

Original Research

Ecologically Friendly, Slow-Release Granular Fertilizers with Phosphogypsum

**Kurmanbek Zhantasov^{1*}, Aitzhan Ziyat¹, Nursulu Sarypbekova²,
Kamilya Kirgizbayeva³, Gani Iztleuov⁴, Manap Zhantasov⁵,
Guzaliya Sagitova⁶, Ayganym Aryn¹**

¹Department of Chemical Technology of Inorganic Substances, M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

²Department of Chemistry and Chemical Technology, M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

³Department of Standardization, Certification and Metrology, L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

⁴Department of Ecology, M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

⁵Department of Oil and Gas Business, M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

⁶Department of Refining and Petrochemicals, M. Auezov South Kazakhstan University, Shymkent, Kazakhstan

Received: 15 July 2021

Accepted: 20 November 2021

Abstract

The paper provides information about phosphogypsum waste from various enterprises and how it can be used in the production of slow-release fertilizer mixtures. Such fertilizer mixes can potentially be used with different types of soil, including acidified soils. Experiments were conducted on phosphogypsum samples from the old and new dumpsites under the Taraz branch of Kazphosphate LLP. All representative samples underwent chemical, mineralogical, thermal gravimetric and differential thermal analyses, as well as Fourier-Transform Infrared (FTIR) spectroscopy and polarized optical microscopy (POM). No significant differences were found in the content of the samples. Phosphogypsum from the old dumpsite contained 87.93% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), 9.10% quartz (SiO_2), 17.55% calcium (Ca), 0.13% potassium (K), 0.35% phosphorus (P), and 0.80% phosphorus pentoxide (P_2O_5). Phosphogypsum from the new dumpsite contained 85.04% gypsum, 10.58% quartz (SiO_2), 19.42% calcium (Ca), 0.14% potassium (K), 0.30% phosphorus (P), and 0.69% phosphorus pentoxide (P_2O_5). The current paper also offers a technological scheme for making a slow-release fertilizer mixture with phosphogypsum.

Keywords: differential thermal analysis, granular fertilizer mixture, internal overburden, microscopy, mineral fertilizer, phosphogypsum, slow release, trace elements, vermiculite, X-ray diffraction

Introduction

Enterprises that operate on natural raw materials and generate solid, liquid and gaseous effluents per hour largely encompass the chemical, metallurgical, mining, heat and power enterprises, and more. In total, post-Soviet countries dump more than 80 billion tons of solid waste, including 1.6 billion tons of toxic and carcinogenic contaminants [1]. Such wastes include phosphorous sludge and electrothermophosphoric slag from the electrothermal production of yellow phosphorus [2-5], as well as *phosphogypsum*, a by-product from the production of phosphoric acid by treating apatite and phosphorites rocks via the chemical process [6-8].

According to experts, enterprises dump about 140 million tons of phosphogypsum, with an annual increase of 14 million tons. Reprocessing rate of phosphogypsum in Kazakhstan is approximately 2 to 4% per year, while in Germany, Belgium and Japan, it is almost 100% [1-4]. Advanced countries (such as the USA, Germany, and Japan) recycle the most phosphogypsum, later used to manufacture cement, paint, and varnishes, and in construction, chemical and agricultural sectors. Due to the climate change [9], the most promising areas for the application of phosphogypsum lie in the field of agriculture (e.g.) reclamation and fertilization. Soil processes can be intensified with a biotechnological approach involving the use of microorganisms to degrade phosphogypsum waste [10].

For 1 ton of extractive phosphoric acid (EPA) produced by reacting sulfuric acid with Karatau phosphorites, about 6 tons of phosphogypsum are generated, the specific surface area of which ranges from 0.15 to 0.24 mm², with a moisture content of approximately 40% [6].

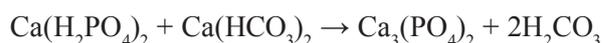
The primary phosphogypsum disposal method in Kazakhstan is landfill disposal, which has a negative impact on the environment. In landfills and dumpsites, phosphogypsum is exposed weathering processes, which cause the phosphogypsum to leach harmful substances into the air, soil, groundwater, and surface water. Besides environmental damage, improper phosphogypsum disposal leads to substantial economic losses (transport and storage costs account for up to 10% of the total cost of the phosphoric acid) [11, 12].

Analysis of the physicochemical properties of phosphogypsum shows that it has an angle of repose around 33 degrees and the bulk density about 1300 kg/m³. Phosphogypsum generally contains, next to calcium sulphate and water, varying amounts of different compounds, such as P₂O₅_{total} (0.74%), N₂O (0.38%), Al₂O₃ (0.087), F (0.081%), and Fe₂O₃ (0.093%), as well as insoluble residues (19.67%) and traces of MgO [3].

