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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**PROCESSING OF SULFUR GASES (H₂S, SO₂, COS) IN
CLAUS STAGE AND CLEANING IN THE LIQUID PHASE**

Speciality: 3303.01 – Chemical technology and engineering

Field of science: Technical

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Dissertation work was performed at the Institute of of Catalysis and Inorganic Chemistry named after Academician M.Nagiyev of ANAS in the laboratory of "Processing of non-ferrous metal mineral raw materials"

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GENERAL CHARACTERISTICS OF THE TOPIC

Urgency and using into practice of the topic. Today, one of the main issues before the country's economy is to develop non-oil sector. From this point of view, along with the acquisition of the main product during the complex processing of mineral raw materials in the country, the protection of environmental requirements, the re-involvement of waste in production is one of the key issues. Thus, along with the extraction of all useful components during the processing of sulfide ores in our country, the sulfur gas to be obtained can be converted more freely into sulfur, gypsum, sulfuric acid, etc. makes it necessary to create new technologies for conversion and to conduct research for its implementation. Also, while previously sulfur-containing gases (oil and gas, non-ferrous metallurgy) were considered waste, free sulfur sources are now considered raw materials due to depletion, and almost 90% of free sulfur and its corresponding compounds are obtained from sulfur-containing gases.

At present, in order to maintain the economic performance of the enterprise in the field of processing of industrial gases containing sulfur, as well as environmental protection issues must be addressed. This requires new research to improve existing technologies. The most widely used method of processing sulfur-containing gases in the world in the Claus method, sulfur-containing gases (COS, SO₂, H₂S) remaining after reduction of metallurgical gases with various reducing agents are converted into free sulfur in two catalytic stages, "hot" and "cold". However, because the Claus process is exothermic and rotating, it is not possible to purify these gases to meet environmental requirements. Despite the fact that the gases left over from the Claus process are recycled in two large catalytic units, the harmful gases still contain harmful sulfur gases.¹ Therefore, in modern times, it is more expedient to conduct research in the liquid phase in order to prevent the loss of some of the free sulfur in the

¹ Fot, S.A. Kalimeneva, O.A., Akimova, M.V. Sources of sulfur losses and ways to improve the efficiency of the Claus and Sulfren units //—Moscow: city No. 11. Gas industry,—2017 No. 11, pp. 106-111.

form of fog, to carry out complete neutralization of gases.

An analysis of the literature review shows that the reagents used to absorb sulfur-containing gases in the liquid phase are either expensive or highly toxic. Therefore, it is important to find and apply more effective, selective, renewable absorbents.

Objectives and tasks of the Research. The object of our research is the complete neutralization of various sulfur-containing gases in the non-ferrous metallurgy and oil and gas industry, their purification to meet environmental requirements, and the conversion of such gases into sulfur and sulfur-containing products.

In order to achieve the set goal, it was necessary to solve the following issues:

- Study of more efficient conversion of hydrogen sulfide in sulfur in the developed model gases and real gases
- Determination of optimal parameters of reduction of SO_2 in methane catalytic reduction products (SO_2 , COS) to H_2S on aluminocobalt-molybdenum (AKM) catalyst and study of oxidation of H_2S in free sulfur in liquid phase
- Absorption and neutralization of SO_2 by red sludge from aluminum industry residues and parallel study of the possibility of dissolution of metal components in sludge
- Exploring the possibility of converting gases containing SO_2 and H_2S into various harmless products by absorbing them with chlorinated lime
- Study of conditions for neutralization of real gases obtained from the reduction of SO_2 on the AKM catalyst by conversion gas with chlorinated lime.

Research methods. Chemical, chromatographic, fluorescent spectrometry analysis methods were used during the work.

The main provisions of the work. Development of basic technological schemes for neutralization of SO_2 , H_2S , COS generated during processing in metallurgy, oil and gas, chemical industry separately and together; Determination of the activity of the catalyst and the optimal parameters of the process in the reduction of sulfur dioxide with methane and conversion gas in the presence of an aluminocobalt-molybdenum catalyst; study of the process of oxidation

of hydrogen sulfide with nitric acid under the condition of regeneration of the oxidizer in the reaction medium; study of conditions of absorption of sulfur dioxide by red sludge; Development of chlorinated lime method for processing hydrogen sulfide separately and in gases with sulfur dioxide.

Scientific innovation of the work. For the first time, a method was developed to oxidize H₂S-containing gases to HNO₃, provided that the oxidizer was regenerated in the reaction medium to sulfur.

Theoretical and practical significance of the research. The obtained scientific and experimental results can be applied for the neutralization of various industrial waste gases containing sulfur (oil and gas, metallurgy, etc.) and the production of industrial products.

Preliminary results can be the basis for the development of new technologies for the processing of sulfur-containing metallurgical gases (SO₂, H₂S, COS).

The proposed waste gas treatment methods are particularly useful for capturing low-concentration gases that are difficult to neutralize.

The results of research on the extraction of useful metal components by neutralizing high-alkaline red sludge for processing and neutralization of SO₂ in metallurgical gases may be the basis for future sludge processing technology.

The personal role of the author. Analysis of the current state of methods of purification of sulfur-containing gases, problem statement, purpose of work, ways to achieve this goal. Substantiation of the applied method, organization and conduct of experiments, analysis of the obtained results, writing of patents, articles and theses, preparation for publication were carried out by the author personally and sometimes with his participation.

Approbation and applied. Based on the results of research on the dissertation, 15 scientific works were published in foreign and national journals, periodicals published in international summary and indexing systems, conference materials, including 2 patents, 7 articles, 6 conference materials.

The materials of the dissertation were discussed at the following scientific conferences. "International Congress Fashmesse

Euro-Eko (Hannover 2015), Satellite conference of the XX Mendeleev Congress on General and Applied Chemistry (Volgograd, 2016), Proceedings of the XXVI Russian Youth Scientific Conference “dedicated to the 120th anniversary of the birth of Academician N.N. Semenov (Yekaterinburg, 2016), Collection of articles on the results of the International Scientific practical conference, “Science, education and innovation” (Kazan 2017), XXI Mendeleev Congress on General and Applied Chemistry. In 6 volumes (St. Petersburg 2019), Proceedings of the XIII International Scientific Conference “Actual Problems of Chemistry” for doctoral students, masters and young researchers dedicated to the 96th anniversary of National Leader Heydar Aliyev (Baku-2019).

Name of the organization where the dissertation work was accomplished.

The dissertation work was accomplished in accordance with the plan of scientific research work carried out at the Institute of Catalysis and Inorganic Chemistry named after academician M.Naghiyev of ANAS (state registration 0115 AZ 2099).

Volume and structure of the dissertation: The dissertation consists of an introduction, 5 chapters, result, a list of references (205). Work 195000 (introduction 8023, Chapter I 44571, Chapter II 17507, Chapter III 34495, Chapter IV 14548, Chapter V 34055, result 3509) consists of a sign and covers 24 tables, 19 graphics, 17 figures.

In the introduction, substantiates the relevance of the dissertation, the purpose of the work, the provisions to be defended, the scientific innovations and practical significance of the work was explained.

