UDC 661.152.3; 349.6

RECYCLING SLAG FROM COMBUSTION OF MSW INTO COMPLEX MINERAL FERTILIZERS USING POOR PHOSPHORITE

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Received 19.03.2022
Accepted 19.05.2022

Abstract: *The article deals with the issue of secondary recycling municipal solid waste (MSW) into complex mineral fertilizers using domestic agricultural raw materials. Used in the recycling were slag from combustion of MSW and poor phosphorite. The nature of the decomposition of phosphorite 50-80% acid H_2SO_4 was studied at an acid consumption rate of 60-110%, of the consumption rate of acid H_2SO_4, which made it possible to identify optimal conditions used also for recycling binary raw materials. The increase in the content of assimilable P_2O_5 has been uncovered in the liquid phase during the recycling binary raw materials in comparison with the decomposition of phosphorite under similar conditions. The role of MSW of slag in increasing the content of assimilable P_2O_5 due to the improvement of conditions for the diffusion of molecules of the formed phosphoric acid to phosphorite particles is explained. The possibility of regulating the characteristics of the obtained complex mineral fertilizers by the ratio of the components of raw materials is shown.*

Keywords*: municipal solid waste, poor phosphorite, recycling, complex mineral fertilizers*
DOI: 10.32737/2221-8688-2022-2-138-144

Introduction

The problems of environmental safety associated with the formation of a significant amount of waste and harmful emissions from various industries, as well as the geometric increase in the accumulation of solid waste cause anxiety of the world community, encouraging researchers to create technologies for the waste recycling process instead of their disposal [1].

The presence of the modern complex for the recycling municipal solid waste (MSW) on the territory of the country, as well as available data from sources of information on the involvement of MSW in the recycling process to obtain complex fertilizers [2-5], have determined the choice of our research to study the possibility of secondary recycling MSW using agricultural raw materials of our country.

Analysis of the chemical composition of the slag obtained from combustion of MSW has revealed the content of such elements as Na, Mg, Si, S, K, Ca, Fe, as well as trace elements Ti and Mn in acceptable amounts to ensure the normal life of plants.

However, a small content of phosphorus (no more than 3%) makes it no possible to allow the use slag of MSW for the production of P-containing fertilizer.

As is known, the main source of phosphorus in the production of P-containing fertilizers are natural phosphorus-containing ores, primarily apatite, non-renewable natural resources from which most modern phosphorus-containing fertilizers are produced. Recently, according to scientists, fears have arisen that the world will soon consume its P-resources and face a catastrophic shortage of phosphorus [6, 7]. Therefore, the attention of researchers turns to the attraction of alternative raw materials for the production of P-containing fertilizer. In this regard, it was interesting to find a source of phosphorus from among the available natural resources of Azerbaijan, which can be used as the second component of mixed raw materials for recycling into complex mineral fertilizers.

Material and research methods

In considering the issues of industrial waste recycling, as well as attracting alternative raw materials instead of apatite for the obtaining complex mineral fertilizers, binary raw material has been used as components:

1. Slag of the Baku plant of the recycling MSW has the following chemical composition:

Na_2O - 5,82; Fe_2O_3 - 10,31; K_2O - 2,27; P_2O_5 - 2,12; CaO - 32,47 SiO_2 - 14,8; Al_2O_3 - 4,12; MgO - 2,42; SO_3 - 2,56; MnO - 0,21; TiO_2 - 0,83.

2. Poor phosphorite which belongs to lean-grade phosphorite, is characterized by low carbonate content, it is high-magnesian MgO content has the following chemical composition, wt.%: CaO – 19.54 P_2O_5 – 14.4; Na_2O – 1.2; K_2O -1.5; MgO – 3.8; Al_2O_3 - 2.6; TiO_2 - 1.01; F – 2.1; SO_3 – 0.15; CO_2 - 2.2; organic compounds – 1.41; H_2O - 1.74; other contents – 2.71.

For the decomposition of raw materials used sulfuric acid with a concentration of 50-80%,

It is known that the mechanical activation of phosphorite concentrates raises the specific surface and changes the physicochemical properties, as well as increases the solubility of phosphorus [8].

In this regard, before the start of the experiments, the raw materials have been subjected to mechanical activation in a ball mill in the attrition mode with a drum rotation frequency of 1200 cycle/m^{-1}, m/s^2 grinding steel balls with a diameter of 6–10 mm. The mass of balls is 0.2 - 0.3 kg when loading one drum with weight of the sample in 10 g, the processing time is 4 minutes.

