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JOINT RECYCLING MSW SLAG AND DRILL CUTTINGS INTO MINERAL FERTILIZERS WITH LEAN-GRADE PHOSPHORITE

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Abstract: *The possibility of joint utilization of municipal solid waste (MSW) slag and drill cuttings by their recycling into complex mineral fertilizers through the use of lean-grade phosphorite as a source of phosphorus has been considered. Also, the recycling of three-component raw materials has been carried out with 50-65% sludge sulfuric acid from the propylene hydration process at 80°C. The consumption rate of sulfuric acid required to obtain mineral fertilizers with a sufficient content of $P_2O_{5assim.}$ has been determined with due regard for the presence of the increased content of sesquioxides in the drill cuttings. Comparative results of the recycling MSW with phosphorite and three-component raw materials confirming the absence of harmful effect of drill cuttings on the recycling process and the role of the nature of the used sulfuric acid on the parameters of the recycling process have been shown.*

Keywords: *MSW slag, drill cuttings, lean-grade phosphorite, recycling, complex mineral fertilizers*
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Introduction

The large tonnage of daily-generated household waste harmfully affects both the environment and human health. The oldest and most common form of MSW managing is underground disposal in landfill, which has become widespread due to a number of advantages, such as simplicity, low investment, high loading capacity and low operating costs. As is known, most of the EU member-countries dispose of more than 50% of their MSW in landfills [1].

In the meantime, landfills contain a huge amount of potentially toxic compounds that can endanger the safety of the environment, pollute the air, soil and water, and thereby threaten human health [2]. In this regard, the efforts of scientists are currently directed to finding ways to recycling solid waste for their use as secondary raw materials. Despite the presence of hazardous waste, innovative solutions that involve the regeneration of materials, especially the reasonable realization by recycling MSW into useful products [3] instead of their disposal are proposed.

One of the examples is the use of waste paper sorted out mixture of municipal solid waste, the recycling of which makes it possible to obtain cellulose nanofibers [4]. It is known that MSW can be recycled in an autoclave at 150°C and a pressure of 0.5 MPa for their subsequent use in the production of building materials as an ingredient [5].

The organic substances contained in MSW make it possible to maintain the balance of organic substances in soils improving their physical and chemical properties thereby increasing soil fertility and carrying out the simultaneous utilization of MSW [6] during their recycling into organomineral fertilizer by composting. A technology has been patented to obtain organomineral fertilizers by recycling the organomineral component of MSW neutralized by geothermal waters [7]. Sulfuric acid-

recycling MSW slag modified with phosphogypsum and natural composition - dolomite, made it possible to obtain complex mineral fertilizers with high mechanical stability [8].

In addition to the use of MSW as a secondary raw material for agricultural needs, the results of the research into the possibility of using drill cuttings in the same direction have been published. Two-year research on agricultural land in France showed the efficiency of using biologically decomposed drill cuttings without harmful effects on soil, ground and surface water [9].

The role of drill cuttings is especially noted in growing fodder "Pennisetum purpureum" on acidic soils. It has been established that a significant increase in grass height and leaf length can be achieved with a dose of drill cuttings not exceeding 5% of the soil [10].

The influence of a mixture of different types of drilling waste on changes in the physicochemical properties of acidic soil, as well as on the growth of red clover (Trifolium pratense L.) has been studied. The addition of drill cuttings into the soil raised the biomass of red clover from 1.5 to 2.5 times due to the soil saturation with bases, alkaline cations (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}), organic substances and the available form of phosphorus [11].

Examples of published results on the utilization of MSW and drill cuttings in solving environmental problems by their recycling into the products useful for the agro-industrial sector played a certain role in choosing the direction of our research.

Material and research methods

Known as an industrially developed region, Azerbaijan like all countries of the world is concerned about environmental problems caused by the accumulation of industrial waste. The following components have been selected as raw materials purposefully approaching to the decision due to the utilization of local industrial waste modified by local natural resources in their recycling into complex mineral fertilizers:

● Slag obtained from MSW incineration of the Baku plant in city waste recycling. According to the data of plant laboratory, the batch used for experiments contained heavy metals within the permissible limits: Cd - 0.09 mg/kg; Ni - 2.1 mg/kg; Cu - 0.32 mg/kg; Pb - 0.17; Hg - traces. The chemical composition of the slag is shown in Fig.1.

