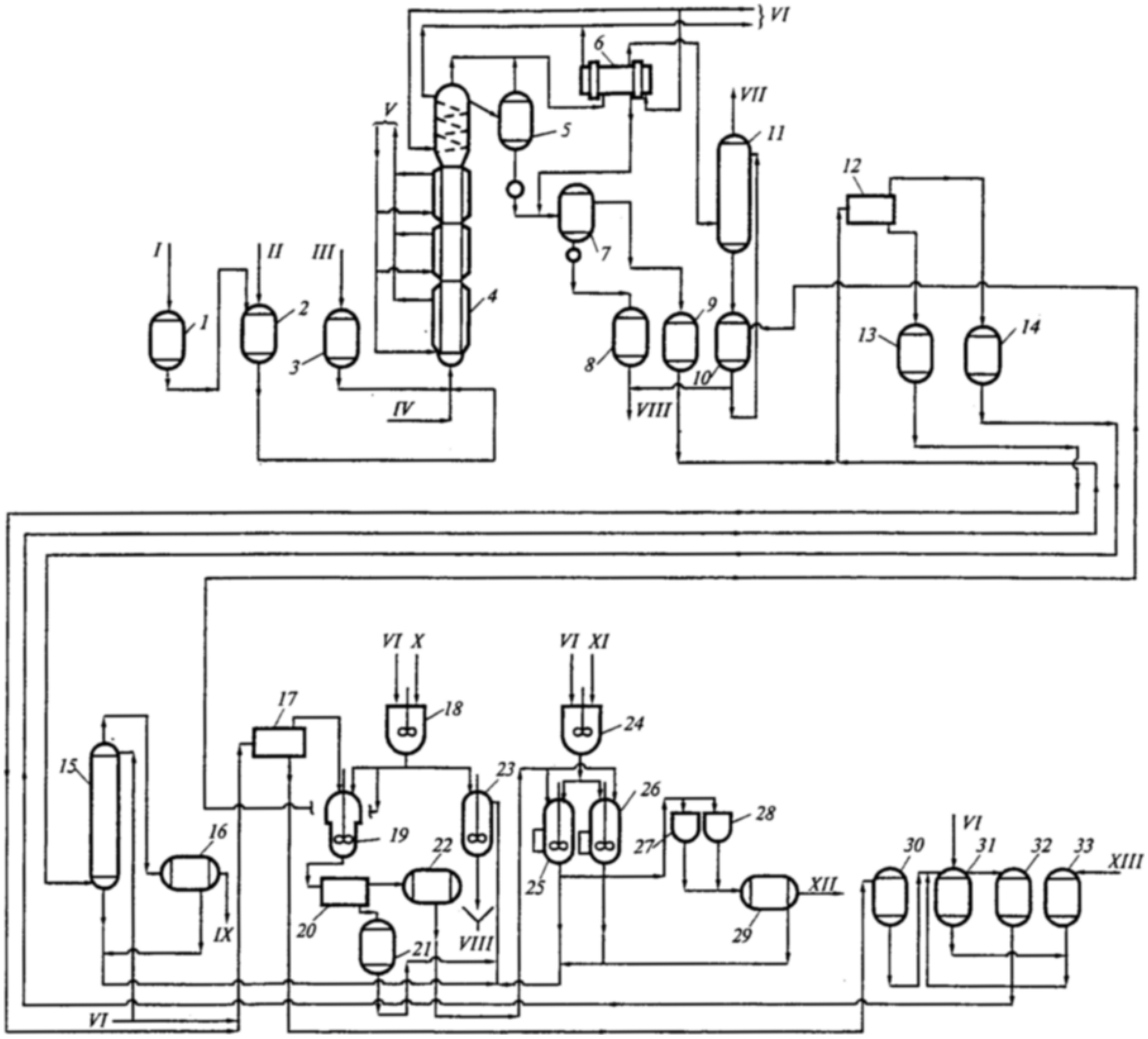

Fig. 2. Process flow plan for the production of sulfoxides by direct oxidation of sulfides in feed, with subsequent recovery of sulfoxides by sulfuric acid extraction: *1-3,8,9,10,13,14,18,19,21-26,30-33)* Tanks; *4)* reactor; *5)* foam knockout; *6)* condenser–cooler; *7,12,16,17,20,29)* settler; *11)* scrubber; *15)* wash tower; *27,28)* filter; *I)* air; *II)* acetic acid; *III)* feed; *IV)* hydrogen peroxide; *V)* heat carrier; *VI)* water; *VII)* waste gas; *VIII)* aqueous phase; *IX)* raffinate; *X)* sodium carbonate; *XI)* sodium sulfate; *XII)* sulfoxide; *XIII)* sulfuric acid.

stage. The second method consists of oxidizing the sulfides directly in the original feed, with subsequent recovery of the sulfoxides by liquid extraction.

There are many possible variants of each method, differing in the nature of the extractant and the oxidation catalyst, the volume of process waste discharge, etc. Therefore, the factual material that has been accumulated does require a critical examination and correlation with respect to methods for obtaining petroleum sulfides and sulfoxides. The sulfide and sulfoxide concentrates are most effective in concentrating rare and nonferrous metals. In this connection, the first commercial schemes for producing these concentrates were developed for the hydrometallurgical industry.

SCHEME I: Production of Sulfoxides by Oxidation of Sulfides Recovered from Feed by Extraction with Sulfuric Acid

The flow plan for this process includes the following stages: Extraction of a sulfide concentrate from a diesel fuel cut by sulfuric acid (spent acid from an alkylation process), distillation of the sulfide concentrate, segregation of the desired fraction

(260-360°C), and oxidation of this fraction to sulfoxides by treatment with hydrogen peroxide. The starting material is a diesel fuel cut from high-sulfur crude, with initial boiling point 190-200°C, end point 355-360°C, and sulfide sulfur content at least 0.8% by weight.

The sulfides are reextracted from the sulfuric acid solution by treatment with a naphtha cut. The acid/feed ratio is 1:2.3 by weight. The reextraction is performed at 25-30°C with a consumption of extractant 10% by volume and water 10% by weight on the extract solution. After separation of the phases, the naphtha layer of the extract is neutralized and washed with water. The naphtha is removed from the washed solution by distillation, and the resulting sulfide product is distilled.