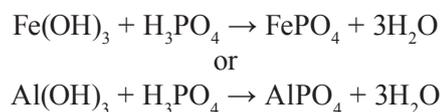
Some authors suggest using neutralized phosphogypsum [5-7], the effect of which lasts 2 years. Sometimes, farmers apply organic-mineral fertilizers, which proceeds the plowing of the land. The mineral

component of such fertilizers may be phosphogypsum (20-25 parts by weight), while the organic component can be represented by the lignin sludge (75-80 parts by weight). These fertilizer mixtures enhance the growth of crops and facilitate the uptake of heavy metals and rare earth metals by plants.

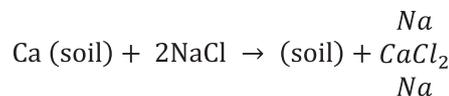
When conducting experimental studies on materials collected from dumpsites, one should keep in mind that under certain moisture and temperature conditions, a reaction can take place with inorganic salts and elements in the soil environment. One example is the reaction between monocalcium phosphate and hydrocarbonate, as shown below:



In an acidic environment, sparingly soluble salts of phosphoric acid can form, such as during the reaction with iron and aluminum hydroxides:

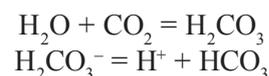


In addition to that, when absorbing any cation from the solution, soil releases an equivalent amount of another cation from the solid phase into that solution (law of conservation of mass). The reaction is as follows:

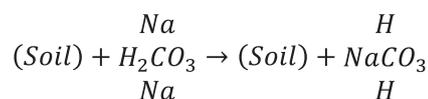


The adsorption strength of monovalent cations increases in the following order: Li⁺ < Na⁺ < NH₄⁺ < K⁺ < Rb⁺, and for divalent cations: Mg²⁺ < Ca²⁺ < Co²⁺. In case of trivalent cations, the adsorption strength increases in the following order: Al³⁺ < Fe³⁺ [13].

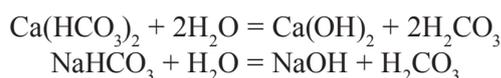
Active acidity is due to the presence of hydrogen ions in the soil solution. The carbon dioxide formed in the soil solution as a result of biological activity has an acidifying effect according to the following equation:



The presence of absorbing sodium ions in the soil solution can lead to the formation of sodium bicarbonate or sodium carbonate. The reaction is as follows:

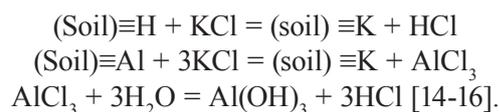


In aqueous solutions, carbonic acid salts undergo hydrolytic dissociation, as shown below:



Because NaOH is a strong base, $\text{Ca}(\text{OH})_2$ is a moderate base, and H_2CO_3 is a weak acid, when carbon dioxide dissolves, the reaction shifts towards an alkaline medium and makes the bases show their properties.

Exchangeable acidity is the amount of hydrogen and aluminum ions that are displaced by the neutral salt when a new complex is added:



The current paper offers a methodology, which can be useful in creating one-time solutions and temporary manufacturing instructions, justifying the fertilization process parameters, deciding on supplemental technical specifications, and collecting input data for project planning and technical-economic assessment of the production.

Experimental

All studies took place between 2020 and 2021 at the M. Auezov South Kazakhstan University (Shymkent, Kazakhstan). Phosphogypsum samples for this study were taken from the old (>17 years) and new (approximately 3 years) dumpsites that belong to the Taraz branch of Kazphosphate LLP (Mineral Fertilizers Plant). All representative samples underwent chemical and mineralogical (X-ray diffraction) examinations, thermogravimetry (TG), differential thermal analysis (DTA), Fourier-Transform Infrared (FTIR) spectroscopy, and polarized optical microscopy (POM). The results of these analyses were used to create a new formulation of a fertilizer mixture.

X-ray diffraction (XDM) data were collected by a D8 Advance diffractometer (Bruker) equipped with a Cu K α radiation source at 40 kV and 40 mA. From X-ray diffraction patterns, the interplanar distances (d values) were calculated. For this, the EVA software was used. Sample decoding and phase identification were carried out using the search-match software and the PDF-2 database.