In the first chapter, in accordance with the content of the dissertation, an analysis of the literature on modern methods and technologies for the processing of sulfur-containing industrial gases is given, and various existing processing directions were analyzed.

The second chapter is devoted to the methodology of the experiments, the characteristics of the reagents taken and the description of the laboratory equipment.

In the third chapter, the oxidation of H₂S under the condition

of regeneration in the reaction medium of the oxidizer (HNO_3) was studied. SO_2 was reduced on the proposed AKM catalyst with methane to obtain a gas mixture containing H_2S and suitable for metallurgical gases. The remaining gases were also reduced to H_2S on the catalyst to oxidize real gases with nitric acid.

Chapter 4 identifies the optimal parameters for the absorption of red gaseous gases containing SO_2 or gases remaining after the Claus process.

In the fifth chapter, the conditions of neutralization of gases containing both H_2S and SO_2 with chlorinated lime and their transformation into gypsum were studied. Optimal parameters of methane reduction with different types of methane conversion products have been found to obtain real gas and achieve high sulfur yield in the first stage of sulfur dioxide processing.

MAIN CONTENT OF THE WORK

Reduction of gases to hydrogen sulfide in the Claus process and oxidation of the latter to free sulfur in the liquid phase

In this method, the process of complete purification of H_2S was carried out without the use of a catalyst, in less time, without obtaining an intermediate product, minimizing the consumption of additional reagents, regenerating the absorbing solution. To achieve this goal, nitric acid is proposed for the first time as an oxidizer of hydrogen sulfide in industrial waste gases. One of the biggest advantages of this process is that since H_2S is a strong reducing agent and HNO_3 is a strong oxidizer, the reaction proceeds very rapidly, and it is possible to regenerate the oxidant (HNO_3) in the reaction medium under normal conditions by giving atmospheric oxygen or pure oxygen. The experiments were performed by mixing a gas (or oxygen) containing 1-100% (volume) H_2S and releasing it from a column containing 10-60% (mass) HNO_3 solution at a rate of 50-200 ml / min with reverse flow at 25-70° C. carried out.

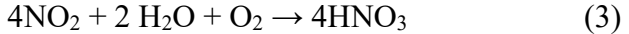
The following reaction occurs:



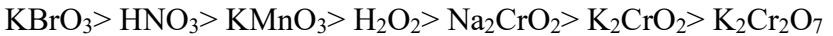
O₂ in the initial mixture reacts with the obtained NO under normal conditions:



NO₂, in turn, is absorbed by water and converted to HNO₃, thus reducing the oxidant.

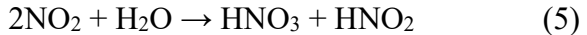
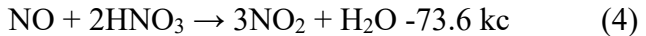


The presence of HNO₃ in the environment further increases the rate of NO oxidation. The oxygen-giving activities of liquid oxidants in this process have been tested experimentally and the following results have been obtained.



As can be seen, HNO₃ has a fairly high activity in the oxidation of NO.

Heterogeneous oxidation of NO to HNO₃ is associated with the following reactions:



If the Cd (CH₃COO)₂ solutions in the drexel placed after the reactor does not turn yellow, this indicates that H₂S has completely reacted, is no longer present, and is completely converted to sulfur. Under the above conditions (25⁰C, φ (H₂S) -20%, ω (HNO₃) ≈30%) the concentrations of HNO₃ solutions before and after the experiment are the same, so nitrogen gases are completely absorbed and converted to nitric acid.

In subsequent experiments, various parameters were added to the process - the rate of gas supply, the concentration of H₂S and HNO₃, temperature, etc. effects have been studied.

As can be seen from table 1, both processes (oxidation and HNO₃ reduction) end at a 100% loss at low concentrations and relatively low gas delivery rates.

It is possible to completely convert H₂S to sulfur of any concentration under given conditions. However, when the concentration of H₂S is higher than 20%, its complete oxidation is not possible due to the large amount of NO obtained at one time. Also, as the gas flow rate increases to 150 ml/min, the recovery rate

of HNO₃ decreases. This is due to the fact that due to the high speed, there is not enough time for complete oxidation of gases.

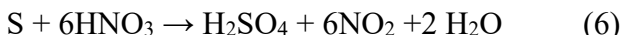
Table 1
Dependence of oxidation of H₂S and reduction of HNO₃
on gas concentration and delivery rate.
(reaction time 30 minutes, temperature 25⁰C)

Gas, ml/min	$\varphi(\text{H}_2\text{S}), \%$	The amount of sulfur obtained, g	S ₂ of H ₂ S conversion rate, %	HNO ₃ recovery, %
50	1	0,021	100	100
	10	0,21	100	100
	20	0,42	100	100
	50	1,07	100	97
	80	1,71	100	87
	100	2,14	100	82
100	1	0,042	10	100
	10	0,42	100	100
	20	0,85	100	100
	50	2,125	100	89
	80	3,42	100	80
	100	4,28	100	68
150	1	0,063	100	100
	10	0,63	100	97
	20	1,26	100	92
	50	3,21	100	81
	80	5,04	100	73
	100	6,42	100	62

As can be seen, the higher the volume fraction of hydrogen sulfide in the primary gas, the lower the efficiency of the process. That is, the complete recovery of nitric acid, which is one of the main goals, does not take place. In the presence of small amounts of H₂S in industrial gases, they are first absorbed by alky-lamines and concentrated, and then processed by the Claus method. However, during oxidation with nitric acid, sulfur can be obtained directly from these gases without condensation.

The study of the temperature dependence of the oxidation of H₂S and the subsequent regeneration of HNO₃ showed that as the temperature increases, some of the H₂S oxidizes to sulfate.

This is due to the reaction (1) to obtain dispersed sulfur with very small particle size. It is known that solid sulfur reacts with hot nitric acid. Dispersed sulfur, on the other hand, reacts more easily with HNO₃, starting at a temperature of 50 ° C, as can be seen from experiments:



The amount of sulfate ions obtained was determined by precipitation in the form of BaSO₄ by gravimetric method. Increasing the temperature to 70° C does not adversely affect the recovery of HNO₃ at the indicated temperature and concentration of the gas (table 2). This can be explained by the increase in the rate of the endothermic (4) reaction with increasing temperature. However, it is not necessary to raise the temperature above 50⁰ C in order to obtain free sulfur.