The desired fraction of the sulfides is oxidized at 70-90°C by hydrogen peroxide (27-30% strength), taken in a 4-8% excess relative to the stoichiometric amount as calculated from the content of sulfide sulfur in the concentrate. The sulfide concentrate recovered by treatment with spent sulfuric acid from an alkylation process will contain sulfonic and carboxylic acids in amounts sufficient for the oxidation without the use of any acidic additives [18].

In practice, oxidation of the sulfide concentrate without a catalyst is convenient, since in this case there is less corrosion of equipment, the oxidized product has a low acidity (below 1.5 g/liter as sulfuric acid), and does not require washing with water. After the oxidation has been completed, the organic and aqueous phases are separated in settlers. A flow plan for this process is shown in Fig. 1.

Spent sulfuric acid from an alkylation process is fed together with water to tank *1* for preparation of the acid solution. The solution is circulated until it is completely uniform. Finished acid solution from tank *1* is fed through the cooler *2*, where it is cooled to 45°C, then to the orifice mixer *4*, with the diesel fuel cut also being fed to this mixer through the cooler *3*.

The resulting mixture passes into the settler *5*, where it is separated into an upper phase (raffinate solution) and a lower phase (extract solution). The raffinate solution flows by gravity to the tank *7*, the extract solution to the tank *6*. The small quantity of extract phase that settles out in tank *7* is drawn off from the bottom and added to the extract solution withdrawn from tank *6*.

The raffinate solution is fed from tank *7* to the mixer *8*, where it is mixed with caustic solution supplied from one of two tanks *11* and *12*, which operate alternately. While caustic solution is being prepared in one of these tanks, solution is circulated from the other tank to the settler *10* to neutralize the raffinate, until the caustic is completely spent. From the mixer *8*, the mixture of raffinate and caustic solution passes through the heater *9*, where it is heated to 50°C, and then to the settler *10*.