The thermal analysis of samples weighted 0.250 g was performed on a simultaneous thermal analyzer STA 449 F3 Jupiter. Before testing, the furnace chamber was evacuated until the vacuum level reached 92% and then purged with an inert gas for 5 minutes. The samples were heated at 10°C/min in a highly purified argon atmosphere and then cooled down at 12°C/min. The total volume of incoming gas was kept within 100 ml/min. The results were processed using the NETZSCH Proteus software.

The Fourier-Transform Infrared (FTIR) spectroscopy analysis was performed on FT-IR spectrometer Avatar 370 in the spectral range 4000-300 cm⁻¹. For this, 2 mg of phosphogypsum powder was mixed with 200 mg of KBr and pressed to form a tablet.

The polarized optical microscopy (POM) was performed on a LEICA DM 2500 P microscope. For this, granular phosphogypsum samples from both the old and new dumpsites were placed in an immersion medium of known refractive index. Meanwhile, the artificial polished sections were prepared to determine the presence of ore minerals in the studied samples.

Mineral fertilizers were tested in accordance with ISO 5316-77, ISO 6598-85, ISO 7497-84, the EAEU technical regulation on the Requirements to Mineral Fertilizers (EAEU TR 039/2016), GOST 4212-76 (Reagents. Methods for preparing solutions for colorimetric and nephelometric analysis), ISO 5316-77, ISO 6598-85, ISO 7497-8, and ISO/IEC 17025-2019.

Future research should examine the effectiveness of the new fertilizer mix using agrochemical tests, including the field, growth, lysimetric and laboratory tests. While the field, growth, and lysimetric tests measure the effectiveness of fertilizers, crop nutrient removal, and losses, the laboratory tests refer to the chemical experiment.

Results

Phosphogypsum Samples from the Old Dumpsite

The phosphogypsum samples from the old dumpsite were placed in an immersion medium and investigated under a microscope. The results show that these samples had 85 to 90% of gypsum. It is a monoclinic mineral with indices of refraction $N_g = 1.529$ and $N_p = 1.520$, optically positive ($2V \sim 58^\circ$). In addition to that, XDM revealed small quantities of quartz and bassanite-like (hemihydrate) phase. The polished section contains copper-bearing minerals: metallic copper, chalcocite, bornite, and pyrite.

Phosphogypsum Samples from the New Dumpsite

Visually, the light gray powdered sample from the new dumpsite is similar to that from the old dumpsite. Under the microscope, both samples turned out to be identical in terms of composition and XDM data. The ore part of the sample was also similar to that from the old dumpsite. The XDM findings are depicted in Tables 1 and 2.

The comparison of data in Tables 1 and 2, reveals 1.5-3% differences in relation to all components. This can be explained by the grinding, which took place in samples from the old dumpsite due to over 40 years of storage.

The thermal analysis of phosphogypsum samples from the old and new dumpsites are depicted in Figs 1 and 2,

Table 1. The mineralogical composition of phosphogypsum from the new dumpsite.

Pattern #	Compound Name	Formula	S-Q
PDF 36-0432	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	85.04%
PDF 79-1906	Quartz	SiO_2	10.58%
PDF 33-0310	Bassanite, syn	$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	4.38%

Table 2. The mineralogical composition of phosphogypsum from the old dumpsite.

Pattern #	Compound Name	Formula	S-Q
PDF 36-0432	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	87.93%
PDF 79-1906	Quartz	SiO_2	9.10%
PDF 00-047-0964	Bassanite, syn	$\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$	2.97%

respectively. The DTA curve in Fig. 2 (old-dumpsite specimen) clearly exhibits the combination of endothermic and exothermic effects on the DTA curve can be attributed to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The first endothermic effect located at 182.9°C indicates dehydration of gypsum to hemihydrate, whereas the

second endothermic effect at 214.5°C corresponds to the complete dehydration of the phosphogypsum. The exothermic effect at 427.7°C can be explained by lattice rearrangement and transformation of di- and hemihydrate gypsum to insoluble anhydrite. The weak minimum at 218.2°C on the DTG curve could indicate dehydration of the hydrated silica gel ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$). In addition to that, the exothermic effect could be a sign of hydrated silica gel crystallization.

The DTA curve in Fig. 1 (new-dumpsite specimen) also shows the combination of endothermic and exothermic effects on the DTA curve can be attributed to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The first endothermic effect located at 186.4°C is due to dehydration to hemihydrate, whereas the second endothermic effect at 216°C is due to complete dehydration. The exothermic effect at 458.2°C can be explained by lattice rearrangement and transformation of dihydrate gypsum to insoluble anhydrite.