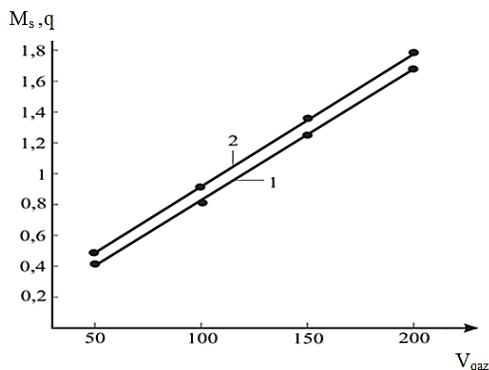
Table 2
Dependence of H₂S oxidation and HNO₃ reduction on
reaction temperature [Vgaz- 50 ml / min, φ (H₂S) -1%]

Temperature, 0C	Conversion rate of H ₂ S,%	Mass of BaSO ₄ obtained, g	Recovery of HNO ₃ ,%
25	100	-	100
40	100	-	100
50	100	0,02	100
60	100	0,035	100
70	100	0,048	100

It was found that the obtained sulfur suspension increased the reaction rate by increasing the contact surface of the gas and liquid. To clarify this, as in previous experiments, a gas containing H₂S is passed through 30% nitric acid (t = 25⁰C, gas delivery rate 100 ml/min). The amount of sulfur in the resulting solution is brought to 10 g/l. Subsequent work is already being carried out at different rates of delivery of a mixture of 10% H₂S and N₂ with a solution of nitric acid containing sulfur suspension to the reactor (figure 1).

It has been found that the presence of a sulfur suspension accelerates both the oxidation of H₂S and the recovery of HNO₃.

Thus, the amount of sulfur obtained in a solution containing a sulfur suspension at the same time and under the same conditions is greater than the amount of sulfur obtained from the oxidation of H_2S to pure HNO_3 . It also allows for the regeneration of HNO_3 to be carried out at relatively high volumes.



**Graphic 1. The dependence of the amount of sulfur obtained on the rate of gas supply.
1-for non-suspension solution, 2-for suspension solution.**

One of the biggest problems in obtaining free sulfur from exhaust gases in the liquid phase is the separation of highly dispersed sulfur from the suspension formed during the process. Typically, the amount of sulfur in such suspensions can vary from 2-3 g/l to 20-30 g/l. In the course of the experiments, it was determined that as the pH of the solution and the amount of sulfur obtained, the viscosity of the solution increases, the free sulfur particles in the obtained suspension enlarge and separate spontaneously from the solution.

The resulting sulfur suspension solutions are neutralized with 0.5 M NaOH solution to the appropriate pH and stored for complete sulfur separation. It was found that as the pH of the solution decreases, less time is required for the separation of sulfur.

A pH of 0.75 corresponds to a 30% solution of HNO_3 , which, as shown earlier, is the optimal concentration for the process (figure 2).

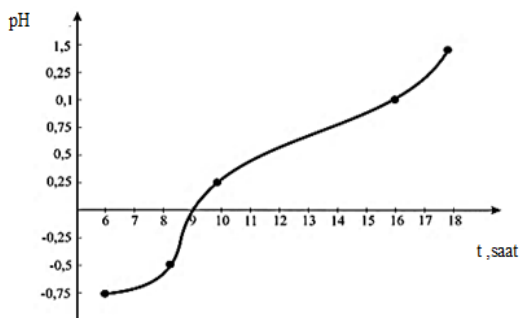


Figure 2 Sulfur release time depending on the pH of the solution.

Based on the results of these experiments, research has been conducted on the proposed principle technological scheme to reduce the number of stages of the existing process and achieve complete neutralization of gases. The process can be schematically shown in figure 1.

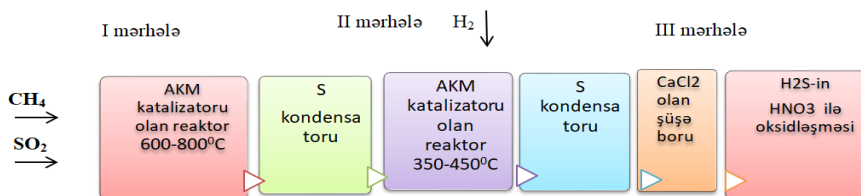


Figure 1 Schematic technological scheme of reduction of sulfur-containing gases to H₂S in the Claus stage and its purification in the liquid phase

The essence of the process is that the SO₂ gas from the combustion furnace is reduced with methane on the proposed AKM catalyst in order to obtain free sulfur. After condensation of the obtained sulfur, the remaining gases—CO, H₂, SO₂, COS, N₂, H₂S are converted to H₂S in the next reactor by transferring H₂ from the outside over the AKM catalyst. Under selected conditions, valuable reductants H₂ and CO are used to react with the remaining SO₂. After condensation of sulfur and water vapor, the H₂S-containing gas is passed through a solution of nitric acid.

The high activity of cobalt-containing catalysts in the process

of SO₂ reduction, especially at a temperature of 350–450⁰C, ie at a temperature of the “hot” Claus stage, is reflected in both our research and literature. On the other hand, since AKM catalyst is manufactured in industry, no additional cost is required for its preparation.

In order to obtain free sulfur and to obtain a gas mixture to be studied in the second stage, SO₂ was reduced with methane on an AKM catalyst at 600–800⁰C with a velocity of 1000 s⁻¹. The VCH₄ / VSO₂ ratio was stoichiometrically taken as a 1: 2 SO₂ concentration of 20% (volume).

It was found that the AKM catalyst has a sufficiently high activity for the reduction of SO₂ and the optimal process temperature is 750⁰C. At these temperatures, maximum conversion of SO₂ on the removed catalyst occurs (table 3).

Table 3

Experimental results on the catalytic reduction of SO₂ with methane (V_{CH₄} : V_{SO₂} = 0.5, φ (SO₂) - 20%, W = 1000s-1)

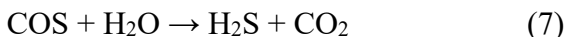
Temperature C ⁰	Dry gas content after stage I *%, volume share						The rate of conversion of SO ₂
	H ₂ S	SO ₂	COS	CO	H ₂	CH ₄	
650	2,90	5,70	0,15	3,10	4,21	0,02	71,50
700	3,24	4,75	0,26	3,65	3,86	0,01	76,25
750	4,10	4,36	0,35	2,84	4,10	0,01	78,20
800	4,86	4,21	0,44	3,26	3,92	0,01	78,95

* The remaining gases are CO₂, N₂.

In order to study the effect of other parameters that will affect the process, the effect of other factors at the found optimal temperature (750⁰C) - volume velocity, ratio of initial reagents and concentration - was studied.

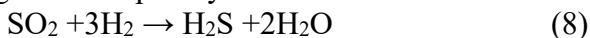
Thus, the temperature 750⁰C, VCH₄: VSO₂ = 1: 2, W = 1000s⁻¹ was determined as the optimal condition in the first stage to carry out the reduction of all sulfur-containing gases to H₂S in the next stage. The volume fraction of gases in the gas mixture obtained under these conditions was as follows (%): H₂S-4.1–2.67; SO₂-4,36–3,76; COS-0.2–0.35; CO-2.84–2.04; H₂-4,14–3,62, the rest N₂

In subsequent experiments, research was carried out to completely convert the remaining SO₂ to H₂S by condensing the free sulfur obtained from the first stage under optimal conditions and separating the gas mixture in the second stage by applying hydrogen gas from the outside on the alumocobaltmolibden catalyst. The water vapor in the gas mixture is not separated on purpose. Because when conducting research with water vapor in the temperature range of COS 400-450⁰C



observed complete hydrolysis by reaction.

