

UDC 631.86:66.094.3:628.4.047

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PRODUCTION TECHNOLOGY FOR ORGANO-MINERAL FERTILIZERS FROM CHEMICAL INDUSTRY WASTE

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This study investigates the potential of using waste from organic synthesis and soda production to produce organo-mineral compositions for agrochemical applications. Thermogravimetric analysis of solid organic waste, X-ray fluorescence determination of its elemental composition, and chemical analysis of the clarified liquid from soda production were conducted. The multi-stage nature of the thermal transformations of the organic waste was identified, with an overall mass loss of about 42 wt.%, due to dehydration, thermal decomposition of the organic material, and partial decarbonization of the mineral phase. The results show that the waste contains significant amounts of calcium, magnesium, iron, and phosphorus compounds, which highlights its potential as a raw material for agrochemical production. Several formulations of organo-mineral fertilizers were developed from the organic concentrate by adding urea and potassium salt to adjust the nutrient ratio. Their physicochemical and agrochemical characteristics were studied, and a basic technological scheme for producing the granulated product was proposed. Field trials on corn and pumpkin crops showed the fertilizer's positive effects on plant growth and crop yield. The results show that incorporating clarified soda production liquid into these mixtures significantly raises soil salinity and alkalinity, thereby restricting their use. The modified composition, which does not use this liquid, exhibits more stable agrochemical properties and a lower risk of secondary salinization. The proposed technology enables the production of organo-mineral fertilizers with a controlled composition and can be used to utilize industrial waste within the circular economy framework.

Keywords: organo-mineral fertilizers, alternative raw materials, modification, agrochemical indicators, waste recovery.

DOI: 10.32434/0321-4095-2026-167-4-96-106

Introduction

A large portion of chemical production facilities in Ukraine and the CIS countries were built between the 1950s and 1980s and are now characterized by outdated technologies that underutilize raw materials. The imperfections in equipment and catalytic systems lead to less-selective target reactions and byproduct

formation. For example, in producing caprolactam and adipic acid, the utilization rate of carbon-containing raw materials often does not exceed 85–90%, with the remaining materials forming a mix of organic byproducts and waste. Similarly, in soda ash production via the Solvay process, the limestone utilization rate is only about 70–75%, leading to the

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accumulation of excess CaCl_2 and other mineral salts in the liquid waste. The long-term operation of such enterprises has led to the formation of millions of tons of various mixtures at sludge storage facilities [1], becoming a problem for the environment and an unused resource [2].

Modern concepts of the circular economy aim to maximize the incorporation of waste into economic cycles by transforming it into valuable products [3–6]. The use of industrial waste for the production of agrochemical products may be particularly promising, as many types of chemical waste contain valuable macro- and micronutrients, including in bioavailable forms.

Within the Siverskodonetsk-Lysychansk urban area, numerous sludge, tailings, and settling ponds for liquid industrial waste of varying sizes remain. These ponds are in very poor technical condition and pose environmental and man-made hazards. Hostilities in eastern Ukraine have resulted in substantial damage to the soil cover and a deterioration of forest ecosystems. Explosions of ammunition, the movement of heavy equipment, fires, and the destruction of industrial facilities have led to soil compaction, the destruction of the humus layer, contamination with heavy metals and toxic substances, and disruptions to natural water regimes [7]. Forests that had worked to protect against erosion and preserve biodiversity were devastated, aggravating the processes of wind and water erosion. Reviving the fertility of these soils is crucial for the region's environmental health, agricultural resuscitation and natural equilibrium. Healthy soils underpin ecosystem resilience, water purification, and carbon sequestration, so they are the bedrock from which a reconstructed area should emerge.

Given the challenges of energy instability, war risks, and rising natural gas prices, there is an urgent need to develop technologies to produce alternative, high-quality, and affordable fertilizers. This should avoid using methane as the primary feedstock for ammonia and nitric acid synthesis, crucial components in the production of ammonium nitrate and urea. The development of new technological solutions, especially those based on waste utilization, will lower fertilizer costs, reduce the carbon footprint, improve the environmental sustainability of agriculture and forestry, and provide a reliable source of nutrients independent of imported energy sources.

The goal of this work is to develop a technology for the comprehensive recovery and use of waste from two types of sludge storage facilities: those from the organic synthesis operations of PJSC «Severodonetsk Azot» (production of caprolactam, adipic acid, crotonaldehyde, methanol, acetic acid, vinyl acetate, etc.) and the soda production of OJSC «Lysychansk

Soda» to produce organo-mineral compositions with various physicochemical and agrochemical properties.