From the settler, the bottom caustic layer is directed to tank *11* or *12*, the upper layer of neutralized raffinate to tank *13*, from which it is fed through the heater *15*, where it is heated to 60°C, to the bottom of the wash tower *14*. Water is fed to the top of this tower. The washed raffinate is collected in tank *17*; and, after settling for one day, it is withdrawn from the unit. The washwater from the bottom of tower *14* is collected in tank *16*, from which it is directed to the wastewater treating system. Also discharged periodically to this same tank is the water that has settled in tank *17*.

Extract solution from tank *6* is fed to the mixer *18*, to which water and a 90-120°C naphtha cut are also fed. The resulting mixture is directed to the settler *21*, from which the bottom layer (a mixture of spent sulfuric acid and tar) passes to the settler *20*. The upper layer from this settler (tar) flows into the tank *19*, from which it is withdrawn from the unit; the lower layer (secondary spent acid) is also withdrawn from the unit. The upper phase from settler *21* (a solution of sulfides in the naphtha cut) is directed to the mixer *22*. Also fed to this mixer is a 1% caustic solution from tanks *24* and *25*, which operate in the same manner as tanks *11* and *12*.

The mixture of the caustic solution with the neutralized solution of sulfides in the naphtha cut passes to the settler *23*. The upper layer from this settler is collected in the tank *26*, from which it is fed to the bottom of the wash tower *27*. The caustic solution from settler *23* passes to tank *24* or *25*; and after the treatment, it is withdrawn from these tanks and is added to the waste streams from tanks *11* and *12*. Water is fed to the top of tower *27* to wash the neutralized solution of sulfides in the naphtha cut. The washwater from the bottom of this tower is combined with the washwater from tower *14*, and the mixture passes to the tank *16* and from there to the wastewater treating section.

The washed solution of sulfides in the naphtha cut flows to tank *28*, from which it is fed to the naphtha stripping tower *31*, which consists of two sections. In the top section, most of the naphtha cut is taken off; in the bottom section, the remainder of the naphtha cut is removed by steam stripping. The vapor from both sections is condensed in the condenser-cooler *32*. The condensate is separated from the water in tank *33*. Water from the bottom of this tank is used in tower *27* as washwater. The naphtha cut passes into tank *34*, from which part of it is directed as reflux to the top section of tower *31*, while the remaining quantity is fed to the mixer *18*.