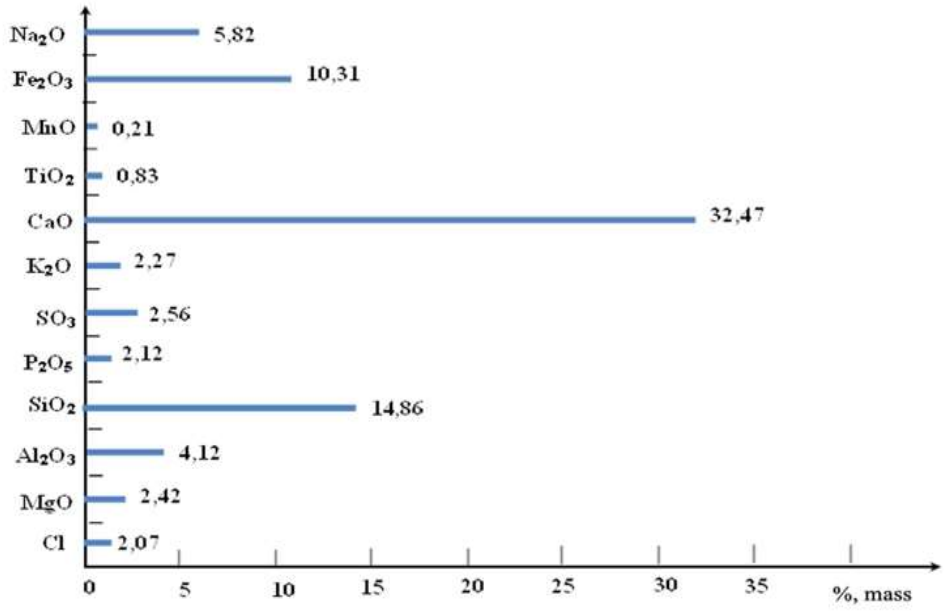

Fig.1. The chemical composition of the MSW slag

● Drill cuttings from the Karadag deposit, well No 1, from a depth of 10 m, mineralogical composition: SiO_2 – 28.4; feldspar - 13.8; montmorillonite, 14.2; elite - 10.1; kaolinite, 10.5; calcite, 6.1; hematite - 6.7; volcanic ash - 10.2. Total concentration of petroleum hydrocarbons in drill cuttings - 15,215 mg/kg.
The chemical composition of drill cuttings is shown in Fig.2.

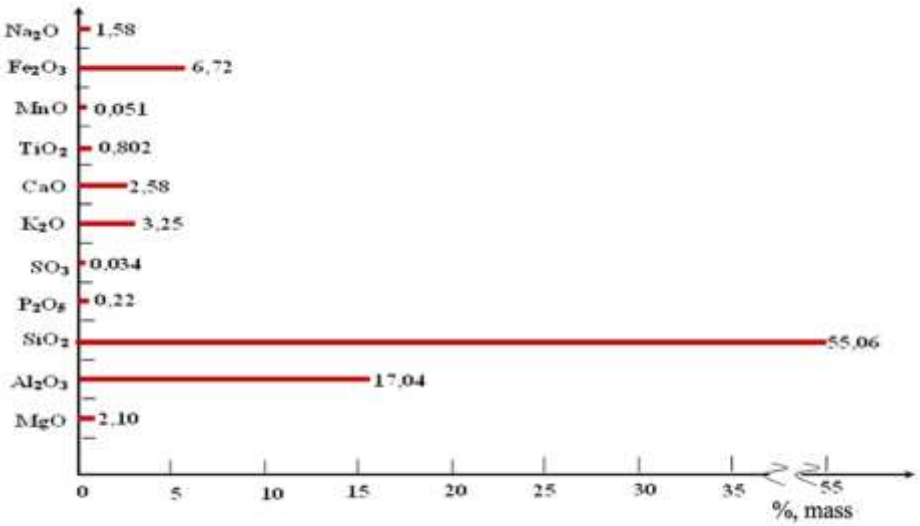

Fig.2. The chemical composition of drill cuttings

● Lean-grade phosphorite
The chemical composition of lean-grade phosphorite is given in fig.3.