Experimental

Solid organic waste was collected from three depths and six locations in the sludge storage basin of organic synthesis plants, and the samples were averaged. The composite sample consists of a heterogeneous mixture of organic substances (C_4 – C_8 dicarboxylic acids and their salts, macro- and microelements in chelated form) and inorganic components (spent catalysts, etc.). The moisture content of the samples ranges from 35–70% wt., depending on the layer depth and storage duration in the sludge storage tank.

The clarified liquid was sampled from the soda production sludge tank using the Solvay method after natural settling (map No. 4). Technical urea (state standard DSTU 7312:2013), potassium chloride (state standard GOST 4568-95), and water were used as additional components.

Thermogravimetric analysis of the organic waste was performed on a Q-1500 D derivatograph of the F. Paulik, J. Paulik, L. Erdey system, with a sensitivity of 500 μV for the TG, DTG, and DTA galvanometers in the temperature range of 20–900°C at a heating rate of 10°C/min in an air atmosphere. The reference sample was $\gamma\text{-Al}_2\text{O}_3$. The sample weight was 100 ± 5 mg.

The elemental composition of the organic waste was determined by EDX 720 spectrometer (Shimadzu, Japan) using X-ray fluorescence (XRF) analysis. The analysis was performed in helium atmosphere at 15 kV and 50 kV, with a measurement duration of 100 seconds for each mode.

Chemical analysis of clarified liquid has been carried out according to standardized methods: density was measured using a hydrometer by DSTU ISO 758:2007, pH was determined potentiometrically (DSTU ISO 10523:2012), chloride content was measured via argentometric titration, sulfate content was determined gravimetrically, and carbonate content was measured by the titrimetric method.

The agrochemical parameters of the products were determined in accordance with the following national standards: total nitrogen content according to DSTU 7911:2015; phosphorus according to DSTU 4114-2002; potassium according to DSTU 7949:2015; and pH according to DSTU ISO 10390:2007.

Results and discussion

Figure 1 shows the thermogravimetric (TG), differential TG, and differential thermal analysis (DTA) of the solid organic waste in question, which suggests that its thermal transitions are of a multi-step nature, consisting of consecutive physical and

chemical processes. The mass loss after the heating up to 850°C is found to be around 42% and this value relates to the total amount of the organic phase, crystallization water and structurally bound water as well as through partial decarbonisation process of the mineral phase.

Within the 50–200°C range, the dehydration process is only physical, including desorption of adsorbed water and removing physically bound water. At this stage, mass loss is between 11–12%. DTG profile displays moderate rates of mass loss with no remarkable exo- or endo-effects, evidencing the absence of major chemical changes in organic matrix. The peak level of moisture elimination occurs at 110–130°C ($DTG \approx -0.2 \dots -0.3\%/^{\circ}\text{C}$), when there is a ratio between the rates of heat and mass transfer and stability of organic basis parts which corresponds to optimal conditions for drying process taking place.

Intensive chemical decomposition begins at temperatures above 180–200°C. Within the 200–400°C range, the main stage of thermolysis of the organic matrix occurs, with a mass loss of 22–24%. The peak decomposition rate is observed at 210–240°C (maximum DTG around 220°C) and is accompanied by a pronounced endothermic effect on the DTA curve. In this range, decarboxylation of dicarboxylic acids, thermal decomposition of their salts, and breaking of σ -bonds between C–C and C–O occur,

leading to the formation of volatile products (CO_2 , CO, and low-molecular-weight organic compounds). The endothermic nature of the process corresponds to the predominance of thermal decomposition reactions over oxidative ones.

A decrease in mass loss ($\sim 3\text{--}4\%$) in the range of 400–600°C is found by correlating with an oxidative decomposition of condensed carbon chains and a transformation of metal-containing organic compounds into stable forms of oxides. This is an exothermic process because oxidation reactions contribute.

At 600–850°C, solid-state processes presumably dominate the transformations of the mineral fraction: partial decarbonation of carbonates and structural rearrangements of amorphous hydroxide-carbonate systems to thermodynamically stable oxide phases comprising CaO and MgO. These processes are associated with a peak of exothermic reaction at $\sim 705^{\circ}\text{C}$ and a further loss in mass meandering 3–4%.