The process of decomposition of raw materials has been carried out in a thermostatic reactor with a volume of 500 ml, in which the calculated amount of sulfuric acid was placed. A milled mixture of MSW slag and phosphorite has been added into the calculated ratios at a temperature of 80°C and stirring for 20 min. After 30-40 minutes the reactor has been placed in an oven, keeping at a temperature of 110 - 120°C for 60 minutes.

The pelletization of the obtained organic mineral fertilizers has been carried out by spheronization method on a plant consisting of an extruder with a matrix cell size of 3 mm, a drum granulator with a rotation speed of up to 40 cycle/m, and a drying cabinet [9].

The qualitative composition of the obtained products has been established by analytical methods to comply with the current state standards (COST). The GST-1 device has been used to determine the static strength of the granules.

Results of the research and their discussion

The recycling phosphates in order to obtain complex mineral fertilizers leads to the transfer of the sparingly soluble phosphorus contained in them into easily soluble compounds by exposing the feedstock to strong mineral acids.

Proceeding from the composition of the raw material which is a mixture of MSW slag and phosphorite, the results of recycling were primarily related to the issue of considering phosphorite as an active raw material, so the first series of experiments have been devoted to the sulfuric acid decomposition of poor phosphorite to thus identify the oriented conditions for the subsequent effective recycling the binary raw materials.

50 g of crushed phosphorite has been used in the experiments.

The influence of the concentration and consumption rate of H_2SO_4 on the parameters of the decomposition process of poor phosphorite has been studied. The results of the experiments are presented in the diagram of Fig. 1.

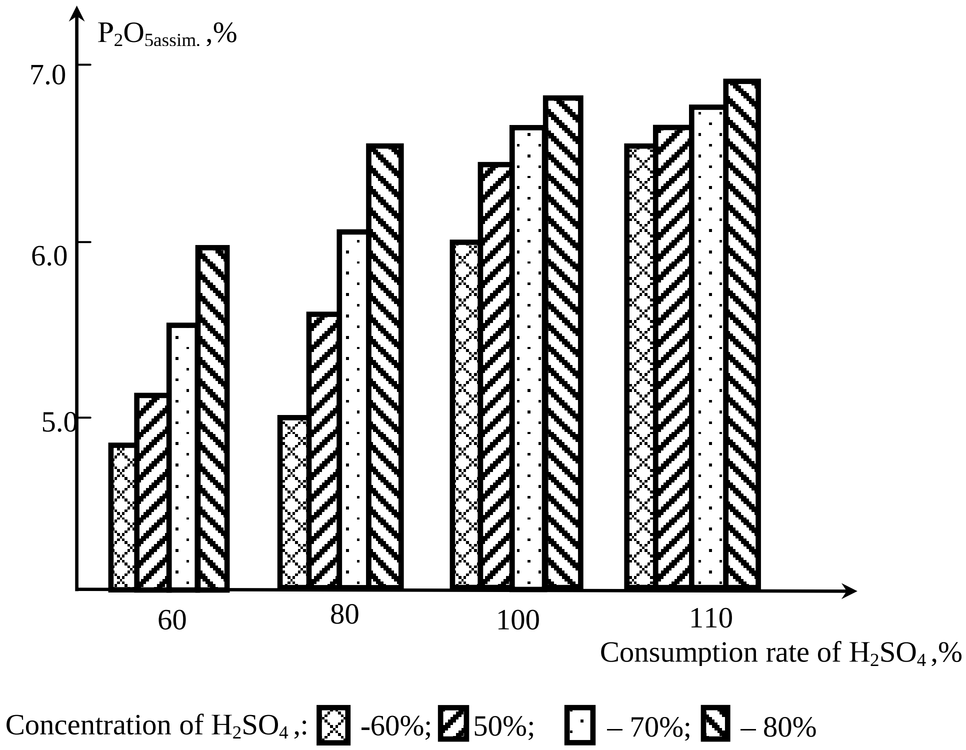

Fig. 1. Influence of concentration and consumption rates of H_2SO_4 on the content of assimilable P_2O_5 in the liquid phase in the recycling phosphorite

The diagram above clearly shows the nature of the decomposition process of phosphorite depending on the conditions, manifesting itself in the fact that the change in the content of P_2O_5 assim in the considered range of consumption rates is not identical. At consumption rates of sulfuric acid equal to 60% and 80%, the difference in the content of assim.P_2O_5 appears quite clearly at acid concentrations of 60%, 70% and 80%, while at concentration of 50%, the changes in the content of assim.P_2O_5 are barely visible.