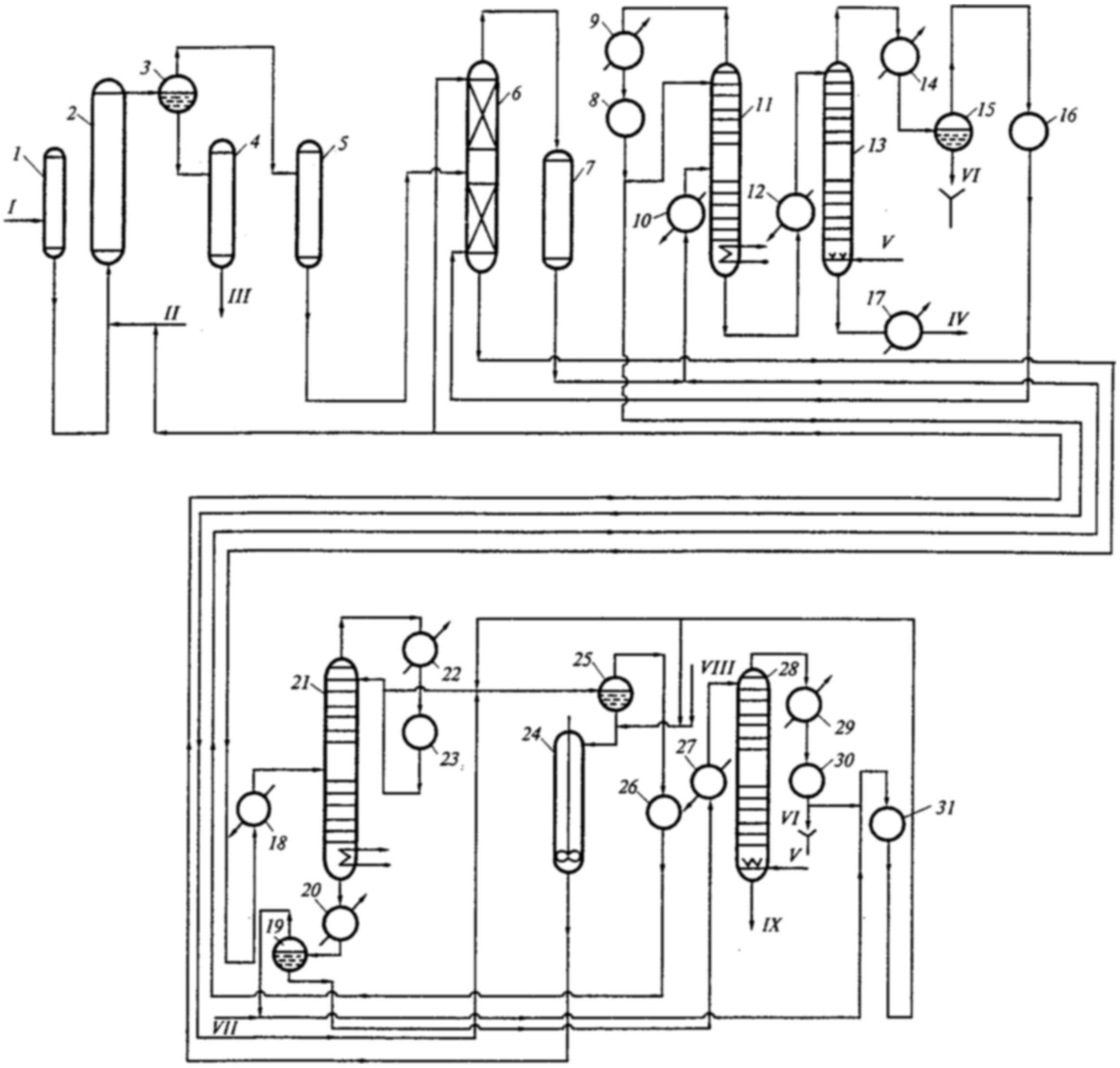

Fig. 3. Process flow plan for the production of sulfoxides by direct oxidation of sulfides in feed, with subsequent recovery by acetone extraction: *1,4,5,7,8,16,23,24,26,30,31)* Tank; *2)* reactor; *3,15,19,25)* settler; *6)* extractor; *9,14,22,29)* condenser–coolers; *10,12,18,27)* heaters; *11,21)* raffinate and extract fractionation towers, respectively; *13)* raffinate stripping tower; *17,20)* coolers; *28)* drying tower; *I)* hydrogen peroxide; *II)* feed; *III)* to wastewater treating section; *IV)* raffinate; *V)* steam; *VI)* water to sewer system; *VII)* fresh water; *VIII)* acetone; *IX)* sulfoxides.

The sulfides, after distilling off the naphtha cut, are withdrawn from the bottom of tower *31* and fed to distillation tower *37*, which is a vacuum tower consisting of two sections. The upper section serves for removal of the head fraction of the sulfides (IBP-260°C) as the overhead product. This vapor stream, after condensation in the condenser–cooler *38*, passes to tank *41*, from which part of the head fraction is fed back to the top of tower *37* as reflux, while the balance quantity is withdrawn from the unit. The still residue from the top section of tower *37* flows into the bottom section.

In the bottom section, the desired 260-360°C fraction of the sulfides is taken as the overhead product by steam distillation. The combined product vapor and steam is condensed in the condenser–cooler *39* and collected in the settler *40*. Water from the bottom of this settler is fed to the top of the wash tower *27*. The sulfide fraction flows over to tank *43*, from which it is directed to oxidation. The still residue from tower *37* is pumped away from the unit through the cooler *42*. Heat is supplied to tower *31* by heaters *29* and *30*, and to tower *37* by heaters *35* and *36*.