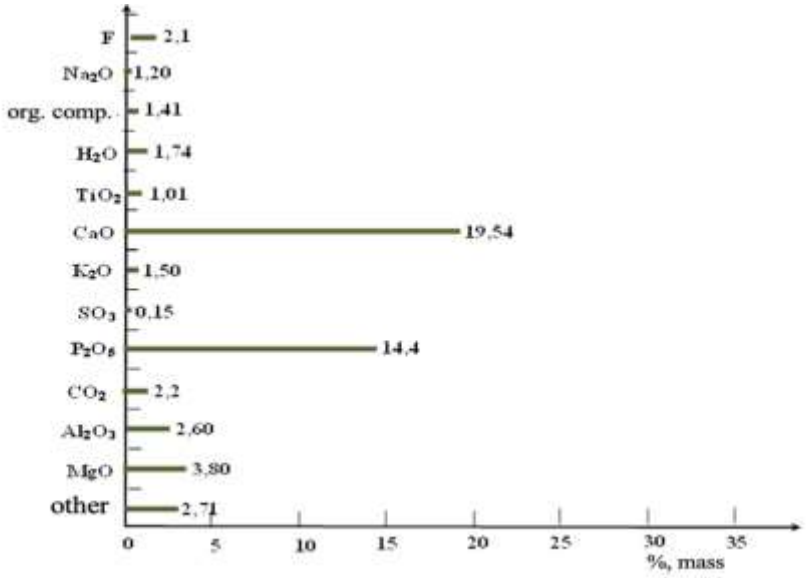

Fig. 3. The chemical composition of lean-grade phosphorite

The recycling of raw materials is carried out via decomposition process by sulfuric acid using spent acid with a concentration of 50 - 65% remained after waste in the hydration process of propylene. The mixed raw material is preliminarily subjected to mechanical processing in a ball mill to a standard grind

corresponding to a residue on a sieve of 0.18 mm.

An estimated amount of sulfuric acid is placed in a thermostated reactor with a volume of 500 ml to decompose the raw material. The milled mixed raw materials in estimated ratios are added at 80°C stirring for 30 min. After 30-40 min, the reactor is placed in an oven, keeping at a temperature of 110-120°C for 1 hour. The resulting sludge is sent for granulation by pelletizing. The obtained granules after drying are separated in a three-tier sieve. The 2-5 mm fraction is sent to the warehouse, the ≤ 2 mm fraction is returned along the recycle line for re-granulation, and the ≥ 5 mm fraction is sent to the granulator followed by reseparation on a sieve.

The static strength of the granules has been determined using an IPG-1 instrument.

Results and discussion

As an industrially developed region Azerbaijan is no exception in terms of the generation of a significant amount of waste and harmful emissions that bring environmental problems. Industrial recycling, recovery and neutralization of production waste are a strategically important direction of the Azerbaijan state policy. On the other hand, the food-based program of the state does not remain unaddressed, which relates to providing the agro-industrial sector with fertilizers and the restoration of land capacity lost due to the exposure of the ground cover to erosion, salinization, anthropogenic environmental impact and other things. Considering both factors, our research has been devoted to the study of the recycling industrial waste in the country involving local agricultural ores.

Previously, we have studied the recycling process of binary raw materials represented as MSW slag and lean-grade phosphorite [12].

The obtained results indicate the possibility of obtaining P-containing mineral fertilizers, the properties of which are regulated by the ratio of raw materials components.

This article reflects the results of studies into the recycling three-component raw materials, in which drill cuttings are used, in addition to MSW slag. Since the raw material contains drill cuttings with a high content of sesquioxides (Al_2O_3 - 17.11%, Fe_2O_3 - 6.76) as a modifier in this series of experiments, it was necessary to determine the consumption rates of sulfuric acid in order to obtain the quantitative content of the components of the resulting mineral fertilizers with appropriate agrochemical standards. The experiments were carried out with raw materials containing 50 g of MSW slag, 50 g of phosphorite, and 20 g of drill cuttings at a decomposition temperature of 80°C. The results of the experiments are presented in Table 1.

Table 1. The effect of concentration and consumption rate of H_2SO_4 on the content of $P_2O_{5assim.}$ in products of joint recycling MSW slag, drill cuttings and lean-grade phosphorite

№	Concentration of H_2SO_4, %.	Consumption rate of H_2SO_4, %.	$P_2O_{5_{total}}$, %	$P_2O_{5_{assim.}}$ %	$\frac{P_2O_{5_{assim.}}}{P_2O_{5_{total}}} \cdot 100$
1	50	80	11. 78	5.77	48.98
2	50	100	10. 87	5.91	54.37
3	50	110	10.12	6.02	59.48
4	50	120	9.93	6.21	62.53
5	50	130	9.71	6.52	67.14
6	50	140	9.33	6.72	72.25
7	50	150	9.15	7.02	76.72
8	50	160	9.12	7.04	77.19

9	60	80	11.91	6.12	51.38
10	60	100	11.04	6.34	57.42
11	60	110	10.36	6.51	62.83
12	60	120	9.77	6.95	71.13
13	60	130	9.53	7.41	77.75
14	60	140	9.33	7.72	82.74
15	60	150	9.18	7.81	85.07
16	60	160	9.23	7.87	85.26