With the transition to the consumption rate of acid that equals to 100%, the nature of the decomposition of phosphorite changed to reflect a sharp increase in the content of assim P_2O_5 for 50% acid, during maintaining the increase in the content of assim. P_2O_5 at average values of the concentrations of the considering interval and decrease in the jump in the increase in the content of assim.P_2O_5 for 80% acid concentration. With respect to the consumption rates of H_2SO_4 equal to 110%, a noticeable continuing increase can be noted only for 50% acid, while a slight increase in the change of the content of assim.P_2O_5 is noted for a more concentrated acid.

This course of events indicates the importance of both characteristics for acid, so the consumption rates should be chosen due to the concentration of H_2SO_4 involved in the process. In the analyzed range of H_2SO_4 concentrations, the acid concentration of 80% at a stoichiometric consumption rate can be taken as the optimal conditions for the recycling of the poor phosphorite.

The obtained results allowed to start studying the use of poor phosphorite in the process of complex recycling together with slag of MSW combustion. The mixture of 100 g of MSW slag and 50 g of phosphorite has been subjected to recycling process at a temperature of 80°C. The experiments have been carried out under conditions similar to the decomposition of phosphorite: the concentration of H_2SO_4 (in %) – 50 -80%, the consumption rate of H_2SO_4 equals to 60, 80, 100 and 110. The results of the recycling are shown in Table 1.

Table 1. The effect of concentration and consumption rate of H_2SO_4 on the content of assim.P_2O_5 in the products of phosphorite recycling together with MSW slag

№	Concentration of H_2SO_4,%	Rate of H_2SO_4,%	P_2O_5total. %	P_2O_5assim. %	$\frac{P_2O_{5_{assim}}}{P_2O_5} \cdot 100\%$
1	50	60	12.27	4.82	39.28
2	50	80	11.72	5.75	49.06
3	50	100	10.93	5.87	53.70
4	50	110	10.12	6.22	61.46
5	60	60	12.13	5.47	45.09
6	60	80	11.01	6.14	55.76
7	60	100	10.85	6.31	58.15
8	60	110	9.61	6.56	68.26
9	70	60	12.37	6.73	54.40
10	70	80	11.36	6.81	59.94
11	70	100	10.27	7.12	69.32
12	70	110	9.56	7.21	75.41
13	80	60	12.43	7.08	56.95
14	80	80	11.48	7.28	63.41
15	80	100	10.51	7.32	69.64
16	80	110	10.43	7.44	71.33

Analysis of the results shown in Table 1 has not revealed any changes depending of the decomposition grade of raw materials on the technological mode of the recycling process used when passing from phosphorite to the mixture of phosphorite with sludge of MSW. Nevertheless, the observed growth in the content of $P_2O_{5assim.}$ as a result of recycling binary raw materials in comparison with the results of recycling phosphorite under the same conditions should be noted. The dependence curves of the P_2O_5assim. content on the concentration of H_2SO_4 have been plotted and presented in Fig. 2 to compare the recycling processes of phosphorite and binary raw materials in using the acid consumption rate equals to 80 and 100% of the stoichiometric standard.

When comparing the dependence curves of the P_2O_5 assim. content during the recycling phosphorite and the co-recycling MSW slag with phosphorite under the same conditions (Fig. 1), the content of P_2O_5assim. rises in the case of recycling binary raw materials. The fact that the distance between the dependence curves of the P_2O_5assim. content for mixed raw materials at 80 and 100% consumption rates decreases relative to the curves characterizing the recycling phosphorite also draws attention. This factor can be explained by combination of two factors. First, mechanical pre-activation of raw materials leads to the weakening of the crystal lattice of both components, thereby contributing to the conversion of P_2O_5 into the water-soluble form [10]. The second factor, in our opinion, can be attributed to the consideration of the role of MSW slag in the recycling process of the considered raw materials due to the mechanism of the process.