The sulfide oxidation process is a batch process. In order to provide continuity of operation, the process is performed by alternating the use of several batch reactors. The desired fraction of sulfides from tank *43*, together with hydrogen peroxide

TABLE 4

Consumption	Process scheme		
	I	II	III
Diesel fuel cut, t/t*	21,684	17,724	13,543
Hydrogen peroxide, t/t	0,344	0,856	0,571
Acetic acid, t/t	—	0,186	—
Spent sulfuric acid from alkylation process, t/t	9,07	—	—
Sulfuric acid (92.5%), t/t	—	0,676	—
Sodium sulfate, t/t	—	0,296	—
Calcined sodium carbonate, t/t	—	0,726	—
Solvent naphtha, t/t	0,07	—	—
Acetone, t/t	0,138	—	0,029
Heptane solvent, t/t	—	—	0.007
Caustic (42%), t/t	0,03	—	0,1
Electric energy, kW·h/t	1366,6	2190	2986
Steam, GJ/t	7,05	2,52	81,6
Water, m^3/t			
chemically treated	16,2	28	5
recirculating	81,3	100	750
Compressed air, m^3/t	82,0	160	—
Inert gas, m^3/t	84,0	100	—

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*Metric tons throughout.

TABLE 5

Index	Sulfoxides obtained by indicated process scheme		
	I	II	III
Density at 20°C, kg/m^3	990	1020	1027,8
Viscosity, mm^2sec			
at 20°C	55,77	121,17	79,88
at 40°C	19,47	31,5	22,93
at 50°C	12,60	18,9	16,40
at 80°C	6,36	6,59	5,39
Temperature, °C			
flash point			
open cup	196	152	152
closed cup	188	145	145
solid point	-55	-30	-50
autogenous ignition temperature	247	241,5	241,0
Sulfur content, wt. %			
total	11,13	11,35	9,62
sulfoxide	7,20	10,66	8,6
Acidity as sulfuric acid, g/liter	0,80	0,56	1,0
Solubility in water, g/liter	7,80	7,6	7,8

from tank *44*, is fed to oxidation in the reactor *45*. The steam that is formed in the oxidation process is condensed in the condenser-cooler *46*. The resulting condensate passes to the settler *47*. To this same settler, upon completion of the oxidation, the oxidized product is fed from reactor *45*. Water from the bottom of settler *47* passes to the tank *48*. The sulfoxides are fed to the finished-product tank *49*, from which they are withdrawn from the unit.

This flow plan is protected by inventor's certificates [19, 20].

The yield and quality of the commercial product and the by-products obtained from the Arlan diesel fuel cut are illustrated in Table 3.

SCHEME II: Production of Sulfoxides by Direct Oxidation of Sulfides in Feed, with Subsequent Recovery by Sulfuric Acid Extraction

This process includes two stages. In the first stage, the sulfides present in the feed are oxidized to sulfoxides by hydrogen peroxide; in the second stage, these sulfoxides are recovered from the oxidized product by extraction with sulfuric acid. The starting material is a diesel fuel cut from high-sulfur crude, with IBP 265-270°C, EP 355-360°C, and sulfide sulfur content no lower than 0.8% by weight.

In this scheme, the volume of feedstock that is subjected to oxidation is considerably greater. Here, stirred reactors are quite ineffective, since the residence of the reactants in the reaction zone requires considerable time. The sulfide oxidation process is intensified by carrying it out in a foam–emulsion regime [21]. A foam reactor has been specially designed for this purpose. The oxidation is performed with a stoichiometric amount of 30%-strength hydrogen peroxide, calculated on the basis of the content of sulfide sulfur in the feed, with the use of glacial acetic acid as a catalyst in amount of 1-5% on feed. When the reaction is performed at 115°C with a superficial air velocity of 0.05 m/sec and an oxidation time of 21 min, the conversion of sulfides to sulfoxides amounts to 70-75%.