Initially, at a temperature of 250-450⁰C, the gas mixture with a volume velocity of 1000s⁻¹ is fed to the reactor loaded with alumocobalt molybdenum catalyst. In the pre-reactor mixer, hydrogen gas is supplied from the cylinder in an amount corresponding to the amount of SO₂ and COS in the mixture. The amount of hydrogen in the gas mixture obtained after reduction with methane and the amount of added hydrogen to completely convert SO₂ to H₂S



The ratio of SO₂: H₂ on the reaction is taken as 1: 3-3.5.

At the beginning of the study, it was observed that the activities of the catalysts change over time under the influence of substances in the reaction medium.

Formation of catalysts takes 0.5-1 hours, depending on the temperature, to become fully “working”. The higher the temperature, the shorter the stationary state of the catalyst.

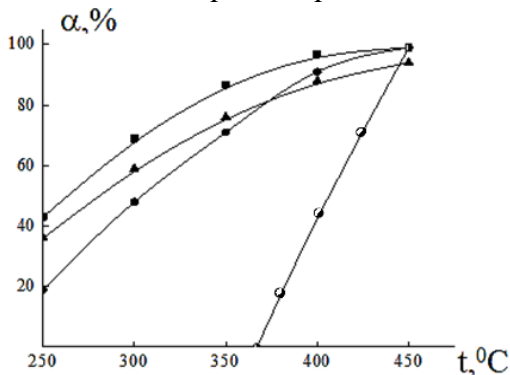
After the catalyst is initially operated in a reaction medium at 400-500° C, the reaction proceeds at a sufficiently high rate at 350-400 ° C.

If the reaction mixture is stopped at 300⁰C and released again through the catalyst at the same temperature, the conversion rate of SO₂ does not change.

Activation of the catalyst at high temperatures in the reaction medium is most likely due to the partial reduction of the contacts over time, which increases with increasing temperature.

The conversion rates of H₂, SO₂, CO and COS gases at 1000 s⁻¹ volume velocity in the temperature range of 250-450⁰ C were studied

on the AKM catalyst processed in the reaction medium for 1 hour. As can be seen from Figure 3, the conversion of SO₂, CO and COS gases at 450⁰ C is completed. The reason H₂ is not fully consumed is that it is taken in more than the required equivalent amount.



Graphic 3 Temperature dependence of conversion rates of H₂S, COS, SO₂, CO, H₂ gases on AKM catalyst
 (■ – SO₂, ▲ – H₂, ● – CO, ○ – COS)

Starting at 375⁰ C, COS begins to hydrolyze with water and interact with SO₂. The optimal volume speed was determined to be 500 s⁻¹.

Previous experiments have shown that it is possible to convert H₂S to complete sulfur with 30% nitric acid in a reactor when the concentration of H₂S in the initial gas mixture is 1-20% (volume) and the gas flow rate is 50-100 ml / min. Therefore, the dry gas mixture obtained from the second stage and containing 6.34-11.64% H₂S, CO₂, N₂ is passed through a 30% nitric acid solution at room temperature. It was found that when a gas mixture containing CO₂, N₂, H₂S is passed through a solution of nitric acid, H₂S is completely converted into sulfur. Thus, other gases do not affect sulfur emissions as expected. H₂S is completely converted to sulfur.

Given that SO₂ may not be fully converted to H₂S due to technological failures, it may be present in SO₂ along with H₂S in the nitric acid solution. Subsequent experiments studied the effect of SO₂ on the oxidation of hydrogen sulfide and the regeneration of nitric acid. (table 4)

Table 4

The degree of conversion of SO₂ and H₂S and the dependence of the regeneration of nitric acid on the amount of SO₂ (t-20-25⁰C)

Gas supply rate to the reactor, ml / min	Volume share in primary gas,% (volume)		Gas conversion rate,%		recovery,% of HNO ₃
	H ₂ S	SO ₂	H ₂ S	SO ₂	
50	11,64	0	100	-	100
50	8,02	0	100	-	100
50	8,21	0,2	100	100	100
50	8,34	0,4	100	100	100
50	8,34	0,6	100	94,72	100

Although H₂S is completely consumed when SO₂-containing gases are fed to the reactor at room temperature, while the rate of gas supply to the reactor is kept constant, complete conversion does not occur when the SO₂ content reaches 0.6%.

Finally, using the method of planning experiments, polynomial regression equations were obtained, which adequately express the process of oxidation of hydrogen sulfide with nitric acid in a given range of parameters. A formal mathematical model of the process is given.

Oxidation of gases (H₂S, COS) remaining after the Claus process to sulfur dioxide and absorption of the latter with red sludge.

One of the methods of processing the sulfur-containing gases left after the Claus process is that these gases are burned to SO₂. In order to neutralize the SO₂ obtained after incineration and SO₂-containing gases in general, research was carried out with the use of red sludge, which is a waste of the aluminum industry. The process can be schematically shown as follows (figure 2).

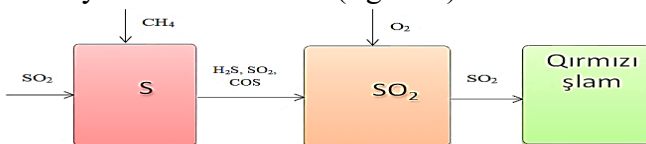


Figure 2 Technological scheme of absorption of sulfur dioxide by red sludge from the combustion of gases remaining after the reduction of sulfur dioxide to free sulfur.

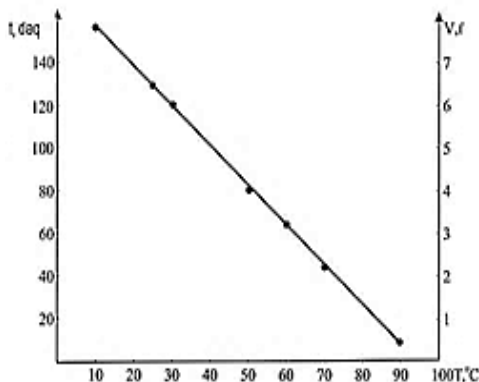
In the city of Ganja, Azerbaijan, 12 million tons of alunite processing and 20 million tons of bauxite processing waste were accumulated in an area of 60 hectares. Despite the fact that this area is covered with soil, it still remains a source of danger.

The average composition of red sludge samples taken from Ganja Clay-soil plant is as follows: 45-47% Fe_2O_3 , 13-18% Al_2O_3 , 3.3-4.4% TiO_2 and a certain amount of V, Zr, Cd, etc. There are metals. As can be seen, the amount of Fe_2O_3 , Al_2O_3 , and TiO_2 in the red sludge is quite large, so their extraction is of great importance.

Red sludge is obtained in the form of horra during industrial processing and has a fairly high pH (10). B: M (solid: liquid) ratios are 1: (3-10). Therefore, pure SO_2 gas is first released from a sample of red sludge with a B: M ratio of 1:10 at a rate of 50 ml / min at different temperatures.