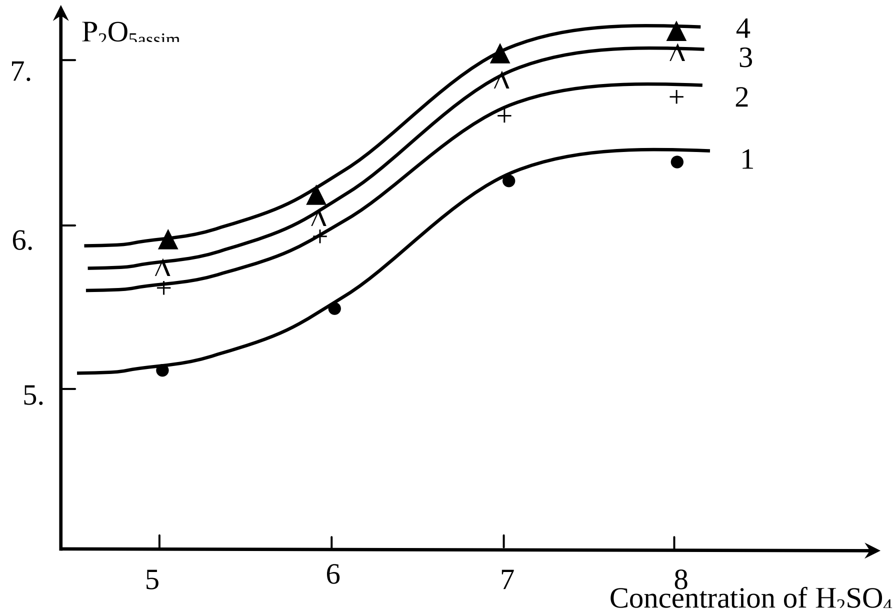

Fig. 2. Dependence of P_2O_5 assim content on concentration of H_2SO_4 at consumption rate of H_2SO_4: for phosphorite 80% - 1, 100% - 2; for phosphorite together with sludge of MSW 80% - 3, 100%- 4

In considering the recycling process of the mixture of MSW slag and phosphorite in the terms of obtaining complex mineral fertilizers, naturally, the preference is given to compositions with a high content of P_2O_5 assim which means that the choice of conditions for the recycling raw materials should ensure the highest possible yield of superphosphate according to the following reaction:

$$Ca_5F(PO_4)_3 + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4{\cdot}2H_2O + HF \quad (1)$$

$$Ca_3F(PO_{4)3} + nH_3PO_4 \rightarrow 5\ Ca(H_2PO_{4)2} + (n-7)H_3PO_4 + HF \quad (2)$$

As is seen from the reaction (1), the first stage of the decomposition process of phosphorite is complicated by the formation of $CaSO_4$. During the decomposition of phosphorite, calcium sulfate formed by reaction (1) is deposited only on phosphorite grains, whereas during the recycling binary raw materials, $CaSO_4$ may also deposit either on the surface of slag particles, or penetrate into the pores and cavities of the surface structure of the particles of MSW slag. In this case, the slag contributes to the decrease in the concentration of $CaSO_4$ molecules that can be deposited on phosphorite grains, taking part $CaSO_4$ “on itself”, setting better conditions for the diffusion of molecules of the formed phosphoric acid to phosphorite particles.

Since, in the case of acid decomposition of the feedstock, the physicochemical properties of the resulting fertilizers depend not only on the conditions of the recycling process, the influence of the qualitative and quantitative composition of the feedstock mixture has been studied. While keeping the amount stable of used MSW slag, the content of phosphorite in the mixed raw materials has been varied. The characteristics of the obtained samples of mineral phosphorus-containing granular fertilizer are given in Table 2.

Table 2. Characteristics of mineral fertilizers in variation of mass ratios of MSW slag: phosphorite

№	Mass ration of MSW slag: phosphorite	P_2O_5total.	P_2O_5 assim.	P_2O_5assim.	CaO	K_2O	Static stability H_2O, MPa	Yield, %	
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 increase in the content of phosphorite in the raw material leads to an improvement in the characteristics of the obtained fertilizer. An increase in the proportion of slag content in the raw material practically does not affect the parameters of the quantitative characteristics of nutrients, while a noticeable increase in the mechanical resistance of the fertilizer attracts attention, which is possibly due to the porous structure of the sintered particles of MSW slag. The obtained results show that it is possible to regulate the qualitative composition of the fertilizer by changing the ratio of the components of the raw material when solving the problem of its use taking into account the agrochemical standards of the need in each nutrient for certain types of agricultural cultures. The identified possibility of co-recycling process of MSW slag using poor phosphorite will simultaneously solve the problems of recycling MSW and provide the agricultural sector of the Republic with complex mineral fertilizers.