The sulfoxides are recovered from the oxidized fraction by extraction with 62% sulfuric acid, with an acid consumption of 1 ton of the monohydrate per ton of sulfoxides. The sulfoxides are recovered from the extract phase either by diluting it to a sulfuric acid concentration of 40% by weight or lower, or by neutralization and subsequent settling of the phases. For neutralization, a 15% sodium carbonate solution is used. In this solution, the sulfoxides separate in the form of a distinct layer, and are directed to a washing operation.

Since the sulfoxide density is very close to that of water, the washing operation is performed with a 10% sodium chloride or 7% sodium sulfate solution in order to ensure layer separation. Since the presence of chloride ions in wastewater is undesirable, the sodium sulfate is preferred. The weight ratio of salt solution of sulfoxides is 2:1. The process flow plan is shown in Fig. 2.

Feedstock from the tank farm and acetic acid from tank *1* are fed to the mixer *2*, from which the feed mixture is pumped to the reactor *4*; hydrogen peroxide from tank *3* is also fed to the reactor *4*. This reactor is an oxidation tower consisting of four sections. Perforated trays are installed ahead of each section. In the first three sections, the feed is oxidized; the fourth section fulfills the function of a condenser–cooler. The reaction sections are jacketed and equipped with thermocouples and sampling cocks. These sections are heated by a heat carrier.

The process operates in the foam regime by feeding air to the reactor *4* from a compressor. The foam that is formed by blowing air through the layer of reactants on a perforated tray passes out of the fourth section of the tower, after cooling, to the foam knockout drum *5*, from which the reaction products are withdrawn to the settler *7*, where they separated into two layers. The upper layer of oxidized product is taken off continuously to the tank *9* and is then directed to the section of the unit for sulfoxide recovery. The lower layer is drained off periodically (as it accumulates) to the tank *8*, from which it is directed to the wastewater treating section.

The gas phase from reactor *4* and the foam knockout drum *5* passes to the condenser–cooler *6*, from which the condensed vapors of steam, acetic acid, and hydrocarbons drain into the settler *7*; the cooled air, which contains a small amount of acetic acid, passes to the scrubber *11*. In the scrubber, the acetic acid vapor is absorbed by a 15% sodium carbonate solution that circulates between the tank *10* and the scrubber. The spent sodium carbonate solution from this tank passes to the wastewater treating section. Fresh sodium carbonate solution enters the tank *10* by gravity flow from tank *18*.

The oxidized product from tank *9* and the water-cut 62% sulfuric acid from tank *32* are mixed and then fed to the settler *12* for phase separation. The light phase of raffinate solution, consisting of partially desulfurized diesel fuel with a small amount of sulfuric acid, passes through the intermediate tank *14* to the bottom of the wash tower *15* for removal of the acid. Water is fed to the top of the tower. The washed raffinate is withdrawn from the bottom of the tower to the settling tank *16*, from which water is discharged periodically to the washwater line, directed from the tower *15* to the neutralizer *23*. The finished raffinate is pumped out of the unit.

The extract solution, consisting of sulfoxides, sulfuric acid, and water, passes from the settler *12* to the tank *13* and then, after dilution with water to an acid concentration of 40%, passes into the settler *17*. Part of the diluted acid from the settler is sent to tank *30* and used to dilute fresh acid in tank *31*. The remainder of this acid, together with the sulfoxides, passes over to tank *19* for neutralization; sodium carbonate solution from tank *18* is also fed to the neutralizer tank. The tanks *18* and *19* are equipped with mechanical stirrers. From tank *18*, the neutralized product passes to the settler *20*, where it separates into two layers. The upper layer of sulfoxides is fed through the intermediate tank *22* to the washing operation; the lower layer of neutralized acid passes through the intermediate tank *21* to tank *23*.

The washing of the sulfoxides with aqueous sodium sulfate solution is accomplished periodically in parallel tanks *25* and *26*, which are equipped with mechanical stirrers. The sodium sulfate solution is prepared in tank *24*. The washwater is directed to tank *23* for neutralization. The sulfoxides, through parallel-operating filters *27* and *28*, are fed to the settler *29*, from which they are withdrawn to the finished product tank farm.