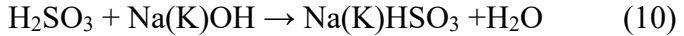
As the temperature increases, the absorption time of the gas and, accordingly, the absorbed volume decrease. If the absorption time at 20°C is 128 minutes and the absorbed volume of SO_2 is 6.6 liters, at 90°C it is 8 minutes and 0.4 l, respectively.

This is explained by the fact that as the temperature increases, the solubility of the gas decreases. Hydrosulfites of metals are also obtained at low temperatures, some of which is used to produce hydrosulfites (figure 4).



Graphic 4 Temperature dependence of sulfur dioxide absorption time and absorbed volume: B: M = 1:10; $\varphi(\text{SO}_2) = 100\%$, Gas = 50 ml / min.

These reaction equations can be summarized as follows:

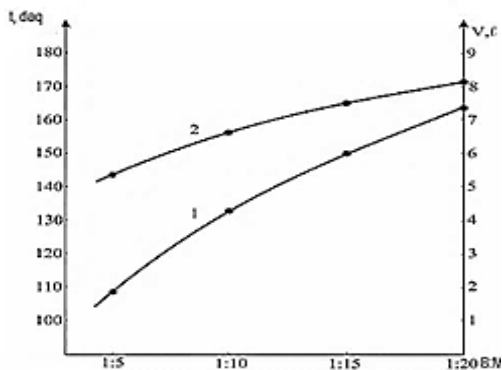


When the temperature is high, the hydrosulfites decompose and the pH of the solution increases. If the pH of the red sludge suspension is initially 10, the pH decreases to 1.84 when SO_2 is absorbed at 25°C and to 6.6 at 90°C . It is known from the literature that the pH of the solution of Al_2O_3 and Fe_2O_3 , which are the main constituents of red cuttings, is less than a quarter.

At 90°C , the pH of the solution is not low enough, so the penetration of metals into the solution is reduced. At 25°C , 36.25% of Al passes into the solution, and at 90°C , 20.89%. One of the noteworthy issues is that iron does not pass into the solution. It is known that one of the biggest problems in the production of aluminum in the processing of alunite, red sludge, clays is the demineralization of aluminate solutions. Under these conditions, iron does not pass into the solution, and in this way it is possible to selectively separate aluminum.

As the B: M ratio increases, the absorption time of SO_2 decreases. In fact, one would expect that as the amount of red sludge increases (B: M ratio), the solution should absorb more SO_2 . However, the opposite effect is obtained. This is due to the well-known sodium hydroalumosilicates (NHAS) in red cuttings. Thus, as the B: M ratio decreases, ie as the amount of water increases, these compounds hydrolyze more. As a result, the amount of alkali in the solution increases, which increases the duration and volume of absorption of SO_2 .

Figure 5. The effect of gas delivery rate on SO_2 absorption is studied. As expected, as the gas delivery rate increases, the contact time of the gas with the liquid decreases and, accordingly, both the absorption time and the absorption volume decrease.



Graphic 5 Dependence of sulfur dioxide absorption time (1) and volume (2) on the ratio B: M: $\phi = 100\%$, $V_{\text{gas}} = 50 \text{ ml / min}$, $t = 25^{\circ}\text{C}$

Raw red taken to verify the validity of this idea

The sludge sample was thoroughly mixed with water at a ratio of 1:30, filtered, and the remaining residue was washed again with water. After 4 consecutive such washes, the pH was equal to 10 in all cases. During subsequent washes, the pH gradually decreases to 7.

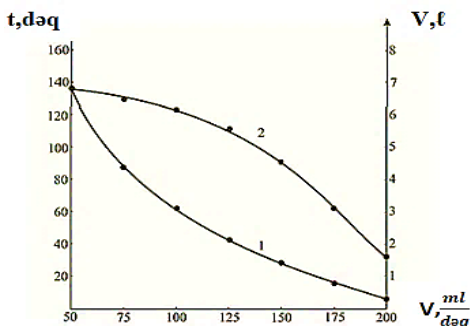
Reducing the B: M ratio makes it easier for Al_2O_3 in the red sludge to enter the solution. When red sludge is treated with SO_2 at 25°C for 2 hours (B: M = 1:10), 36.25% of Al_2O_3 and 52.85% at 1:30 pass into the solution. Although the solubility of Al_2O_3 increases with increasing B: M ratio, its concentration in solution decreases.

6.8 l SO_2 is absorbed in 138 minutes when the gas is injected into a 300 ml red sludge suspension at room temperature at a rate of 50 ml / min (B: M = 1:10). This means that the absorption capacity of the suspension is 9.8 l/h. If we take into account that the volume of SO_2 from the exhaust gases is 1.5-2%, then 1 l red sludge suspension (B: M = 1:10) 659 l can neutralize industrial waste gas, which is a large enough number for such processes.

When the rate of gas supply to the reactor is increased from 50 ml/min to 200 ml/min, the amount of absorbed gas decreases sharply from 6.9 l to 0.4 l.

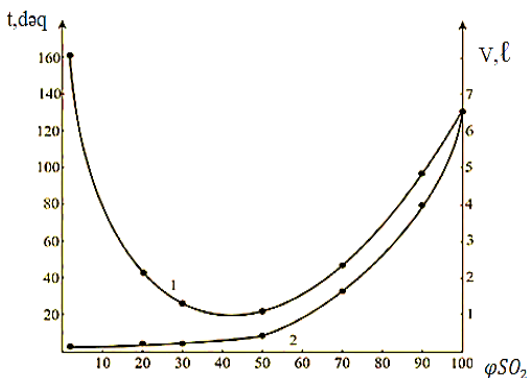
To study the effect of the initial SO_2 gas concentration on the absorption time and the amount of sulfur dioxide absorbed, experiments were performed with a B: M ratio of 1:10, gas delivery

rate to the reactor $V_{\text{gas}} = 50 \text{ ml/min}$, and suspension temperature $t = 25^\circ\text{C}$ (figure 6).



Graphic 6 Dependence of sulfur dioxide absorption time (1) and volume (2) on the rate of gas mixture delivery to the reactor. B: $M = 1:10$; $V_{\text{gas}} = 50 \text{ ml / min}$, $t = 25^\circ\text{C}$.

During the experiments, the absorption time first decreases from 160 to 22 minutes with increasing SO_2 concentration, and then gradually increases. This is explained by the fact that as the amount of SO_2 in the primary gas increases, the process of alkaline neutralization in the solution begins. The neutralization process is completed at a point where the concentration is 40% and the absorption time is 22 minutes (figure 7).



Graphic 7 Dependence of sulfur dioxide absorption time (1) and volume (2) on SO_2 concentration (B: $M = 1:10$; Gas = 50ml / min, $t = 25^\circ\text{C}$).

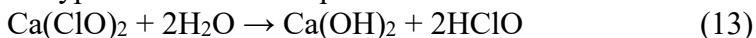
Studies show that red sludge suspension is suitable for capturing and neutralizing SO₂ in various concentrations. Since it was necessary to maintain the temperature and the concentration of SO₂ in the solution at a relatively high level in order to increase the yield of metal compounds in the red sludge, it was decided to carry out further experiments in an autoclave. In the future, in this way neutralization of SO₂ of any concentration obtained during the processing of sulfide ores in the country, and Al, Fe, as well as Ti, Zr, V, etc. can be used in the purchase of precious metals.