References

1. Maina S., Kachrimanidou V., Koutinas A. A roadmap towards a circular and sustainable bioeconomy through waste valorization. *Current Opinion in Green and Sustainable Chemistry*. 2017, vol. 8, pp. 18–23. https://doi.org/10.1016/j.cogsc.2017.07.007
2. Geraybeyly S.A., Ismailova R.A. Study of possibility of recycling slag of MSW combustion to complex mineral fertilizers. *Chemical safety*. 2021, vol. 5, no 2, pp. 138-147. https://dOI: 10.25514/CHS.2021.2.20008
3. Pat. RF 2663020 (published in 2018). The utilization method of municipal solid waste (MSW) using double-encapsulation technology, providing 100% environmentally friendly utilization of MSW.
4. Pat. RF 2241554 (published in 2004). The recycling methods of municipal solid wastes.
5. Pat. RF 2294319 (published in 2007). The recycling methods of municipal solid wastes.
6. Steven J. Van Kauwenbergh, Mike Stewart and Robert Mikkelsen. World reserves of phosphate rock-a dynamic and unfolding story. Beller Grops. 2013, vol 97, no. 3. pp.18-20.
7. Prem S. Bindraban, Christian O. Dimkpa, Renu Pandey. Exploring phosphorus fertilizers and fertilization strategies for improved human and environmental health. *Biology and Fertility of Soils*. 2020, vol. 56, pp. 299–317.
8. Tonsuaadu K., Kaljuvee T., Petkova V., Traksmaa R., Bender V., Kirsimae K. Impact of mechanical activation on physical and chemical properties of phosphorite concentrates *International journal of Mineral Processing*. 2011, vol. 100, pp. 104-109.

9. Skovorodnokov P.V. Features of the granulation process of organomineral fertilizers by the pelleting method / P.V.Skovorodnikov, M.V.Cherepanova. Bulleten of the Tomsk Polytechnic University, Tomsk: 2019, vol. 330, no 9, pp. 51-59.
10. Shatilo V.I., Minakovsky A.F. Acid-free activation of Vyatka-Kama phosphate meal in the presence of nitrogen- and potassium-containing salts. *Proceedings of the National Academy of Sciences of Belarus, Chemical series*, 2019, issue 55, no 4, pp. 464–471. https://doi.org/10.29235/1561-8331-2019-55-4-464-471

BƏRK MƏİŞƏT TULLANTILARININ (BMT) YANMA ŞLAKININ «KASIB» FOSFORİTLİ KOMPLEKS MİNERAL GÜBRƏLƏRİNƏ EMALI

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Xülasə: Məqalə yerli aqrofiliz xammalından istifadə etməklə bərk məişət tullantılarının (BMT) təkrar emalı əsasında kompleks mineral gübrələrin alınmasına həsr edilmişdir. Emal prosesində bərk məişət tullantılarının yanma şlakından və "kasıb" fosforitlərə aid olan Naxçıvan fosforitindən istifadə edilmişdir. Fosforitin 50-80%-li H_2SO_4 ilə turşunun 60-110%-li sərfiyyat normasında parçalanma xarakteri öyrənilərək optimal şərait müəyyən edilmişdir və o, həmçinin binar xammalın emalı üçün də istifadə olunmuşdur. Binar xammalın emalı zamanı maye fazada P_2O_5-in mənimsənilən miqdarının analoji şəraitdə fosforitin parçalanması zamanı olan miqdar ilə müqayisədə daha yüksək olması müəyyən olunmuşdur. P_2O_5-in mənimsənilən miqdarının artmasında bərk məişət tullantılarının şlakının rolu izah olunmuşdur ki, bu da əmələ gələn fosfat turşusunun molekullarının fosforit hissəciklərinə diffuziyası üçün şəraitin yaxşılaşması ilə əlaqədardır. Alınan kompleks mineral gübrələrin xüsusiyyətlərinin xammal komponentlərinin nisbəti əsasında tənzimlənməsinin mümkünlüyü göstərilmişdir.

Açar sözlər: bərk məişət tullantıları, "kasıb" fosforit, emal, kompleks mineral gübrələr.

ПЕРЕРАБОТКА ШЛАКА СЖИГАНИЯ ТБО В КОМПЛЕКСНЫЕ МИНЕРАЛЬНЫЕ УДОБРЕНИЯ С ПРИВЛЕЧЕНИЕМ БЕДНОГО ФОСФОРИТА

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Аннотация: Статья посвящена вопросу вторичной переработки твердых бытовых отходов (ТБО) с использованием местного агрорудного сырья в комплексные минеральные удобрения. В процессе переработки использован шлак сжигания ТБО и бедный фосфорит. Изучен характер разложения фосфорита 50 -80 % -ной H_2SO_4 при норме расхода кислоты 60–110%, позволивший определить оптимальные условия, использованные также для переработки бинарного сырья. Выявлено увеличение содержания P_2O_5 усв. в жидкой фазе при переработке бинарного сырья по сравнению с разложением фосфорита при аналогичных условиях. Объяснена роль шлака ТБО в повышении содержания P_2O_5 усв, связанная с улучшением условий для диффузии молекул образовавшейся фосфорной кислоты к частицам фосфорита. Показана возможность регулирования характеристики полученных комплексных минеральных удобрений соотношением компонентов сырья.
Ключевые слова: твердые бытовые отходы, бедный фосфорит, переработка, комплексные минеральные удобрения.