Fresh acid is fed to tank *33*, from which it is directed to tank *31* for mixing with diluted acid from tank *30*. The finished 62% sulfuric acid passes over to tank *32*, from which it is fed to the extraction operation.

This flow plan is protected by a patent [22] and an inventor's certificate [23].

The respective yields of sulfoxides and raffinate are 5.7% and 92.3% on feed; their respective total sulfur contents are 11.35% and 1.5% by weight, and sulfoxide sulfur contents 10.66% and 0.15-0.18% by weight.

SCHEME III: Production of Sulfoxides by Direct Oxidation of Sulfides in Feed, with Subsequent Recovery by Acetone Extraction

A significant disadvantage of the two schemes thus far considered is the use of acids, both in the sulfide oxidation stage and in the sulfide or sulfoxide extraction stage. Therefore, attempts have been made to develop new, ecologically clean, closed-cycle methods for obtaining petroleum sulfides and sulfoxides. As a result of a series of studies reported in [24], an ecologically clean scheme has been developed for sulfoxide production.

The oxidation of sulfides with hydrogen peroxide is performed in the presence of catalytic quantities of acetone. Acetone is also used to extract the sulfoxides from the oxidized product. When acetone is used simultaneously as a catalyst and an extractant, the technology of sulfoxide production becomes much simpler. The process flow plan is shown in Fig. 3.

Feedstock from the tank farm, hydrogen peroxide from tank *1*, and acetone are fed to the reactor *2*. The reactor consists of a pipe designed to ensure interaction of the immiscible liquids. The reactor parameters (length and diameter) and the reactant feed rates are determined by calculation. Sulfides are oxidized to sulfoxides in the reactor. After the oxidation is completed, the reaction products are withdrawn to the settler *3*, where they are separated into two layers. The upper layer, the oxidized product, is withdrawn to the tank *5*; the lower aqueous layer is drained to the wastewater tank *4*, from which it is sent to the treatment section.

Oxidized product from tank *5* is fed to the middle of the extractor *6*, which is a column-type vessel, set up for countercurrent extraction. The solvent, water-cut acetone, is fed to the top of the extractor, and the wash solvent (heptane fraction) is fed to the bottom of the extractor.

As a result of the use of two solvents with very little mutual solubility, the sharpness of separation of the feed components is increased and phase separation is improved; this facilitates the operation of the extractor. Water-cut acetone is used as the extractant. The dilution with water reduces the solvency of the acetone, thus tending to improve the layering of the phases in the reactor as a consequence of the greater density difference.

The raffinate solution, consisting of partially desulfurized diesel fuel, acetone, and the heptane fraction, is withdrawn from the top of the extractor. It passes to the tank *7*, from there through the heater *10* to the fractionation tower *11*. The azeotrope of acetone and heptane taken from the top of this tower is condensed in the condenser–cooler *9*. The condensate is collected in tank *8*, from which part is returned to the tower as reflux and the balance is taken off to the settler *25*.

The bottom product from the fractionation tower is a residue consisting of raffinate and heptane that was not distilled off with the azeotrope. This bottom product passes through the heater *12* to the stripping tower *13*, with steam fed to the bottom of this tower. The heptane and water vapor from the top of the stripping tower are condensed in the condenser–cooler *14*. The condensate passes to the settler *15*, where it is separated into two layers—an upper heptane layer and a lower water layer. The water is discharged to the sewer system; the heptane flows by gravity to tank *16*, from which it is fed to the bottom of the extractor *6*. The raffinate from the bottom of the stripping tower passes through the cooler *17* and is withdrawn from the unit.

The extract solution from the bottom of the extractor *6* is fed through the heater *18* to the fractionation tower *21*. The stream from the top of this tower consists of vapors of acetone and heptane that are present in the extract solution. After condensation in the condenser–cooler *22*, this solvent mixture is collected in tank *23*, from which part of the product is fed back to tower *21* as reflux, and the balance is fed, together with the azeotrope from tower *11*, to the settler *25*.