The following findings may be due to the presence of silicic acid ($n\text{SiO}_2 \cdot m\text{H}_2\text{O}$): a DTA minimum located at 143°C and a weak exothermic effect on the dDTA curve with a peak at 196°C. First, dehydration took place at 143°C with the formation of silica gel, which then crystallized at 196°C. A weak DTG maximum at 201.7°C may be due to oxidation of the ferrous iron. A DTG minimum at 207.7°C and a weak exothermic effect on the dDTA curve with a peak at 1009.1°C may

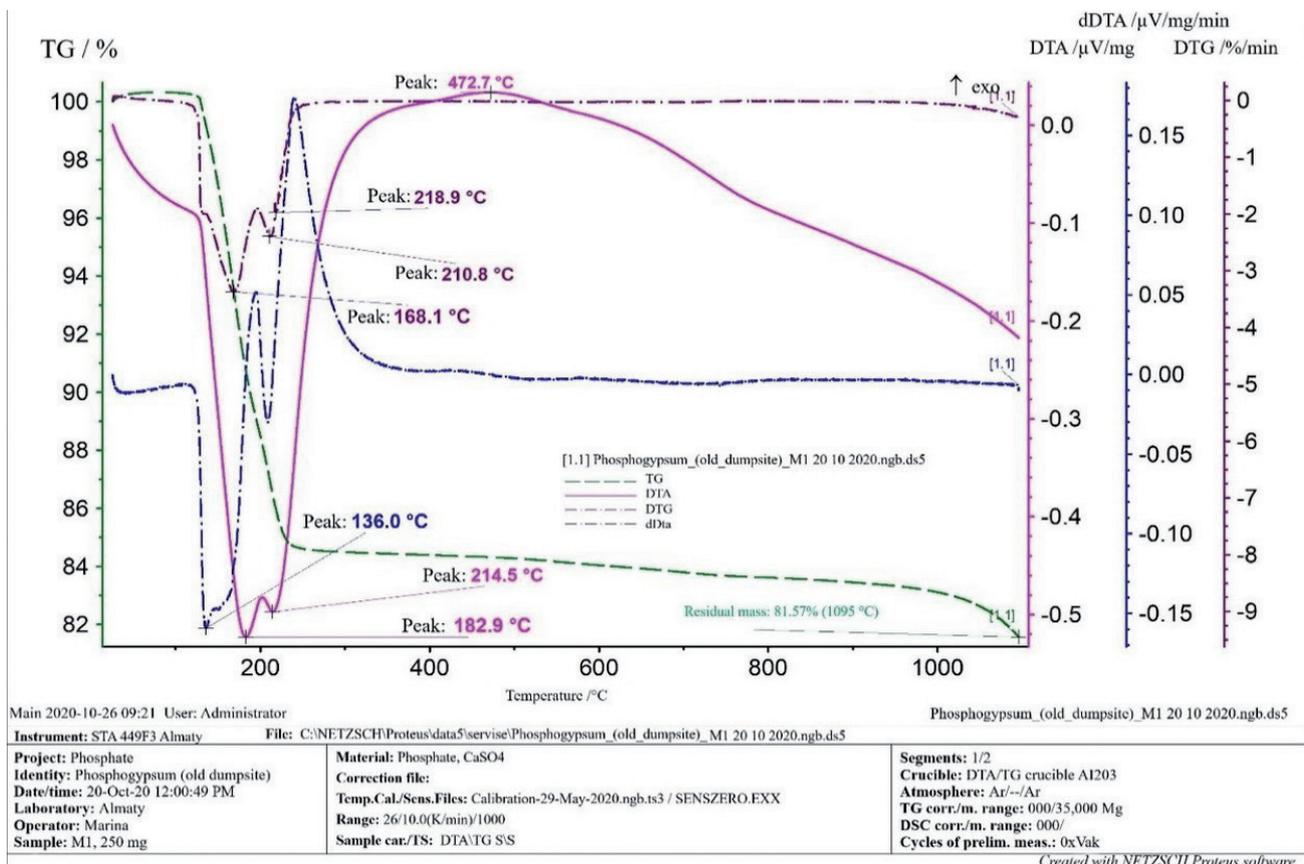


Fig. 1. The thermal analysis of phosphogypsum from the old dumpsite.