Based on the obtained results presented in Table 1, it should be noted that both concentration and consumption rate of H_2SO_4 affect the process of formation of water-soluble phosphorus-containing compounds in recycling the mixed three-component raw materials (phosphorite + MSW + drill cuttings) under consideration, as well as in recycling the two-component raw materials (phosphorite + MSW). At the same concentration, the content of P_2O_{5assim} in the decomposition products increases with an increase in the consumption rate. So, for example, at 50% concentration of sulfuric acid, an increase in the consumption rate of sulfuric acid from 80 to 160% leads to an increase in the degree of extraction of P_2O_{5assim} from 48.98 to 77.19%. In this case, at a consumption rate of 150 and 160%, the values of $P_2O_{5assim.}$ differ by an insignificant amount, which allows us to conclude that it is not advisable to increase the acid consumption rate above 150%. The same pattern is also characteristic when proceeding to the analysis of the results obtained under the conditions of using 60% concentration of sulfuric acid.

The obtained results are consistent with the well-known results of studies [13], confirming the need in raising the consumption rate of sulfuric acid for the recycling phosphate raw materials when the content of sesquioxides increases in it.

When we planned experiments for the recycling three-component raw materials with the simultaneous presence of MSW slag and drill cuttings, there was no confidence in the possibility of obtaining positive results.

Nevertheless, a comparative analysis of the obtained results with the data of previously reviewed experiments in terms of the recycling of lean-grade phosphorite with MSW made it possible to refute the existing doubts. The results obtained under same conditions, namely, when using sulfuric acid of 50-60% concentration corresponding to the concentration of spent acid taken from the propylene hydration device have been used in comparison. Comparison of the results is presented in table 2.

Table 2. The dependence of the P_2O_{5assim}.value on the composition of raw materials and recycling conditions

Raw materials	P_2O_5 assim., %			
	Concentration of H_2SO_4/ stoichiometric flow of H_2SO_4, %			
	50/80	50/100	60/80	60/100
Phosphorite	5.23	5.67	5.59	6.09
Phosphorite + MSW	5.75	5.87	6.14	6.31
Phosphorite + MSW +Drill cuttings	5.77	5.91	6.12	6.34

The results given in Table 2 show the possibility of recycling phosphorite in the presence of both MSW slag and the combined presence of MSW slag with drill cuttings to obtain $P_2O_{5assim.}$ values with the same order and close magnitude. Such results are indicative of the fact that addition of drilling slag into the composition of raw materials does not complicate the recycling process even despite the presence of an increased content of sesquioxides in the drill cuttings.

At first glance, the arisen contradiction between the well-known requirement to increase the consumption rate of sulfuric acid when the raw material contains a slightly increased content of sesquioxides and the obtained experimental data in terms of $P_2O_{5assim.}$ content remaining at the same level when drill cuttings are addedunder the same other conditions obliged us to find the fact that explains the obtained result.

When comparing the recycling conditions of the compared compositions of raw materials, the only difference is in the use of spent acids taken from different chemical processes. As the analysis of the spent acid from the propylene hydration unit showed, it (acid) contains organic compounds that are surface-active substances (surfactants), the molecules of which contain a sulfo group: isopropyl sulfate 0.25 - 0.30%; diisopropyl sulfate - 0.3 - 0.4%; isobutyl sulfate - 0.12 - 0.15%; diisobutyl sulfate - 0.2%.

The presence of sulfogroup-containing compounds in the reaction medium, which is the only difference in the used technological mode made it necessary to check this fact in order to affirm its effect on the process parameters.

The decomposition of raw materials containing phosphorite, MSW slag and drill cuttings with 50 and 60% technical sulfuric acid was carried out to test our assumption.
Comparative results obtained using commercial sulfuric acid and spent sulfuric acid from hydration
a propylene unit are shown in Fig.4.

The graphic images of the decomposition process of raw materials with MSW slag, drill cuttings and phosphorite presented in Fig.3, when using the same consumption rates of 50 and 60% H_2SO_4, which has a different nature, allowed us to accept the fact that the use of spent H_2SO_4 from a propylene hydration unit containing alkyl sulfates causes to increase in effectiveness of raw material decomposition.

