REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

DEVELOPMENT OF TECHNOLOGY FOR PROCESSING OF INDUSTRIAL WASTES IN AZERBAIJAN WITH USE OF LOCAL RESOURCES

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Field of science: Technical sciences

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GENERAL CHARACTERISTICS OF WORK

Actuality of the topic and degree of development of the topic. The formation of significant amounts of waste and hazardous emissions from various industries create environmental problems in many countries. Being an industrially developed region, Azerbaijan is not an exception in this regard. Industrial recycling, utilization and neutralization of industrial wastes is a strategically important direction of the state policy of the country, one example of which is the improvement of municipal domestic waste (MSW) management.

An equally important issue under the government's scrutiny is the provision of food to the population. The strategic roadmap for the production and processing of agricultural products, approved by President Ilham Aliyev in August 2017, calls for improving the supply of mineral fertilizers to agricultural producers. Solving this issue will increase the production capacity of agricultural products, market development and rural well-being.

Considering both factors that play an important role in the economy of the country, the chosen topic dedicated to the development of processing technology of local raw materials, represented by industrial wastes, as well as natural resources of Azerbaijan to obtain complex mineral fertilizers, is very relevant. The obtained results will be aimed at solving the problems related to the utilization of industrial wastes, simultaneously increasing the efficiency of the agro-industrial sector of the Republic.

Developed modern technologies for obtaining fertilizers undergo difficulties related to their transportation and storage. In this regard, it seems quite adequate to use local resources for the development of fertilizer production technologies. At the same time the issues related to the creation of ecological technologies, not affecting the environment, increasing the sustainability of food safety were put at the head of the solution.

Object and subject of the research. In the dissertation work, the **objects of research** were solid waste (SW), drilling cuttings and waste from industrial enterprises of Azerbaijan, represented by agroforestry and thermal waters, local natural resources.

The subject of the research is the technology of obtaining fertilizers using solid waste, the development of the technological regime of the raw material processing process and the principle of operation of recycling facilities, and the determination of the properties of the raw material components.

Research aims and objectives. The main aim of the research is to study the possibilities of involving industrial waste as secondary raw materials in the processing together with local agricultural ores and modifiers for the development of technologies for obtaining organic-mineral and complex mineral fertilizers.

To achieve the main aim, the following issues were set and resolved in the dissertation work:

- substantiation of the choice of non-traditional raw materials from the industrial waste of Azerbaijan and local natural resources in order to develop new technologies for the production of fertilizers;
- determination of the conditions for the preliminary preparation of raw materials for subsequent processing;
- establishment of the technological mode of the process of processing the separated raw materials: the duration of the process, the consumption of raw materials components, the concentration of acid, the mode of granulation;
- revealing the relationship between the composition of raw materials and the characteristics of the obtained samples of fertilizers;
- development of schematic diagrams of technological installations for recycling used raw materials.

Research methods. Laboratory studies were carried out using a thermostatically controlled reactor, a ball mill SLM-1, a rotating thermostatic drum reactor with a jacket for granulation, and a tubular furnace for drying granules. Determination of the quantitative composition of the obtained products was carried out by calculation and analytical methods in accordance with the current state standards. To determine the strength of the granules, an IPG-1 device was used; to determine the pH of the samples, a potentiometric device HI 2211-02 was used.

The main provisions submitted for defense:

- the first developed technology for the production of organo-mineral fertilizers using the organic component of MSW, previously neutralized by geothermal waters of the Lerik region, coming to the surface with a temperature of 25-75°C, containing H_2S;

- experimentally established possibility of obtaining K- and Si-containing organomineral fertilizers based on the organic component of solid wastes (SW), by modification with phonolite and montmorillonite, respectively;

- the established nature of the influence of temperature, process duration, concentration and consumption rate of nitric, sulfuric and phosphoric acids on the degree of extraction of the main useful components during the processing of drill cuttings together with local kaolin clays.

- parameters of technological modes of processes for obtaining complex mineral fertilizers by sulfuric acid decomposition of Nakhichevan phosphorite, MSW incineration slag with phosphorite, a mixture of MSW incineration slag and drill cuttings with phosphorite;

- revealed dependence of the content of P_2O_5 in processed products on the concentration and consumption rate of H_2SO_4, as well as the composition of the used raw materials;

- parameters of the technological process of processing complex raw materials, represented by SW slag, dolomite and phosphogypsum into complex mineral fertilizers: the quantitative composition of the mixed raw materials, the concentration of sulfuric acid and the temperature of the reaction medium;

- substantiation of the role of SW slag and the amount of dolomite introduced into the composition of raw materials to increase the static strength of the granules of the obtained complex mineral fertilizer;

- developed technological schemes for the processing of industrial waste in Azerbaijan and local natural resources for the production of organomineral and complex mineral fertilizers.

Scientific novelty of the research.

1. The dependence of the degree of separation of the main components of organic-mineral, as well as complex mineral fertilizers

on the technological parameters of the processing process has been determined.

2. For the first time, based on the experimental results, a method for obtaining organic-mineral fertilizers by processing organic components of BT neutralized using geothermal waters containing H_2S has been developed.

3. A technology for obtaining complex mineral fertilizers based on the joint processing of kaolin clays of drilling mud with acid has been developed.

Scientifical and practical significance of the research.

The theoretical significance of the work lies in the fact that the proposed methods of solid waste disposal allow us to build a unique model of the functioning of a closed system for the production of organomineral fertilizers, the input parameters of which are industrial and domestic solid waste, geothermal water, local mineral resources and organic raw materials of the Republic.

Based on the results of the conducted research, technological schemes for the production of organic-mineral and complex mineral fertilizers have been developed for the implementation of technologies. Fertilizer samples have been obtained, the content of which corresponds to the requirements for fertilizers produced in industry in terms of the amount of nutritional components, which is of great **practical importance**. The developed technologies ensure the utilization of local industrial waste.

Author's personal contribution. The applicant directly participated in planning and making experiments, analytical control of the obtained samples, discussion of the results, and preparation of research materials for invention applications, publications in scientific journals, and conference reports.