Absorption of gases remaining after the Claus process in chlorine-lime suspension.

This chapter is devoted to the capture and neutralization of industrial gases containing H₂S and SO₂. Thus, the most popular method of processing sulfur-containing gases is a mixture of H₂S, SO₂ in the gases left after the Claus process.² This does not meet environmental requirements. In this regard, the use of chlorinated lime, produced on an industrial scale and proposed for the first time as a chemisorbent, for the purpose of neutralization of sulfur-containing gases was carried out.

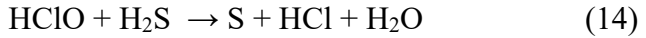
Chlorinated lime used in the experiments is made in Russia and has the following composition: Ca(ClO)₂·CaCl₂·2Ca(OH)₂ contains 32% (mass) of “active chlorine” (hypochlorite).

4-6 minutes after the gas mixture comes into contact with the solution, a white suspension of sulfur is formed and gradually turns yellow. Based on this, it can be concluded that under normal conditions, first the physical absorption of H₂S occurs, and then the chemical interaction with the components of the solution. Thus, Ca(ClO)₂ is a salt formed from strong base and weak acid, so it hydrolyzes to hypochloric acid in aqueous solution:

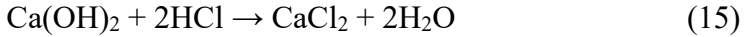


Since the obtained HClO is a very strong oxidizer under normal conditions, and H₂S is a strong reducing agent, the following reaction takes place:

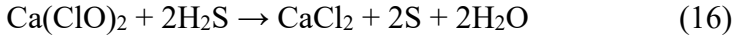
² Golubeva, I.A., Khairullina, G.R. Analysis of the production of gray by Klaus's method in oil and gas enterprises of Russia, unsolved problems // NefteGasoKhimiya.2017.



HCl is neutralized by Ca(OH)_2 obtained by hydrolysis



The final equation can be written as:



The obtained sulfur is separated by decantation. The decantate is filtered, washed and dried. The capacity of the absorbent for sulfur is 12 grams of sulfur/dm³·h. SO₂ in the gas mixture is absorbed by Ca(OH)_2 in solution.

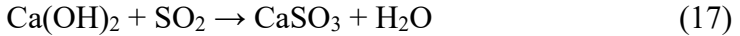


Table 5
Distribution of sulfur in reaction products depending on temperature (by mass%)

t, °C	S	CaSO ₃	CaSO ₄
20	6.90	9.13	83.97
40	2.52	9.48	88.00
50	-	9.81	90.19
60	-	9.81	90.19

$\text{HClO} \rightarrow \text{HCl} + \text{O}$. The resulting atomic oxygen is a stronger oxidizer, oxidizing H₂S to sulfite and sulfate ions.

As the B: M ratio increases, the absorbency of the absorbent increases. When B: M = 1: 2.5, the absorption capacity of the absorbent due to sulfur is 34 grams of sulfur/dm³ per hour. Experiments show that when the ratio of B: M is more than 1: 2.5, it is difficult to mix the solution in the laboratory, and therefore further research is carried out in the ratio B: M = 1: 2.5.

Figure 8 shows the dependence of the absorption time of a gas mixture on its consumption rate.

Absorption time is the retention time of H₂S and SO₂ of a chlorinated lime solution in a given B: M ratio. As can be seen, as the velocity increases from 10 ml/ min to 100 ml / min, the absorption time decreases due to the large amount of H₂S and SO₂ given per unit time.

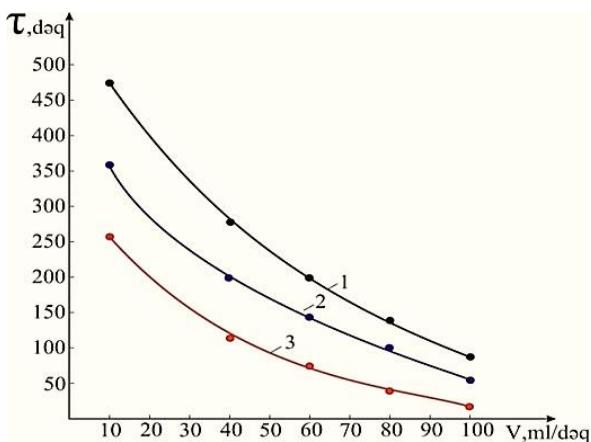


Figure 8 Absorption time dependence of the absorption time of the gas mixture. Curves 1,2,3 for model I, II, III gases, respectively. B: M = 1: 2.5, t = 50°C

The same can be seen with increasing concentrations of gases in the mixture (models I, II, III). Thus, the lower the viscosity, the longer the absorption lasts.

A study of the temperature dependence of the absorption time showed that the absorption time decreases to 50° C with increasing temperature. And then it changes almost insignificantly. This is explained by the fact that up to 50°C the interaction of H₂S and SO₂ with the absorbent components is completed.

Thus, as a result of the experiments, it can be said that chlorinated lime can be used to neutralize low-concentration sulfur-containing gases.

Starting from 1961, the current Institute of Catalysis and Inorganic Chemistry of ANAS under the leadership of academician H. Shahtakhtinsky studied in detail the reduction of SO₂ with various reducers, including natural gas conversion products. However, all research has focused on increasing the sulfur output during reduction, creating new and more active catalysts used in these processes. Sulfur gases contained in the exhaust gases have not been completely neutralized.

To complete all this work, the optimal parameters for the

reduction of SO₂ to free sulfur on the AKM catalyst, an industrial catalyst that we first offer with natural gas conversion products, have been determined. Then, the effect of various factors on the absorption of sulfur gases by chlorinated lime obtained under the optimal conditions by abandoning the Claus process was studied. The process can be shown schematically as follows (figure 3).



Figure 3 Schematic technological scheme of absorption of the remaining gas mixture (H₂S, SO₂, N₂, CO₂) with chlorinated lime after reduction of SO₂ with conversion gas

The studies were conducted at a temperature of 250-450⁰C, a volume velocity of 500-2000 s⁻¹ and the ratio of the final components (CO + H₂): SO₂ = 2. The analysis of Table 6 shows that the maximum yield when reducing the conversion of sulfur dioxide obtained by various methods with gas is between 350-450⁰C.