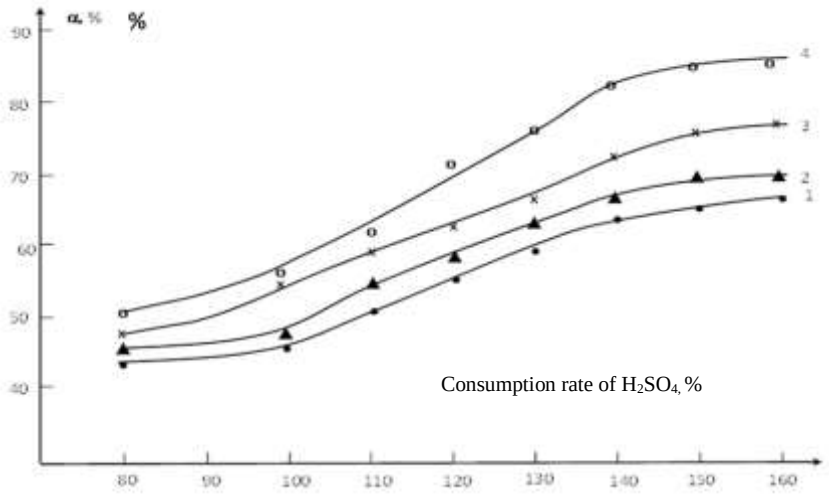

Fig. 4. The dependence of the decomposition coefficient of raw materials containing MSW slag, phosphorite and drill cuttings on the consumption rate of H_2SO_4: 1 - 50% technical H_2SO_4; 2 - 60% technical H_2SO_4; 3 – 50% spent H_2SO_4; 4 - 60% spent H_2SO_4

By our estimate, the present esters with surface-active properties led to the foaming of the reaction mass that resulted in the formation of gaps and macro-capillaries, thereby improving diffusion in phosphorite particles. In addition, the present ethers reduce the surface-tension of the solid particles while weakening the sealing crust of calcium sulfate and accelerating the decomposition process of phosphorite.

The possibility of studying the joint recycling MSW slag and drill cuttings will help to some extent solving the utilization problem of these production wastes. Furthermore, it will be possible to add an additional amount of K, Na, Mg, Mn, Ba to the composition of mineral fertilizers, each of which plays a certain role in plant life.

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BƏRK MƏİŞƏT TULLANTILARI (BMT) ŞLAKI VƏ ZƏİF FOSFORİT İLƏ QAZMA ŞLAMLARININ MİNERAL GÜBRƏLƏRƏ BİRGƏ EMALI

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Xülasə: Fosfor mənbəyi kimi zəif fosforitin istifadə olunması ilə BMT (bərk məişət tullantıları) şlakı və qazma şlamının mürəkkəb mineral gübrələrə emal imkanları nəzərdən keçirilmişdir. Üç komponentli xammalın emalı propilenin hidratlaşması prosesindən 50-65%-li işlənmiş sulfat turşusu ilə 80^{o}C temperaturda həyata keçirilmişdir. Qazma şlamında biryarımlıq oksidlərin yüksək miqdarının mövcudluğunu nəzərə alaraq, $P_2O_{5\ mən.}$-nin kifayət qədər miqdarı ilə mineral gübrələrin alınması üçün tələb olunan sulfat turşusunun sərfiyyat norması aşkar edilmişdir. Qazma şlamının emal prosesinə zərərli təsirinin olmamasını sübut edən fosforit ilə BMT və üçkomponentli xammalın müqayisəli emal nəticələri göstərilmişdir. İstifadə olunan sulfat turşusunun təbiətinin emal prosesinin göstəricilərinə təsir rolu əsaslandırılmışdır.
Açar sözlər: BMT şlakı, qazma şlamı, zəif fosforit, emal, mürəkkəb mineral gübrə

СОВМЕСТНАЯ ПЕРЕРАБОТКА ШЛАКА ТБО И БУРОВОГО ШЛАМА С ОБЕДНЕННЫМ ФОСФОРИТОМ В МИНЕРАЛЬНЫЕ УДОБРЕНИЯ

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Аннотация: Рассмотрена возможность совместной утилизации шлака ТБО (твердые бытовые отходы) и бурового шлама переработкой в сложные минеральные удобрения с использованием обедненного фосфорита в качестве источника фосфора. Переработка трехкомпонентного сырья осуществлена 50-65% отработанной серной кислотой с процесса гидратации пропилена, при температуре 80°С. Учитывая присутствие в буровом шламе повышенного содержания полуторных оксидов, выявлена норма расхода серной кислоты, необходимой для получения минеральных удобрений с достаточным содержанием $P_2O_{5усв}$. Приведены сравнительные результаты переработки ТБО с фосфоритом и трехкомпонентного сырья, подтверждающие отсутствие вредного воздействия бурового шлама на процесс переработки. Обоснована роль природы используемой серной кислоты на показатели процесса переработки.
Ключевые слова: шлак ТБО, буровой шлам, обедненный фосфорит, переработка, сложные минеральные удобрения.