Approbation and implementation. The main results of the dissertation work were reported and discussed at meetings of the Academic Council of Azerbaijan State Oil and Industry University, as well as at the following international and regional conferences and congresses, including: The 36th National and the 3rd International Geosciences Congress (Iran, february, 2018); Международная научная конференция «Перспективы инновативного развития

химической технологии и инженерии» (Сумгаит, 2019); International Conference «Scientific research of the SCO countries: synergy and integration» (Beijing, China, November 19, 2019); İnternational conference «Actual problems of chemical engineering, dedicated to the 100th anniversary of the Azerbaijan State Oil and Industry University» (Baku, 2020, 24-25 december); LXXX Международная научно – практическая конференция «Инновационные подходы в современной науке» (Москва, октябрь, 2020).

The results obtained in the dissertation work can be applied in the structural divisions and services of the Ministry of Ecology and Natural Resources of Azerbaijan, in commercial enterprises engaged in waste disposal, as well as in scientific and industrial institutions engaged in the development and preparation of various types of fertilizers.

The organomineral fertilizer proposed in the dissertation work was introduced in an agricultural area of the village of Khalach, Salyan district (the act of testing the obtained sample is indicated in the appendix of the dissertation).

Name of the organization where the dissertation work was carried out. The dissertation work was carried out at the department "Petrochemical technology and industrial ecology" of the Azerbaijan State Oil and Industry University.

The total volume of the dissertation is expressed in characters, with the volume of each structural section of the dissertation indicated separately. The dissertation is presented in 158 pages of printed text.The dissertation is presented in a text of 183291 characters in total, with the introduction consisting of 17240 characters, Chapter I consisting of 62385 characters, Chapter II consisting of 19806 characters, Chapter III consisting of 23744 characters, and Chapter IV consisting of 60116 characters.

MAIN CONTENTS OF THE WORK

The introduction presents the general state of the problem, justifies the relevance of the topic of the dissertation work, and specifies the goals and objectives of the study, notes the scientific novelty and practical significance of the work. The main provisions to be defended are formulated.

The first chapter examines the impact of municipal solid waste on the ecological state of the environment, provides an analysis of studies on the formation of such waste, and notes the factors affecting the amount of their accumulation. A schematic representation of the ways in which hazardous components penetrate into the environment at unregulated landfills is given. It is noted that municipal solid waste has a fairly similar composition regardless of the place of origin, the main components of which are paper, glass, organic residues, plastic, fabrics, metal objects, and their quantitative composition may differ depending on the climatic zone and season. This chapter also presents the main characteristics of municipal solid waste and methods of their disposal using various technologies. It is also indicated here that when determining the choice of a method for disposal of municipal solid waste that ensures environmental safety and compliance with sanitary standards provided for humans, it is necessary to have information on the fractional composition of municipal solid waste, physical characteristics, calorific value and moisture content. Priority areas in the field of environmental protection in Azerbaijan are noted, determining the state policy in the field of ensuring ecological balance in nature, providing for the use of waste as secondary raw materials. The article analyzes the current state of issues related to the production of complex fertilizers. The characteristics of raw materials and their preparation for use in the production of organomineral and complex mineral fertilizers are given. The existing directions of fertilizer production technology are considered, both with the use of traditional raw materials and with the involvement of production waste and natural resources in the processing, and process flow charts for the production of complex fertilizers. The shortcomings associated with

existing complex process flow charts and limitations in the use of depleted phosphate raw materials are noted.

The second chapter presents the characteristics of the raw materials selected for the production of complex fertilizers. The processing involves waste generated by the life of the population, industry and natural resources of Azerbaijan: organic component of waste processed at the Baku Waste Utilization Plant (Balakhany); waste incineration slag; drilling mud from a depth of 10 m, well No. 1 of the Karadag field; spent sulfuric acid from oil refining processes; combined phosphorite of the Nakhchivan Autonomous Republic; dolomite from the Boyanata (Gobustan) mountain rock; kaolin clays of the Khizi, Siyazan and Lerik deposits; montmorillonite; phonolite, limestone from the Shurabad deposit; thermal water from a spring in the Lerik region containing H_2S, waste from the production of phosphoric acid - imported phosphogypsum of grade A-2.

An experimental method for removing inorganic and organic components (glass, metal, plastic, building materials, paper, bones, etc.) from municipal solid waste is presented. This chapter also describes the methods for preparing raw materials, including preliminary neutralization of the organic component of municipal solid waste using the Berman method for analyzing organic fertilizers for the presence of helminth larvae. The degree of neutralization was determined by the difference in the readings for the presence of pathogens in the raw materials and after the neutralization process in the mixture. The control methods for assessing the qualitative and quantitative composition (titrimetric method for determining total nitrogen, photoelectrocolorimetric method for determining total phosphorus, photometric method for determining total potassium, complexometric method for determining calcium and magnesium, method for determining the mass fraction of Fe_2O_3 and Al_2O_3, potentiometric method for determining the pH of samples) of the obtained samples of complex fertilizers used in this study are specified. It is shown that studying the properties of the obtained samples, such as the content of nutrients, pH of organomineral fertilizers, static strength of granules will help to select a specific type of fertilizer. At the end of the chapter, it is noted that the results of the

proposed experiment will allow choosing the appropriate composition of fertilizer for application to the soil when growing a particular type of agricultural crop, taking into account the type of soil to obtain high yields.

The third chapter reflects the results of research on the processing of the organic component of SW, represented by food waste of animal and plant origin, wood, paper residues.

Preparation of raw materials included treatment of SW with geothermal water coming to the surface with a temperature of 75°C. containing H_2S. Given the use of Berman's method[1] to analyze SW samples for the presence of helminth larvae, in addition to the influence of the temperature factor, the dependence of the degree of decontamination on the volume of the used salt solution was studied. Comparison of the results of experiments on neutralization of SW with a blank solution and with geothermal waters containing 1% H_2S in the temperature range of 25-75°C made it possible to establish the influence of the factor of H_2S presence on the degree of neutralization.

A series of experiments examined the effect of the concentration of H_2S dissolved in geothermal water on the degree of decontamination of SW. Analysis of the obtained curves of dependence of the degree of neutralization on temperature showed that when using geothermal water with H_2S content above 5%, a shift of the maximum neutralization point towards the axis of ordinates is observed, while indicating the possibility of almost complete neutralization when the H_2S content in geothermal water increases at a lower temperature (Figure 1). This can be explained by the fact that we used geothermal waters with pH = 8.6 provide the presence of more than 90% of hydrogen sulfide in the form of hydrosulfide ion HS^-, thereby increasing the concentration (H+) and resulting in increased efficiency of neutralization from pathogens[2].