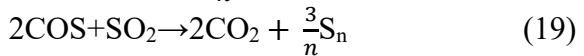
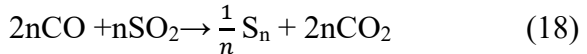
**Table 6
Distribution of gases and the rate of conversion of SO₂ in the products of reduction of sulfur dioxide by methane conversion products. (W = 1000 s-1, N = 2)**

	°C	Volume share of gases in reaction products,%							Conversion rate of SO ₂ ,%
		O ₂	H ₂ S	CO	COS	CO ₂	H ₂	N ₂	
Carbon dioxide (1:1)	250	9,36	-	2,82	0,03	13,42	0,12	74,25	53,16
	300	3,73	0,51	4,23	0,01	14,43	-	77,09	81,31
	350	2,12	2,50	1,31	-	14,99	-	79,08	89,40
	400	2,32	4,62	-	-	14,72	-	78,34	88,36
	450	2,14	6,89	1,16	-	15,08	-	74,73	89,29
Oxygen (1:2)	250	8,47	-	2,03	0,01	10,72	-	78,77	57,65
	300	3,31	2,19	3,42	-	10,51	-	80,57	83,46
	350	2,34	3,65	0,27	-	10,36	-	83,38	88,30
	400	1,82	8,73	-	-	11,75	-	77,7	90,92
	450	2,04	10,36	-	-	12,26	-	75,34	89,78

Continue table 6

Water vapor (1: 3)	250	6,15	0,59	1,23	-	8,62	0,04	83,37	69,27
	300	2,47	5,52	2,61	-	8,10	0,01	81,29	87,66
	350	1,29	9,28	-	-	8,03	-	81,4	93,54
	400	0,9	15,63	-	-	7,88	-	75,54	95,27
	450	1,71	22,75	-	-	7,78	-	67,76	91,45

In the range of COS 350-450⁰ C it is not observed at all.



This is because the optimal temperatures of reaction (18) and reaction (19) coincide.

The results of the research were analyzed and the conversion of CH₄ to water vapor was preferred, and the effect of various factors on the conversion rate of SO₂ was studied in the process of reduction of methane by water vapor conversion products. This is because the catalyst (GIAP-8) does not carbonize only when methane is converted to water vapor. The composition of the gas mixture obtained under optimal conditions was as follows (volume,%): SO₂ - 1.2-1.4, H₂S-9.2-9.3, CO₂ -8.0-8.3, N₂-rest.

The gas mixture is first passed through condensers connected in series and filled with Rashig rings to capture sulfur. It is then purified from water vapor by passing through glass tubes containing CaCl₂.

The gas mixture is fed to the reactor under normal conditions (20–25⁰C) and at different temperatures at a rate of 50 ml / min, the ratio of the mass of chlorinated lime to the mass of the liquid (water) B: M = 1:10. Since all three of the acid gases in the gas mixture (H₂S, SO₂, CO₂) interact with the Ca (OH) 2 in the suspension, and the solubility of H₂S in water is close to that of CO₂, competition must occur between them. However, the conversion of H₂S to sulfur occurs very rapidly because the hypochlorite ion formed in the solution is ClO- a strong oxidizing sulfide ion and a strong reducing agent. Therefore, selectivity for H₂S is achieved and competition is eliminated. It has been found that under normal conditions, sulfur-free sulfur occurs in the form of CaSO₃ and CaSO₄. All three

substances are available at temperatures up to 50°C. After 50°C, the reaction products do not contain free sulfur. An increase in temperature after 60°C does not change the ratio of CaSO₃ and CaSO₄ obtained. It can be concluded that if the reaction is carried out under normal conditions, it is more expedient to obtain free sulfur from H₂S, and it is not necessary to add lime to chlorinated lime. The remaining gases (CO₂ and SO₂) can be absorbed by lime in the second reactor. By raising the temperature to 50° C, all three gases can be absorbed simultaneously, and sulfur-containing gases can be converted into a gypsum product by blowing air from the solution.

The combined absorption of H₂S, CO₂ and SO₂ depends mainly on the pH of the solution.

It is known that the higher the pH of the solution, the easier it is to absorb sour gases. Therefore, the absorption time of chlorinated lime varies depending on the pH (Figure 8)

The pH of the chlorinated lime solution used was 9. The pH gradually decreases as the primary gases pass through the suspension. At pH 4.2, the suspension loses its ability to absorb.

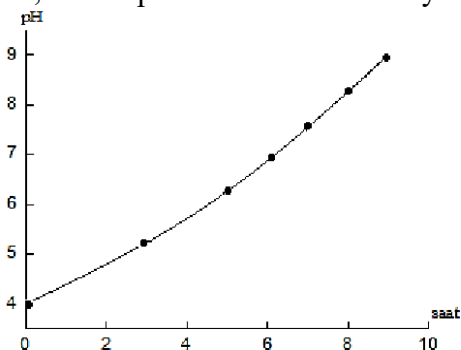


Figure 8 PH dependence of the absorption time of gases with chlorinated lime. (B: M = 1: 2.5; t = 50°C; V gar = 100 ml / min)

It has been found that a pH below 9 dramatically reduces the absorption capacity of H₂S. A pH above 9 dramatically increases the absorption capacity of SO₂ and CO₂, which reduces the rate of H₂S's interaction with Ca (ClO) 2. It has also been found that maintaining the pH in the range of 8-9 reduces the absorption of CO₂ relative to

SO₂. It can be concluded that in order to completely capture the more toxic SO₂ and H₂S, the pH can be maintained at a level suitable for SO₂ and H₂S by adding lime, and if it is necessary to capture the absorbed CO₂, a second reactor with lime suspension can be installed after the main reactor. This offer is also advantageous in terms of security. Thus, if there is any defect in the technological process, other toxic gases are trapped in this reactor.

In this chapter, using the planning method of experiments, polynomial regression equations are derived, which adequately express the basic technological process involving the reduction of sulfur dioxide with conversion gas to free sulfur and the absorption of the remaining gas mixture (H₂S, SO₂) with chlorinated lime. A formal mathematical model of the process is given in width.

Result

1. Along with the purification of sulfur-containing gases in the products of non-ferrous metallurgy and oil and gas industry to meet environmental requirements, new methods of obtaining useful products such as sulfur and gypsum have been developed. Depending on the composition of the exhaust gases, sulfur dioxide, hydrogen sulfide, or a mixture of both, three basic technological schemes are given. Two of them have been patented [2, 8].
2. The reduction of sulfur dioxide to sulfur on the alum-cobalt-molybdenum catalyst was studied and its high conversion rate (79-84%) was achieved. Optimal process parameters were found: $t-750^{\circ}\text{C}$, $V_{\text{ch4}}: V_{\text{so2}} = 0.5$, $W = 1000\text{s}^{-1}$ [5].
3. Research was carried out to convert H₂S into a gas-H₂S by adding H₂ on the AKM catalyst in the Claus stage to a mixture of sulfur dioxide and COS and H₂S gases formed during the reduction of sulfur dioxide to sulfur. AKM catalyst was found to be highly active in this process. When the temperature is 400-450⁰ C, $W-500\text{ s}^{-1}$, the conversion of COS and SO₂ to H₂S is 100% [9].
4. The method of oxidation of H₂S in HNO₃ to sulfur in model and

real gas mixtures and parallel regeneration of HNO₃ in the reaction medium was developed. Optimal conditions for complete oxidation of H₂S and 100% regeneration of HNO₃ (t-25⁰C, gas delivery rate V = 100 ml / min; W_{hno3}-30%) were found. Spontaneous flotation of sulfur was found to occur when the pH = -0.75 and the amount of sulfur in the suspension was 8-10 g / l [12].