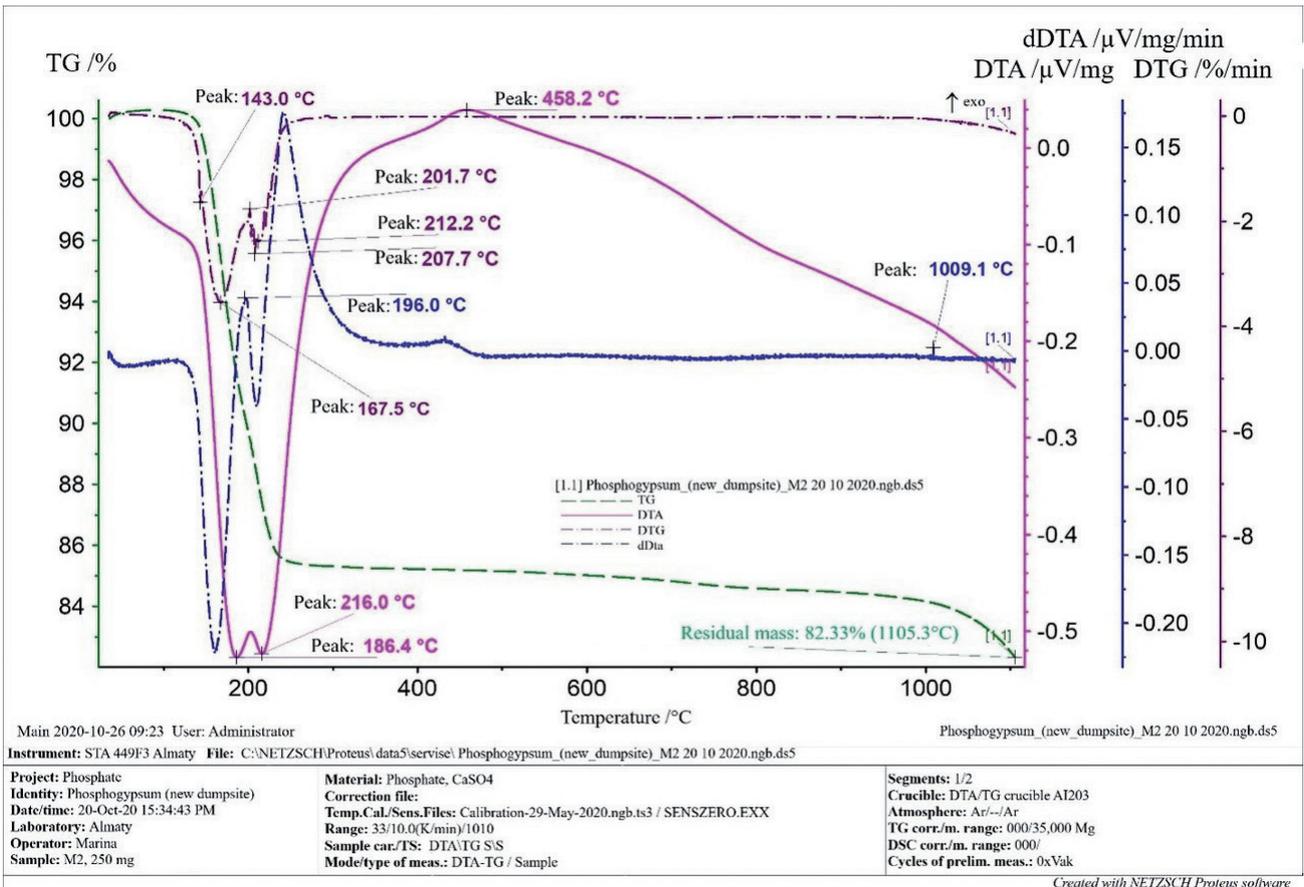


Fig. 2. The thermal analysis of phosphogypsum samples from the new dumpsite.

be associated with the presence of a small amount of aluminum phosphate ($Al_3[PO_4](OH)_6 \cdot 6H_2O$). In this case, dehydration may be seen at 207.7°C with the formation of an amorphous substance, the presence of which leads to the amorphous phase crystallization at 1009.1°C.

The FTIR analysis of phosphogypsum samples from the old dumpsite (Fig. 3) indicated the presence of gypsum ($CaSO_4 \cdot 2H_2O$) and quartz (SiO_2). The well-defined peaks of gypsum can be seen at 3548, 3496, 3404, 3244, 1686, 1621, 1145, 1115, 1004, 669, and 602 cm^{-1} .