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[1] ГОСТ Р 54001-2010. Национальный Стандарт РФ. Удобрения органические. Методы гельминтологического анализа (утв. и введен в действие приказом Федерального агенства по техническому регулированию и метрологии от 30 ноября 2010 г. №591-ст). – М.: Стандартинформ, 2020. с.10.

[2] Линник, Л.И. Химия воды и микробиология: конспект лекций для студентов / Л.И. Линник, - Новополоцк: ПГУ, - 2015- 235 с.

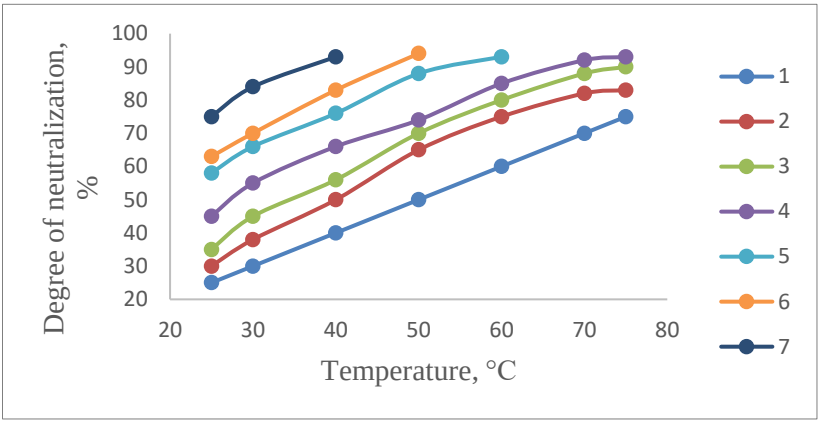


Figure 1: Dependence of the degree of decontamination of SW on the temperature when using: 1 - blank solution: 2 - geothermal water containing 1% H_2S; 3- 7 - geothermal water containing 3.5, 10, 13,18% H_2S

The technological parameters of the process of processing the decontaminated organic component of SW, together with phonolite into organomineral fertilizers have been studied [18]. On the basis of experimental data the technology of obtaining potassium-containing organomineral fertilizers was developed, including the following stages:

- decontamination of the organic component of SW by geothermal water containing H_2S;
- mixing of the decontaminated organic component with crushed phonolite;
- drying of the resulting pulp for 1.5-2 hours at 100-110°C;
- introduction of crushed shell rock into the resulting mass until a neutral environment is provided;
- pelletizing;
- drying the granules to a residual moisture ≤ 1-2%.

Experimentally obtained data confirmed the dependence of the content of the main components in the obtained fertilizer mass ratio of raw material components. The obtained samples contain nutrients in amounts that meet the requirements and have a sufficiently high static strength (tab.1).

Table 1

Characteristics of the obtained K-containing fertilizer

Mass ratio of the organic component of SW: phonolite, g	Content of components, masses. %					Static strength of granules, kgf/cm2
	N	K_2O	P_2O_5	CaO	MgO	
90:10	0,51	6,2	0,42	18,42	1,63	19
80:20	0,49	6,5	0,48	18,83	1,69	21
70:30	0,46	6,9	0,51	19,25	1,76	23
60:40	0,41	7,3	0,53	19,37	1,82	24

Taking into account the inexhaustible reserves of SiO_2-containing clay minerals in Azerbaijan, as well as the porous structure of siliceous minerals capable of adsorbing nutrients, giving mixtures based on them prolonging properties, the recycling of the organic component of MSW together with montmorillonite, which contains 69.90% SiO2, was studied (tab.2). Samples of Si-containing organomineral fertilizers are obtained by the technology developed for obtaining K-containing fertilizers based on SW and phonolite.

Table 2

Characteristics of granules with 1% SiO2 in the raw material depending on the duration of pelletizing

Duration of granulation, Sec	Yield of granules of the commercial fraction (3-5 mm), mass. %	Average granule strength, N/gran	Average granule size, mm
30	83,06	19,0	3,8
60	84,61	19,6	3,7
90	85,8	20,1	3,8
120	86, 5	20,6	3,9
150	87,2	21,2	4,0
180	86,9	19,8	3,8

On the example of obtaining Si organic fertilizers, it was interesting to determine the conditions of granulation, which provide sufficient strength of granules (Figure2).

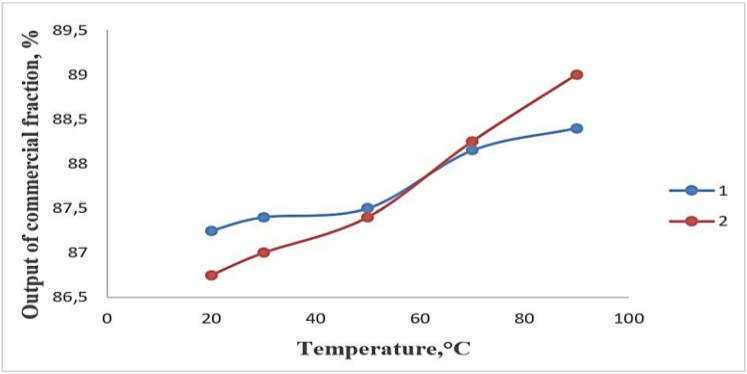


Figure 2: Influence of pelleting temperature on the static strength of pellets

The influence of the duration of pelleting of the pulp on the characteristics of the pellets was studied at room temperature in the time interval of 60 – 180 s and subsequent drying at 105°C with the introduction of 1% SiO_2 in the composition of raw materials. The effect of temperature on the formation of pellets with 1% SiO_2 in the raw material was studied in the temperature range from 30 to 90°C with a pelletizing duration of 150 s.

Although the value of static strength was directly dependent on temperature, it was not excluded that there was a factor to improve this value at the same temperature. In this regard, the effect of the SiO_2 content in the raw material on the value of mechanical strength was studied. The granulation was carried out for 150 s in the temperature range of 50 - 70◦C, introducing montmorillonite in the feed in the amount ensuring the SiO_2 content in the feed equal to 3 - 5 %. It was found that the optimal strength of the pellets provides a combination of varying the SiO_2 content in the raw material with the temperature of granulation (Figure 3).

The effect of increasing the content of silicon oxide in the raw material to increase the mechanical strength of pellets can be explained as follows. As a result of temperature transformation of the organic

component of SW, organic compounds are formed, which penetrate into the spaces between the layers of elementary packages of montmorillonite structure, representing lamellar micropores. The resulting complex contributes to an increase in the mechanical strength of the granules.