From the bottom of tower *21*, a two-phase mixture of sulfoxides and water drains through the cooler *20* to settler *19*, which is positioned below the level of the tower; here, it is separated into an upper aqueous layer and a lower sulfoxide layer. The aqueous layer from settler *19* is fed first to tank *31* and is then, after mixing with distillates from towers *11* and *21*, passes into the settler *25* for dilution of the acetone.

The mixture in the settler is separated into two layers—an upper heptane layer with small amounts of acetone, and a lower layer consisting of water-cut acetone with a small amount of heptane. The upper layer drains into tank *26*, from which it is fed into the feed line of the fractionation tower *11*. The lower layer, acetone, flows by gravity into tank *24*, from which it is fed to the top of extractor *6* and to the reactor *2*.

The sulfoxides from the settler *19* pass through the heater *27* to the steam-stripping drying tower *28*, which operates under vacuum. Steam is fed to the bottom of this tower; water vapor is taken from the top and is condensed in the condenser–cooler *29*. The condensate is collected in tank *30*, from which it is discharged to the sewer system or, if necessary, is directed to tank *31* to make up water losses. The dried sulfoxides from the bottom of tower *28* are taken off to the finished product tank.

This unit includes a system for preparation of the aqueous solution of acetone. Water, through tank *31*, is directed to the stirred tank *24*. The required quantity of fresh acetone *VIII* is also fed to this tank. The water and acetone are mixed for 15 min at 40°C. In starting up the unit, water-cut acetone is fed to the extractor *6* and reactor *2*.

This flow plan is protected by inventor's certificates [25, 26].

The respective yields of sulfoxides and raffinate are 7.45% and 90.91% by weight on feed; the respective total sulfur contents in these products are 9.62% and 1.3% by weight, sulfoxide sulfur 8.6% and 0.08-0.1% by weight.

TECHNOECONOMIC COMPARISON OF SCHEMES FOR THE PRODUCTION OF SULFOXIDE CONCENTRATE

The results obtained in the operation of experimental and semicommercial units using these process schemes are presented in Table 4.

Scheme I. Significant disadvantages: High specific consumption of sulfuric acid (more than 9 tons of sulfuric acid are required to obtain 1 ton of sulfoxides); formation of large amounts of tar, which is a viscous product with a high content of sulfur (up to 10% by weight); removal of tar from the surfaces of the vessels requires periodic washing with solvents and subsequent distillation to recover the solvent from the tar.

Principal advantages: Reuse of spent sulfuric acid as an extractant that exhibits high selectivity in the separation of sulfides and hydrocarbons and is very stable, so that it can be regenerated repeatedly; high density of sulfuric acid, which favors rapid and clean layering of phases; ready availability and low cost of sulfuric acid; low manufacturing cost of sulfoxides, and small capital investment; possibility of obtaining a sulfide concentrate as a commercial product.

Scheme II. Disadvantages: Somewhat greater capital investment; need for treating acid discharges; difficulty in utilization and regeneration of dilute (40%) acid. Advantages: Higher yield of sulfoxides; lower consumption of sulfuric acid; operation of reactors in the foam–emulsion regime, simplifying the mechanical design of the continuous process and tending to give a significant increase in the reaction rate, owing to the highly developed interfacial contact surface.

Scheme III does not have any of the disadvantages of Schemes I and II. Advantages: High selectivity in oxidation of the sulfide; use of acetone as a catalyst and also as an extractant (the acetone is a low-boiling material that is thermally and chemically stable, low-cost, readily available, and low-toxicity; it is readily regenerated from the extract and raffinate solutions); high recovery of sulfoxide; small volume of process discharges; formation of contaminated water only in the stage of sulfide oxidation, in amounts smaller than the quantity of sulfoxide product by a factor of 1.5-2; absence of any production wastes (tar, gas discharges, etc.).

The sulfoxides obtained by the different process technologies will meet the specification requirements in all respects (Table 5). The raffinates obtained through Schemes I-III, after hydrotreating, can be used as a component of diesel fuel. Production of sulfoxides from petroleum raw material, using any of these three schemes, can be set up on the base of equipment already available in refineries and petrochemical plants.

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