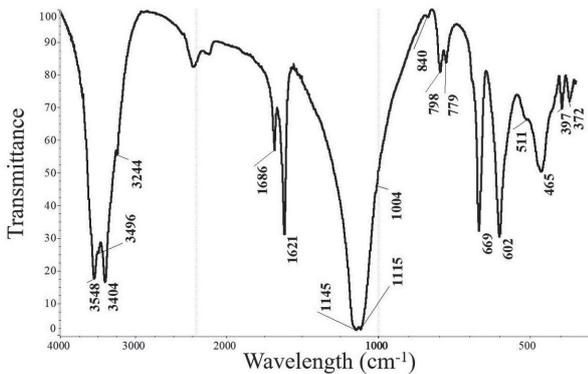


Fig. 3. FTIR spectroscopy results for phosphogypsum from the old dumpsite.

602 cm^{-1} . The peaks of quartz are located at 798, 779, 511, 465, 397, and 372 cm^{-1} .

The FTIR spectrum of phosphogypsum from the new dumpsite (Fig. 4) shows insignificant deviations in relation to peaks depicted in Fig. 3, but the composition of both samples is similar: gypsum ($CaSO_4 \cdot 2H_2O$) and quartz (SiO_2). This time, the well-defined peaks of gypsum can be seen at 3554, 3494, 3409, 3244, 1684, 1621, 1148, 1116, 1005, 669, and 602 cm^{-1} . The peaks of quartz are located at 798, 779, 511, 469, 398, and 374 cm^{-1} .

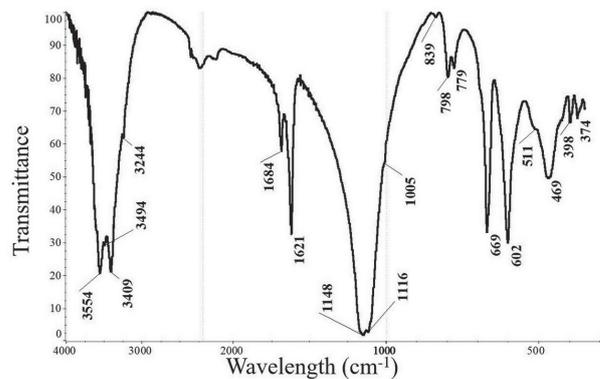


Fig. 4. FTIR spectroscopy results for phosphogypsum from the new dumpsite.

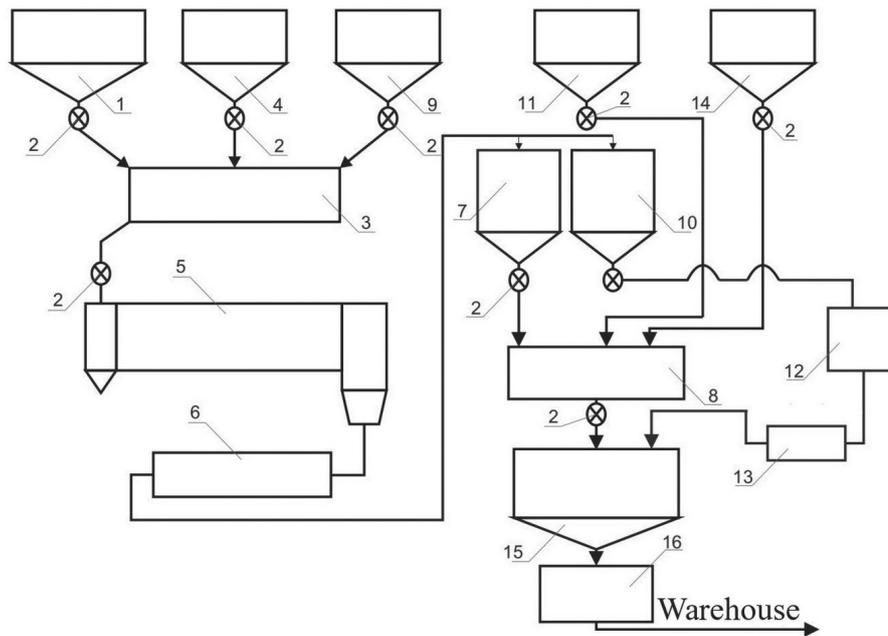


Fig. 5. Manufacturing process of phosphogypsum-containing fertilizer mixtures: 1, 4, 7, 9, 10, 11, 12, 14, and 15 – bins; 2 – proportioning feeder; 3 and 13 – mixers; 5 – drum furnace; 6 – cooler; 8 – grinding mill; 16 – bagging machine.