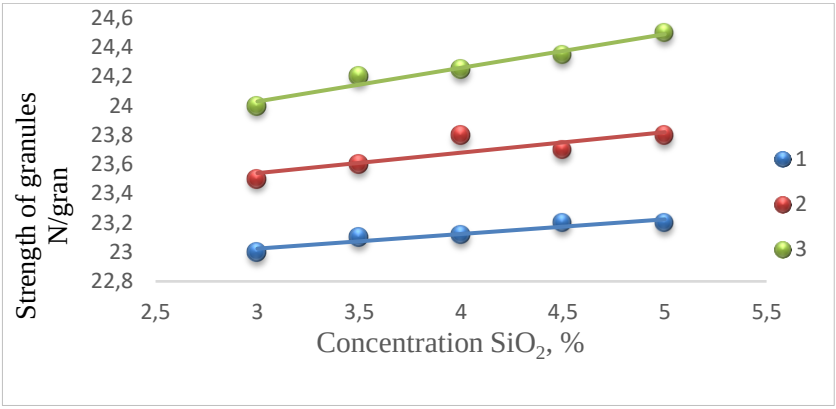


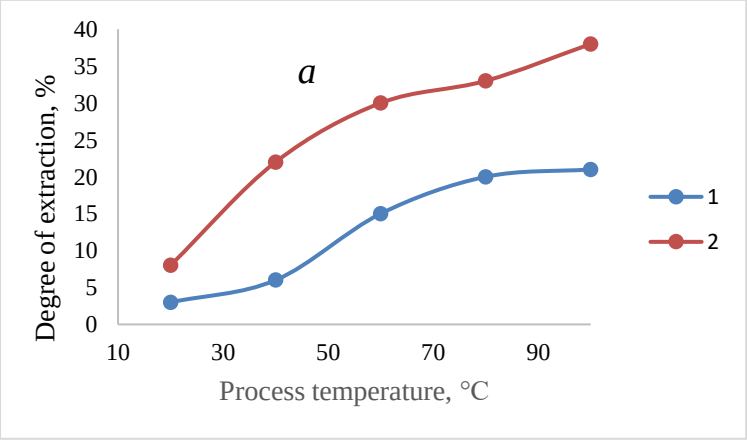
Figure 3. The dependence of the strength of Si-organic fertilizer granules on the concentration of SiO_2 at temperature: 1 -50˚C; 2 - 60˚C; 3 - 70˚C.

The fourth chapter presents the results of processing of industrial wastes of Azerbaijan and local agro-ore raw materials into complex mineral fertilizers. The raw material was a mixture of drill slag with kaolin clay of Khyzy deposit in a mass ratio of 1:1. To process the selected raw materials used HNO_3 27-35% concentration - a waste product of the process of electrochemical polishing of steel and alloys with electrolyte. For dilution of nitric acid to the required concentration the mine (field) waters of copper mines of the Gedabey region of Azerbaijan containing such microelements as Cu, Zn, Ni, Mn were used.

Influence of temperature, duration of process and concentration of a mineral acid on a degree of extraction of the basic useful components present in the received mineral fertilizer is investigated. The degree of extraction of Al_2O_3 and Fe_2O_3 was taken as an indicator of efficiency of mineral decomposition.

Analyzing the obtained data, it should be noted that the dependence of extraction degree of Fe_2O_3 and Al_2O_3 with the increase of concentration from 10% to 35% increases to a certain level, the curve has an inflection corresponding to the maximum value of extraction degree. For Fe_2O_3 the maximum degree of extraction reaches 21%, and for Al_2O_3 39% at 25% concentration of nitric acid (Figure4).

With further increase in the acid concentration the degree of extraction of components from raw materials decreases. Regarding the time of the process of raw materials' minerals decomposition, it can be stated that for maximum extraction of components it is enough to process the raw materials within one hour. Studies on the processing of drilling mud mixture with Khizi clay using H_2SO_4 and H_3PO_4 acids have revealed a similar pattern of dependence of the extraction degree of Fe_2O_3 and Al_2O_3 on the considered technological parameters. To identify the significance of the qualitative composition of clay for the acid decomposition of minerals included in the composition of the studied raw materials, the decomposition of clays from the Lerik and Siyazan deposits was carried out with HNO_3 and H_2SO_4 acids under optimal conditions for processing Khizi clay (Figure 5).



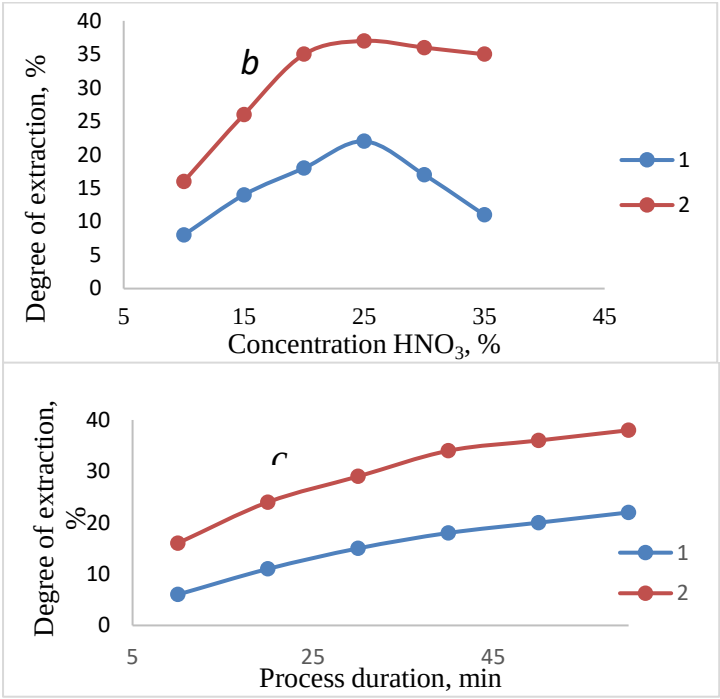


Figure 4: Dependence of Fe_2O_3 (1) and Al_2O_3 (2) extraction degree in solution on process parameters: a - temperature; b - concentration of HNO_3; c - process duration.