5. The method of absorption of H₂S, COS gases in the gas mixture obtained after reduction of SO₂ in metallurgical gases with various reducers to sulfur by absorption of sulfur dioxide (or from other sources) with the residue of Ganja GTK was applied. Temperature 25-90⁰C, gas supply rate 50-200 ml / min, B: M = 1: 2.5 - 1:20, in experiments with SO₂ residue 1-100% (volume), complete neutralization of SO₂ sludge confirmed for suitability. As a result of the absorption of SO₂, a number of metals (Al, Ti, V, Cr, Mn, Mg, Ni) in the sludge were found to be in solution when the pH was below 4. This was proposed as a method of hydrometallurgical processing of these metals [6].
6. In order to achieve high sulfur yield, the reduction of SO₂ on the AKM catalyst by various ways of conversion of natural gas (CH₄, O₂, H₂O) products (CO, H₂) was studied. As a result, the catalyst was found to be carbonized in other conversion methods, so the process was focused on methane with water conversion products. Optimal conditions were selected at 400-450⁰C, W = 1000 s⁻¹, (CO + H₂): SO₂ = 2: 1 [13].
7. For the processing of model gases and real gases obtained after reduction of SO₂ by conversion gas, the method of chemo-basis with chlorinated-lime and chlorinated-lime + lime mixture was developed, bypassing the traditional Klaus method. The effect of various parameters (temperature, gas supply rate, pH, B; M ratios) on the process was studied. It was found that S, CaSO₃ and CaSO₄ are obtained in solution at temperatures up to 50C, and CaSO₃ and CaSO₄ at high temperatures. It was found that the optimal pH was 8-9 for gases containing H₂S and SO₂, and that the suspension lost its absorbency when the pH was <4.2 [11].

When B: M = 1.25, the absorption capacity of the suspension for H₂S, SO₂, and CO₂ gases in real gases was found to be 63.8 g / ℓ ·. The method is patented [10, 15].

8. Based on the results of the research, adequate expression of the main technological processes in the range of parameters, including both the oxidation of hydrogen sulfide with nitric acid, the reduction of sulfur dioxide to conversion gas to free sulfur and the absorption of the remaining gas mixture (H₂S, SO₂) with chlorinated lime polynomial regression equations are derived. A formal mathematical model of the process was obtained.

Published works related to the dissertation:

1. Ahmedov, M.M., Ibrahimov, A.A., Vekilova, R.M. "Utilization of exhaust sulfur dioxide gases of metallurgical production by catalytic method"// Internationaler Kongress Fachmesse Euro-Eko Hannover Programm abstracts, – December, – 2015, – p.8-9.

2. Əhmədov, M.M. Hidrogen-sulfiddən kükürdün alınması üsulları, patent a 20140012, Azərbaycan Respublkası / İbrahimov Ə.A., Vəkilova R.M. – 2016.

3. Ахмедов, М.М., Ибрагимов, А.А., Векилова, Р.М. Переработка красного шлама с использованием диоксида серы. // Проблемы теоретической и экспериментальной химии, тезисы докладов XXVI "Российской молодежной научной конференции", посвященной 120-летию со дня рождения академика Н.Н. Семенова, – Екатеринбург, – 2016, – с398-399.

4. Ахмедов, М.М., Ибрагимов, А.А., Векилова, Р.М. Утилизация сероводорода азотной кислотой и рециклинг последнего в реакционной среде // V Международная конференция Школа по химической технологии, Сателлитная конференция XX Менделеевского съезда по общей и прикладной химии, – Волгоград: – 2016, – том 1, – с.184-185.

5. Ahmedov, M.M. Oxidation of hydrogen sulfide with nitric acid till sulphur and reduction of oxidizing agent at reaction medium / A.A.Ibrahimov, R.M.Vekilova, N.A.Abbasova // Azərbaycan kimya jurnalı, – Bakı: – 2017. №2, – s.20-24.

6. Ибрагимов, А.А. Поглощение диоксида серы суспензией красного шлама / М.М.Ахмедов, Р.М.Векилова, Н.И.Аббасова // Нефтепереработка нефтехимия, – Москва: – 2017. 11, – с.41-44.

7. Ахмедов, М.М., Ибрагимов, А.А., Векилова, Р.М. О возможности утилизации отходящих сернистых газов хлорной известью // Сборник статей по итогам Международной научно практической конференции, "Наука, образование и инновации" – Москва: – 2017. – часть 2, – с.169-170.

8. Əhmədov, M.M. Qazların hidrogen sulfid və kükürd dioksiddən təmizlənməsi üsulu patent a 20150092, Azərbaycan

Respublikası / İbrahimov Ə.A., Vəkilova R.M., Həmidov R.H. – 2017.

9. Əhmədov, M.M. Kükürd-dioksidin təbii qazın konversiya məhsulları ilə alümokobaltmolibden katalizatoru üzərində reduksiyası / M.M.Əhmədov, Ə.A.İbrahimov, R.M.Vəkilova // Azərbaycan Texniki Universiteti, “Elmi əsərlər”, – 2018. №2, – s. 168-174.

10. Əhmədov, M.M. Az qatılıqlı kükürd qazlarının xlorlu əhənglə absorbsiyası / Ə.A.İbrahimov, R.M.Vəkilova, R.H.Həmidov // – Bakı: Kimya problemləri, – 2018. (16), №3, – s.369-375.

11. İbrahimov, Ə.A. Kükürd tərkibli qazların xlorlu əhənglə udulmasına reaksiya mühitinin təsiri / Ə.A.İbrahimov, R.M.Vəkilova // – Bakı: Azərbaycan Texniki Universiteti, “Elmi əsərlər”, – 2019. №1, – s. 148-153.

12. Vəkilova, R.M. Alümokobaltmolibden katalizatoru üzərində kükürd tərkibli qazların emalı və maye fazada tam zərərsizləşdirilməsi // – Bakı: Azərbaycan Texniki Universiteti, “Elmi əsərlər”, – 2019. №2, – s.177-180.

13. Vəkilova, R.M. Kükürd-dioksidin kükürdə və hidrogen-sulfidə qədər katalitik reduksiyası və axrincının maye fazada tam zərərsizləşdirilməsi // – Bakı: Azərbaycan Texniki Universiteti, “Elmi əsərlər” – 2019. №3, – s. 173-177.

14. İbrahimov, Ə.A., Vəkilova, R.M. Kükürd tərkibli qazların emalı üsulu// Ümummili lider Heydər Əliyevin anadan olmasının 96-cı ildönümünə həsr olunmuş doktrant, magistr və gənc tədqiqatçıların “Kimyanın aktual problemləri” XIII Beynəlxalq Elmi Konfransının Materialları, – Bakı, –15-16 may, – 2019. – s.228-230.

15. Ибрагимов, А.А., Векилова, Р.М. Утилизация сернистых газов хлорной известью // XXI Менделеевского съезда по общей и прикладной химии. – Санкт-Петербург, – 2019. В 6 т., Т.2а, – с.226.

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