Discussion

Due to moderate solubility of gypsum in water (2.5 g/l), some researchers assigned it a modest role in displacing exchangeable sodium [17]. However, when interacting with the alkali soil, it becomes more soluble in water due to the binding of calcium ions, and the increase is substantial. In dynamic conditions when a solution moves through the illuvial zone of the alkali soil due to capillary action, the water solubility of gypsum is somewhat similar to that of phosphogypsum. In stationary conditions, which correspond to the interaction of Na/Ca and Na with clays and loams, the water solubility of gypsum is 1.2-5.7 times higher. Theoretically, the solubility index of gypsum increases if the following conditions are met: increased constants

of sodium-calcium exchange, decreased solid-to-liquid ratio, and increased exchange capacity. An increase in the solubility of gypsum in a liquid phase during its interaction with clays is largely associated with a shift in dissolution equilibrium towards new portions. It is apparently due to the absorption of one of the products of the reaction with calcium ions by the absorption complex, as well as ion pair formation.

Technology of Phosphogypsum-Containing Fertilizer Production

Based on the results of the study above, a production line was designed to produce granular fertilizer mixes with phosphogypsum that would improve the properties of soil. A granular fertilizer flow chart

Table 3. Material balance for complex fertilizer manufacturing process.

Input quantity			Output quantity		
Raw material	kg	%	Output	kg	%
Phosphorite fines from phosphorus production and/or thermal phosphorite treatment	670	67.0	Complex-mixed, slow-release mineral fertilizer mixture	990	99.0
Vermiculite	115	11.5			
Internal overburden of brown coal	100	10.0			
Phosphogypsum	65	6.5			
Brown coal	50	5.0			
Total	1000	100	Mechanical losses	10	1.0
Total			Total	1000	100

captured in Fig. 5 gives details on the production process of granular fertilizer mixtures with phosphogypsum.

To reduce environmental load, as well as fuel and energy costs associated with phosphorite processing, manufacturers may use electrostatic precipitators to trap calcination dust generated at 950-1100°C and phosphorite fines from phosphorus production caught in a cyclone during agglomeration. Another alternative is calcined vermiculite, which manufacturers may get from other providers on a contractual basis. To improve the quality of spread of phosphogypsum-containing fertilizer mixtures, manufacturers should use soap stock from alkaline refining as a binder [18].

Based on the material balance calculations, a report was made (Table 3), which showcases the quantities of all materials that will enter and leave the proposed production line.

Under the proposed production model, the manufacturing process of phosphogypsum-containing fertilizer mixtures has four steps:

(1) **Phosphorite processing.** A proportioning feeder 2 supplies a pre-set quantity of phosphorite fines (size fraction, 0-5 mm) from a bin 1 to a mixer 3, where they are mixed together with tared fines of brown coal, fed from another bin 4. After mixing, the fines enter a rotary drum furnace 5, in which they undergo drying at a temperature of 150-350°C and thermal treatment at 850-950°C. A calcined product then enters a cooler 6 in which it cools down to 40°C before traveling to a collection bin 7 mounted in front of a grinding mill 8.

(2) **Vermiculite processing.** Natural vermiculite from a bin 9 and small fines of brown coal (size fraction, 0-5 mm) from a bin 4 are mixed together in a mixer 3. The burden mixture is then fed to a rotary drum furnace 5 for drying and calcination at temperatures of up to 950°C, and then to a cooler 6, so that it cools down to 40°C. A cooled product is transported to a separate bin 10.

(3) **Grinding and mixing of individually prepared components.** The calcined phosphorite from a collection bin 7 and internal overburden fines (size fraction, 0-5 mm) from a bin 11 are sent to a centrifugal-elliptical ball mill for grinding until a fraction of less than 0.1 mm. After grinding, the product enters an intermediate bin 12 where it waits to be sent to a mixer 13. The phosphorite-based granules are mixed with phosphogypsum from a bin 14 and calcined vermiculite from a bin 10. Once mixed, the product is sent to a final bin 15 where it is kept before transportation to a bagging machine 16.

(4) **Bagging.** The fertilizer mixture is bagged and sent to a warehouse for storage.

Conclusions

This study examined phosphogypsum specimens from the old and new dumpsites. No significant differences were found in the chemical and

mineralogical composition between them. According to the results of the XDM mineralogical analysis, both phosphogypsum samples contain gypsum (87.93% vs 85.04%, respectively), quartz (9.10% vs 10.58%, respectively); basanite (2.97% vs 4.38%, respectively). The TG/DTA analysis indicated the presence of insignificant temperature peaks. This finding coincides with the results of the FTIR spectroscopy. The current paper also offers a technological scheme for making a slow-release fertilizer mixture containing a phosphate substance, vermiculite as a water-retaining component, internal overburden with trace elements, and phosphogypsum as a neutralizer to reduce soil acidity and salinity.

Conflict of Interest

The authors declare no conflict of interest.