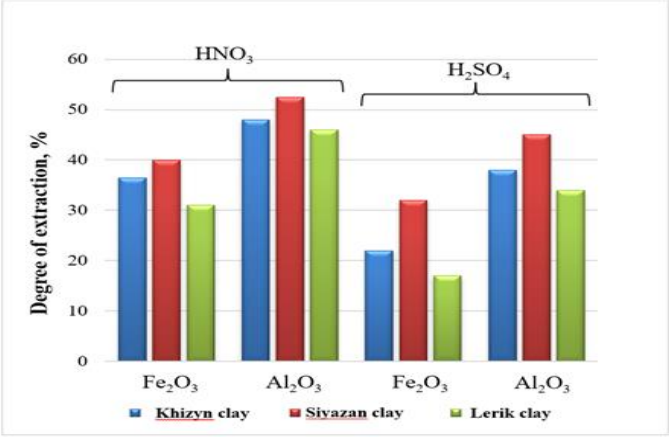


Figure 5: Extraction of Al_2O_3 and Fe_2O_3 depending on their deposit and the acid used: - Khizyn clay; - Siyazan clay; - Lerik clay

In this case, the kink on the curves of dependence of extraction degree on concentration for all acids can serve as reduction of the ratio between liquid and solid phase, which leads to increase of pulp viscosity and, consequently, to decrease of diffusion speed of hydrogen transfer to undecomposed rock particles.

It was found that at the acid decomposition of both HNO3 and H2S04 acids clays of different deposits do not manifest themselves uniquely in the same processing conditions. To explain this fact, guided only by the chemical composition of clays is not possible, meanwhile, the petrographic studies could give an unambiguous answer, as the influence on the properties of minerals of their internal structure (crystal structure), as well as the conditions of their formation and origin is known. The high K_2O content approaching 10% predetermined the use of phonolite as a modifying additive for obtaining K-bearing mineral fertilizers (tab.3).

Table 3

Characteristics of N, K-containing mineral fertilizer

№	Correlation Drill slag: clay; phonolite	The content of the components, mass. %					
		N	P_2O_5	K_2O	Na_2O	MgO	CaO
1	1:1:0,25	32,1	0,21	7,2	0,48	0,52	0,67
2	1:1:0,5	31,6	0,22	7,6	0,43	0,48	0,53
3	1:1:0,75	30,8	0,24	8,1	0,41	0,45	0,44
4	1:1:1	30,1	0,26	9,3	0,45	0,38	0,39

The influence of the ratio of the components of raw materials on the content of the main components in the obtained samples has been studied. On the basis of the obtained results about the possibility of processing of drilling mud together with local kaolin clays, the basic technological scheme of complex processing of these raw materials has been developed (Figure 6).

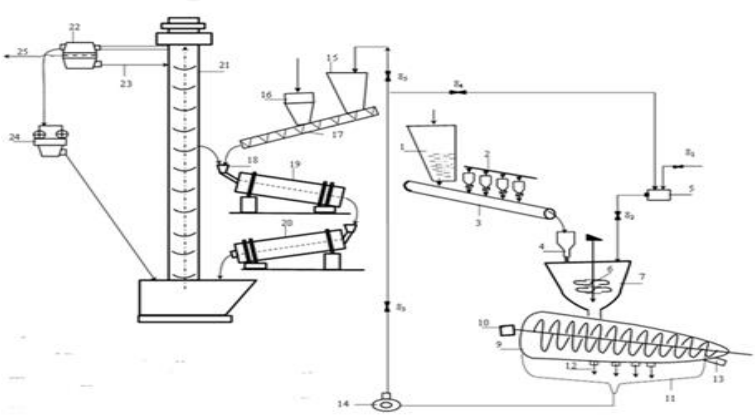


Figure 6. Basic technological scheme for drilling mud processing together with clay: Drilling mud hopper - 1, clay hopper - 2, conveyor - 3, batcher - 4, acid tank - 5, mixer - 6, reactor - 7, adjusting tap - 8, screw press - 9 with shaft -10 , liquid phase collection chamber - 11, holes for liquid phase discharge - 12, outlet pipe for meliorant - 13, pump - 14, tank for liquid phase - 15, bunker with coquina - 16, screw - 17, drain - 18, pelletizer -19, drying drum - 20, elevator - 21, sieve - 22, retort line - 23, crusher - 24, product line - 25.

Presence of phosphorite with phosphorus content from 12 to 15%, characterized by low carbonate (2-2,5%) with MgO content of 3,8% on the territory of Azerbaijan in Nakhichevan AR, allowed to expand the raw materials base for production of complex mineral fertilizers. We were tasked with studying the possibility of processing raw materials that would include SW incineration slag and Nakhichevan phosphorite.

Proceeding from a composition of raw materials, results of processing, first of all, will be connected with a question of consideration of phosphorite as an active raw material, therefore the first series of experiments has been devoted to sulfuric acid decomposition of Nakhichevan phosphorite with the purpose of revealing the approximate conditions of the subsequent effective processing of binary raw materials. Nakhichevan phosphorite was preliminarily subjected to mechanical processing in a ball mill to a standard grinding, corresponding to the residue on the sieve 0.18 mm. In the experiments, 50-80% H_2SO_4 was used, with a rate of 60 - 110%

of stoichiometric. Processing of raw materials was carried out at 80°C (Figure7).

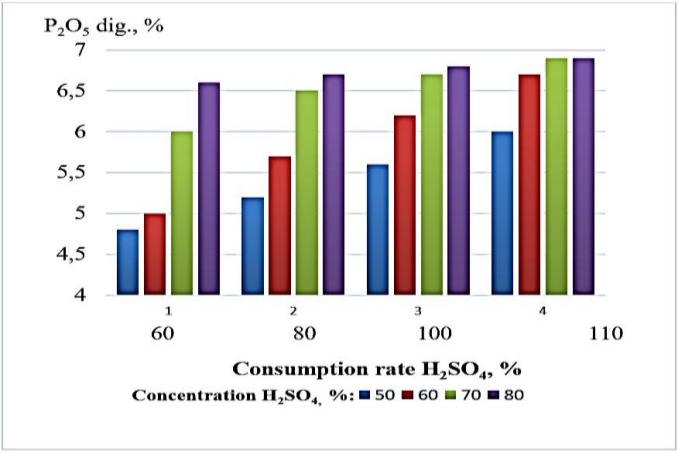


Figure 7. Influence of concentration and rate of consumption of H_2SO_4 on the content of $P_2O_{5dig.}$ in the liquid phase during processing of phosphorite

The presented diagram shows the nature of the process of decomposition of phosphorite, depending on the conditions, conditioning the importance of both characteristics. When deciding on the choice of rate should be based on the concentration of H_2SO_4 involved in the process. In the investigated interval of concentration of sulfuric acid for optimum conditions of processing of Nakhichevan phosphorite it is possible to accept concentration of acid equal to 80% at stoichiometric rate of consumption.