References

1. ILYIN A.P. Modern Problems of Inorganic Chemical Engineering; Ivanovo State University of Chemical Technology: Ivanovo, **2011**.
2. ZHANTASOV K.T., SHAPALOV S.S., BERZHANOVA D.S., KADIRBAYEVA A.A., ZHANTASOVA D.M., ALTEEV T., MIRZAEV A.A. Production of Glyphosate Using Waste From Phosphorus Production and Organic Compounds. M. Auezov South Kazakhstan State University: Shymkent, **2018**.
3. ERSHOV V.A. The problem of comprehensive Karatau phosphorite processing. Fosfornaya promyshlennost [Phosphorus production], **3** (8), 16, **1972**.
4. ZHANTASOV K.T., AIBALAEVA K.D., FRANGULIDI L.K., BARLYBAEV M.R., BERZHANOV D.S., YURCHENKO B.N., ZHANTASOV M.K. Technological equipment for yellow phosphorus production (textbook). International Journal of Applied and Fundamental Research, **3** (2), 199, **2014**.
5. VANDEN NEST T., RUYSSCHAERT G., VANDECASTEELE B., COUGNON M., MERCKX R., REHEUL D. P availability and P leaching after reducing the mineral P fertilization and the use of digestate products as new organic fertilizers in a 4-year field trial with high P status. Agriculture, Ecosystems & Environment, **202**, 56, **2015**.
6. CHAUDHARY S., DHERI G.S., BRAR B.S. Long-term effects of NPK fertilizers and organic manures on carbon stabilization and management index under rice-wheat cropping system. Soil and Tillage Research, **166**, 59, **2017**.
7. ZHANTASOV K.T., ISKANDIROV M.Z., AIBALAEVA K.D., ALTEEV T.A., NOVIK D.M., ZHANTASOVA, D.M. Modern Technologies for Processing Mineral Raw Materials: A Textbook; M. Auezov South Kazakhstan State University: Shymkent, **2015**.
8. CHERNYSH Y., YAKHNENKO O., CHUBUR V., ROUBÍK H. Phosphogypsum recycling: A review of environmental issues, current trends, and prospects. Applied Sciences, **11** (4), 1575, **2021**.
9. TRIFI H., NAJJARI A., ACHOUAK W., BARAKAT M., GHEDIRA K., MRAD F., SAIDI M., SGHAIER H.

- Metataxonomics of Tunisian phosphogypsum based on five bioinformatics pipelines: Insights for bioremediation. *Genomics*, **112** (1), 981, **2020**.
10. BELYUCHENKO I.S. RF Patent No. 2423812. Method to Improve the Agrophysical Properties of Soil (A01B7 9/02, 2011), **2011**.
 11. IVANITSKIY V.V., KLASSEN P.V., NOVIKOV A.A., STONIS S.N., EVENCHIK S.D., YAKOVLEVA M.E. Phosphogypsum and Its Use; Khimiya: Moscow, **1990**.
 12. YANG R., SU Y., WANG T., YANG Q. Effect of chemical and organic fertilization on soil carbon and nitrogen accumulation in a newly cultivated farmland. *Journal of Integrative Agriculture*, **15** (3), 658, **2016**.
 13. TANIRBERGENOV S., SAPAROV A., SULEYMENOV B. Methods of increasing productivity and environmental sustainability of cotton on irrigated light gray soils of the South Kazakhstan region. In International Congress on "Soil Science in International Year of Soils"; Sochi, Russia, 405, **2015**.
 14. FARAHANI S.S., RAJABIPOUR A., KEYHANI A., SHARIFI M. Energy use and economic analysis of NPK-15: 8: 15 fertilizer granulation process in Iran. *Journal of the Saudi Society of Agricultural Sciences*, **16** (3), 265, **2017**.
 15. CAMERON K.C., DI H.J., MOIR J.L. Nitrogen losses from the soil/plant system: a review. *Annals of Applied Biology*, **162** (2), 145, **2013**.
 16. BAZHIROVA K.N. Development of an Energy-Saving Technology for the Production of Mechanically Activated, Slow-Release Mineral Fertilizers; Shymkent, **2015**.
 17. ZHANTASOV K.T., BAZHIROV N. S., BISHIMBAEV V.K., BAZHIROV T.S., ZHANTASOV M.K., BAZHIROVA K.N., OMAROV B.T., NALIBAEV M.I. Patent RK No. 31226. Method to Grind Phosphorus-Containing Materials. Decision on Patent Under Application No. 2013/1487.1, dated July **28**, 2014, **2014**.