The following stage of experimental researches foresaw research of character of processing of binary raw material, representing a mix of Nakhichevan phosphorite with slag from incineration of solid waste. A mixture of 100 g of SW slag and 50 g of phosphorite was subjected to processing at a temperature of 80°C. Experiments were performed under conditions similar to phosphorite decomposition. To compare the processing of phosphorite and binary raw materials (SW slag and phosphorite) using the rate of acid equal to 80 and 100% on the obtained data we built curves of dependence of

P_2O_5dig. in the obtained samples on the concentration of H_2SO_4 (Figure8).

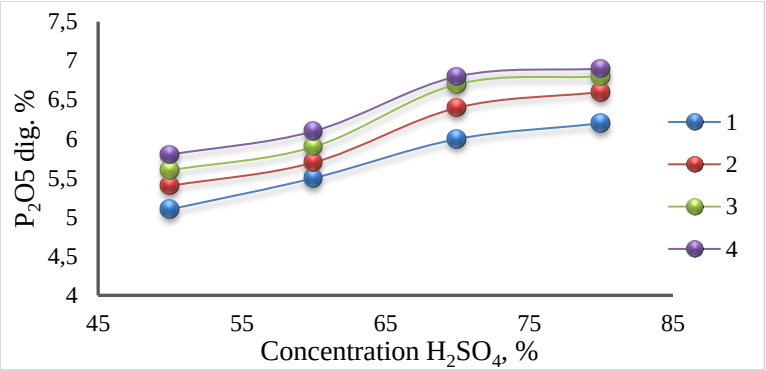


Figure 8. Dependence of P_2O_5 content on H_2SO_4 concentration at H_2SO_4 rate of 80%: for phosphorite -1, for phosphorite combined with SW slag - 3; at H_2SO_4 rate of 100%: for phosphorite -3, for phosphorite combined with SW slag - 4.

When comparing the curves of dependence of P_2O_{5dig}. content in processing phosphorite and joint processing of SW slag with phosphorite under the same conditions, the increase of P_2O_{5dig}. content in case of binary raw materials processing is observed. Also noteworthy is the fact that the distance between the curves of dependence of P_2O_5 digestible content for binary raw materials at 80 and 100% flow rates decreases relative to the curves characterizing the processing of phosphorite. This pattern reflects the absence of the negative effect of the presence of SW slag in the binary feedstock.

The obtained results can be explained by two factors. First, carrying out a preliminary mechanical activation of phosphorite leads to a softening of its crystal lattice, promoting the transition of P_2O_5 in a water-soluble form. The second factor, in our opinion, can be attributed to consideration of the role of SW slag in the processing of the raw materials in question. If in the decomposition of phosphorite the calcium sulfate formed in the first stage is deposited only on the phosphorite grains, the processing of binary raw materials can also result in deposition of $CaSO_4$ either on the surface of slag particles, or

penetration into pores and hollows in the surface structure of SW slag particles. In this case, the slag helps to reduce the concentration of $CaSO_4$ molecules capable to precipitate on phosphorite grains by taking a part of $CaSO_4$ on itself, creating better conditions for the diffusion of molecules of the formed phosphoric acid to phosphorite particles.

The influence of the ratio of components of binary raw materials (SW slag + phosphorite) on the characteristics of the obtained fertilizers by varying the content of phosphorite under optimal process conditions: temperature 80°C, the concentration of acid 80% at 100% rate of consumption (table 4) .

According to the results obtained, increasing the content of phosphorus in the raw material leads to improved characteristics of the resulting fertilizer [14]. The increase in the proportion of slag in the raw material has almost no effect on the quantitative characteristics of nutrients, while drawing attention to a tangible increase in the mechanical strength of the fertilizer, which is probably due to the porous structure of sintered particles of SW slag.

Table 4

Characteristics of mineral fertilizers by varying the mass ratio of SW slag: phosphorite

№	Mass ratio of SW slag: phosphorite	P_2O_5.%	P_2O_5 усв.%	P_2O_5 св.%	CaO	K_2O	H_2O	Output, %	Static strength, MPa
1	50:10	14,2	12,2	2,3	23,5	2,6	2,1	89,0	1,6
2	50:20	14,8	12,6	2,4	24,2	2,9	2,2	90,3	1,9
3	50:30	15,4	13,2	2,6	25,1	3,0	2,2	90,6	2,2
4	50:40	15,9	13,6	2,9	25,4	3,3	2,4	91,2	2,4
5	50:50	16,2	13,9	3,3	25,7	3,7	2,5	91,7	2,6
6	60:50	16,3	13,8	3,3	25,8	3,7	2,6	91,7	3,1

The study of the chemical composition of the liquid phase showed the presence of both free phosphoric acid and sulfuric acid,

the presence of which, even after granulation, will limit its use on some types of soil. In this regard, to regulate acidity, if necessary, local crushed shell rock ($CaCO_3$) was added to the resulting pulp as a neutralizing additive before the granulation stage. To avoid losses of water-soluble P_2O_5, and to prevent the process of retrogradation, the amount of added shell rock was determined by the pH value, bringing it to a value of 6.5-7.

Continuing research on identifying opportunities to attract local industry waste processing for the production of mineral fertilizers, along with SW slag and phosphate, drilling mud was introduced into the composition of raw materials. Used sulfuric acid with 50-65% concentration of propylene hydration process was used in the processing of raw materials. The process of decomposition of three-component raw materials was carried out in the conditions of processing of a mixture of SW slag with phosphorite at a temperature of 80°C, the rate of sulfuric acid, equal to 100-110 of stoichiometry.

Comparison of the results of recycling raw materials with industrial wastes under the same conditions showed the possibility of obtaining P_2O_{5dig} values of the same order and close in value, exceeding the value of P_2O_{5dig} in the processing of phosphorite (tab.5). The introduction of drilling mud into the composition of raw materials does not complicate the process of processing, despite the presence of increased content of halide oxides in the drilling mud.

Table 5

Dependence of P_2O_5dig. value on the composition of raw materials and processing conditions

Raw material	$P_2O_5dig.$			
	Concentration H_2SO_4 / Consumption rate H_2SO_4			
	50/80	50/100	60/80	60/100
Phosphorite	5.23	5.67	5.59	6.09
Phosphorite + SW	5.75	5.87	6.14	6.31
Phosphorite + SW + Drilling mud	5.77	5.91	6.12	6.34

The obtained results obliged to find the factor, which allowed to keep P_2O_5 value when adding to the binary raw materials of drilling mud. Under the conditions of processing of the compared compositions of raw materials the only difference is the difference in the use of spent acids from different chemical processes. In order to confirm the assumption about the role of origin of the used sulfuric acid, the decomposition of a mixture of phosphorite, MSW slag and drilling mud with 50 and 60% technical sulfuric acid under similar conditions was carried out (Figure9). Comparative results obtained with the use of both acids confirmed the efficiency of raw material decomposition using spent sulfuric acid from the propylene hydrolysis unit.

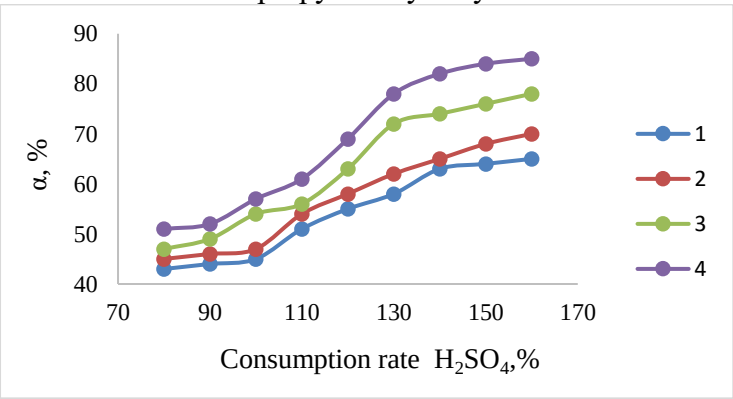


Figure 9. Dependence of the coefficient of decomposition of raw materials containing SW slag, phosphorite and drilling mud on the rate of H_2SO_4:

1 - technical 50% H_2SO_4; 2 - technical 60% H_2SO_4;
3 - waste 50% H_2SO_4; 4 - waste 60% H_2SO_4

The analysis of the spent acid from the propylene hydration unit showed the presence of organic compounds: isopropyl sulfate 0,25 - 0,30%; diisopropyl sulfate - 0,3 - 0,4%; isobutyl sulfate - 0,12 - 0,15%; diisobutyl sulfate - 0,2%. The present ethers, having surface-active properties, can promote foaming of the reaction mass, forming gaps and macrocapillaries, thereby improving diffusion to the phosphorite particles. In addition, the present ethers reduce the surface

tension of solid particles, thereby weakening the compacting crust of calcium sulfate and accelerating the process of phosphorite decomposition.

Based on studies on the possibility of recycling phosphorite as a mixture with SW slag, as well as three-component raw materials with drilling mud, the basic technological scheme was proposed. Installation of the unit includes the use of standard equipment, and the scheme provides for the use of equipment for feeding modifying additives if it is necessary to introduce microelements into the fertilizer (Figure 10).

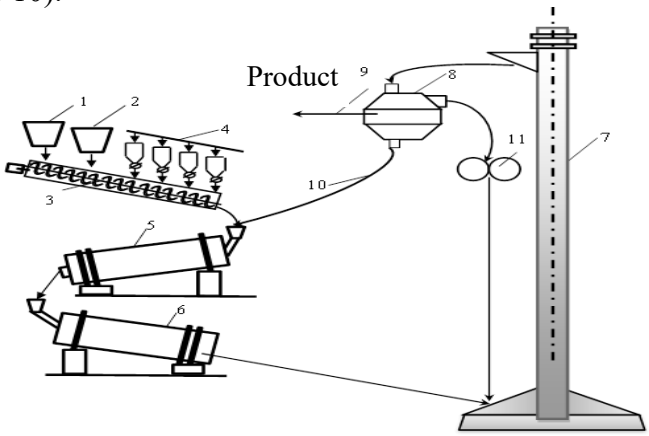
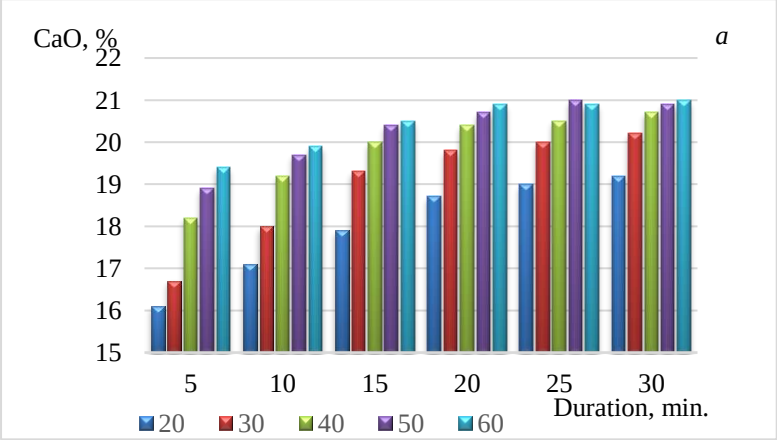


Figure 10. Basic technological scheme of SW slag and drilling mud utilization: sulfuric acid tank - 1, SW slag tank - 2, auger-3, modifiers hoppers - 4, granulator - 5, dryer - 6, elevator - 7, tier sieve - 8, finished product line - 9, retort line - 10, crusher - 11.

The processing of three-component feedstock containing SW slag, dolomite and phosphogypsum has been studied [15]. Grinded feedstock up to particle size of 5-10 mm was subject to decomposition with sulfuric acid, being a waste product of an oil refinery, and its concentration was increased to 10 - 20 %. Consumption rate of sulfuric acid was taken as 100% of stoichiometry. With the purpose of revealing of interrelation of regimes of process on characteristics of received fertilizers the importance of variation of technological regimes has been studied.

It was found that the order of mixing of reagents does not affect the ratio of the obtained liquid and solid phases. Time changes of process direction under the influence of such technological parameters as H_2SO_4 concentration and process temperature were investigated.

The picture of the temperature dependence of CaO accumulation, identical in character as for 10%, as well as for 20% concentration of sulfuric acid, reflecting two areas. In the time interval of 5-20 min intense accumulation of calcium oxide is observed. With transition to the temperature interval of 20 - 30 min, a barely perceptible accumulation of calcium oxide is observed, confirming the completion of dolomite decomposition. The character of the influence of sulfuric acid concentration on CaO accumulation in the solid phase depending on the decomposition process temperature indicates a decrease in oxide accumulation throughout the temperature range when passing from using 10% concentration of H_2SO_4 to 20% concentration (Figure11).



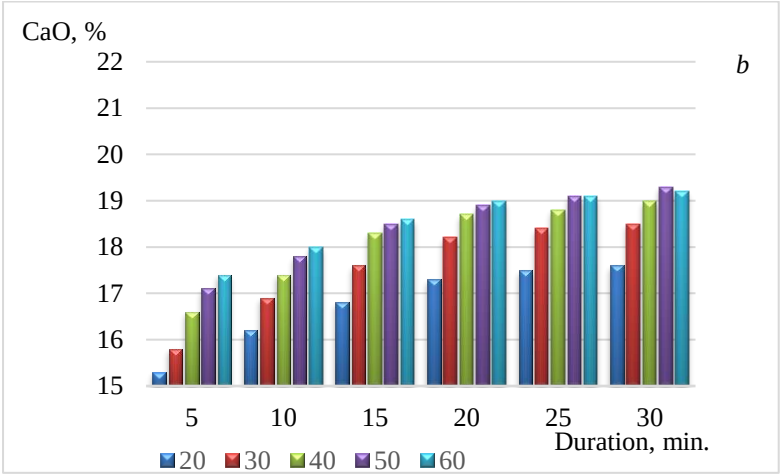


Figure 11. Effect of process parameters on CaO accumulation : а) 10% H_2SO_4; б) 20% H_2SO_4

Such character of changes shown at the diagrams can well be explained by the fact that full dissociation of sulfuric acid is achieved when the density of H_2SO_4 approaches the density of water, i.e., when the acid is strongly diluted. Increasing the acid concentration increases the calcium content in the liquid phase, namely in the form of $CaHSO_4$. Given that in obtaining a complex fertilizer priority is the content of $CaSO_4$, which in contrast to leaching $CaHSO_4$ will remain in the soil, the efficiency of the process will be provided by using 10% sulfuric acid.

Summarizing the experimental results obtained, it should be noted that the optimum conditions of technological parameters of the studied raw materials processing in the considered intervals can be taken as acid decomposition of 10% H_2SO_4 in the temperature range of 40-50°C for 20-25 minutes. Under these conditions the influence of raw material components ratio on the composition of the obtained mineral fertilizer samples was studied (tab.6).

Table 6
Characteristics of fertilizer depending on the composition of raw materials

№	Content of components of raw materials, g			Oxide content, wt, %				Static strengths of pellets, kgf/cm^2
	SW slag	Phospho-gypsum	Dolomite	CaO	MgO	P_2O_5	K_2O	
1	50	25	25	13,0	2,15	0,21	0,12	21,2
2	60	25	25	15,2	2,18	0,22	0,12	21,9
3	70	25	25	18,1	2,21	0,24	0,13	22,4
4	80	25	25	19,7	2,24	0,25	0,14	23,2
5	90	25	25	20,2	2,25	0,27	0,16	23,9
6	100	25	25	20,4	2,27	0,29	0,16	24,4
7	100	50	25	27,7	2,23	0,31	0,18	24,6
8	100	25	40	23,8	2,68	0,29	0,17	27,2
9	100	25	50	24,1	2,85	1,29	0,18	27,8

As the results of the experiments showed, the increase in dolomite content led to an increase in the strength of granules up to 27.8 kgf/cm^2. It seems to us that the result obtained may well be explained by the fact that the slag obtained as a result of high-temperature processing of SW contains enlarged sintering particles. The surface structure of such particles will retain depressions and pores when crushing them, thus providing the slag with the role of a binder for raw material components. As a result of intensive interaction of powdered dolomite with the slag surface, the viscosity of the mixture increases, leading to the strength of the granules.

The conducted research revealed the processing conditions of the selected raw materials, with the possibility of regulating the characteristics of the samples of the obtained complex fertilizer. The developed methods and technological schemes will allow to receive fertilizers with obviously required quality with use of local natural resources in a combination to the industrial wastes of Azerbaijan.

CONCLUSIONS

1. The possibility of using Azerbaijan's surface geothermal waters with a temperature of 25-75°C containing H_2S for neutralization of the organic component of MSW was studied. The influence of H_2S concentration on the degree of neutralization with regard to temperature was established, showing a shift of the maximum degree of neutralization towards a decrease in the temperature of geothermal water when the concentration of H_2S increases, which will expand the geography of the choice of sources used.

2. For the first time the technology of receiving of organomineral fertilizers with involvement in processing of the neutralized organic component of SW by geothermal waters of Azerbaijan containing H_2S with use as the modifier of a local phonolite and a shell rock for neutralization of the received pulp is developed.

3. The possibility of using montmorillonite as a modifier at processing of an organic component of MSW for obtaining of Si - organomineral fertilizers, and also its role in increase of static strength of granules is established.

4. Influence of temperature, process duration, concentration and consumption rate of nitric, sulphuric and phosphoric acids on the extraction degree of the main useful components present in the obtained mineral fertilizers at processing of drilling mud together with the local kaolin clays has been determined. The possibility of using phonolite as a source of potassium as a raw material modifier is shown.

5. Optimal conditions for sulfuric acid processing of Nakhichevan phosphorite together with SW incineration slag and phosphorite have been revealed. It is determined that the content of P_2O_{5dig} in the processed products depends on the concentration and rate of H_2SO_4, as well as the composition of the used raw materials.

6. The qualitatively controlled process of joint processing of SW slag, dolomite and phosphogypsum into complex mineral fertilizers by varying the composition of mixed raw materials, concentration of sulfuric acid and temperature of the reaction medium has been carried out. The role of SW slag and the amount of dolomite introduced into

the raw material composition on increasing the static strength of the granules obtained complex mineral fertilizer is substantiated.

7. Fundamental technological schemes enabling the processing of industrial wastes of Azerbaijan and local natural resources into complex mineral fertilizers have been proposed.

8. The developed technology will allow solving the issue of import substitution by own production of organomineral and complex mineral fertilizers, representing an exceptional dependence for the organomineral complex in solving the food program.

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Personal contribution of the applicant in joint works with co-performers

[7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18] – independent work of the author

[1, 2, 3, 4, 5, 6] – setting the task, developing the procedure for processing solid waste and disposal methods, conducting experimental experiments, analysis and evaluation of the results belongs to the author

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