Thus, a clear temperature distinction has been established between the zone of physical dehydration (up to 180–200°C) and the zone of chemical degradation of the organic matrix ($>200^{\circ}\text{C}$). This served as the basis for selecting the temperature regime for the heat treatment stages. The operating range of 110–130°C for evaporation and drying of the concentrate ensures intensive moisture removal while fully preserving the organic component, remaining

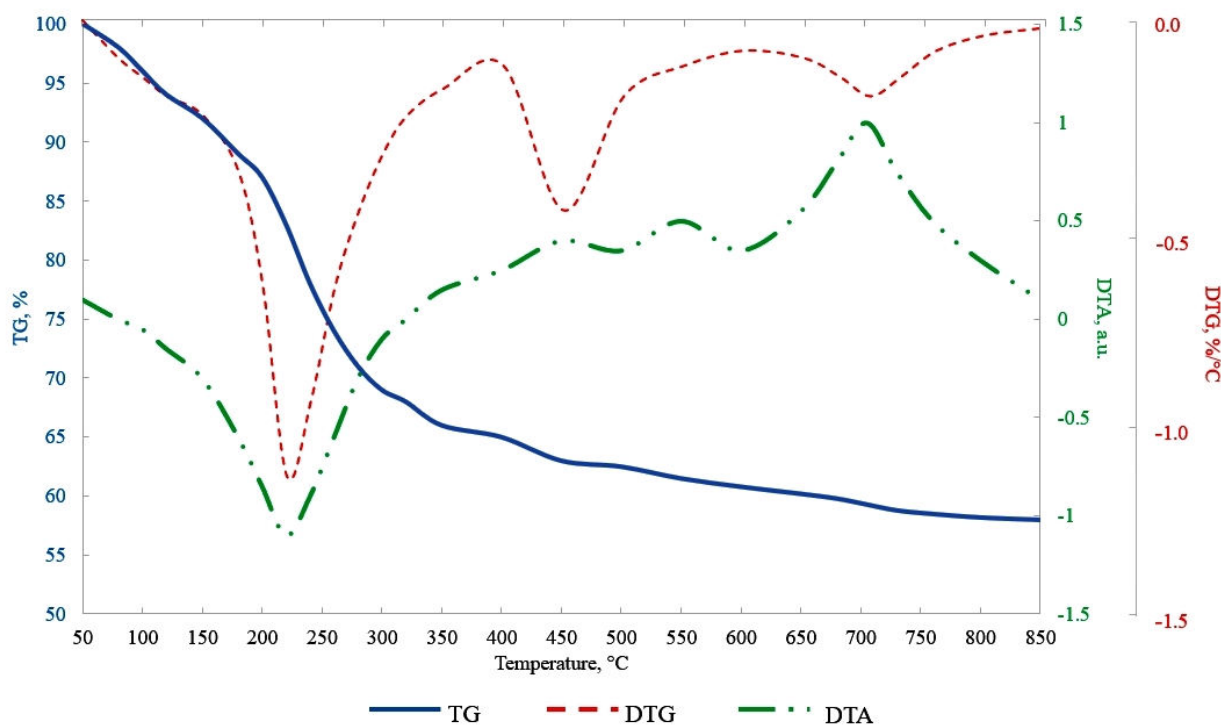


Fig. 1. Thermograms (TG, DTG, DTA) of solid organic waste

50–70°C below the temperature at which thermal destruction begins.

XRF analysis of the inorganic fraction of this waste (Table 1) revealed high levels of magnesium and calcium oxides, which are attributed to the use of lime and dolomite ($\text{CaMg}(\text{CO}_3)_2$) to neutralize acidic effluents and adjust the pH of process solutions at organic synthesis plants. The presence of phosphorus and iron oxides makes the waste a valuable raw material for the production of products with agrochemical properties. The calcium-to-magnesium ratio in the oxides, approximately 1.2:1, will ensure balanced plant nutrition with these elements.

The clarified liquid is characterized by high mineralization (271 g/L) and contains soluble salts of calcium, magnesium, and sodium, as well as sulfates and chlorides (Table 2). The presence of ammonium ions (0.5 g/L) makes it possible to use this liquid as a minor source of nitrogen in fertilizers. However, the high chloride and sulfate levels may result in excessive salinity in the final product. The pH of the liquid indicates a moderately alkaline environment.

Thus, the concept of combining solid organic waste with clarified liquid from soda production (in a mass ratio of 1:(0.04–0.7) on a dry matter basis) will allow for the utilization of the advantages of both components: the solid waste contains macro- and micronutrients, some of which are present in the form of organic salts of dicarboxylic acids, which enhances their bioavailability to plants, while the clarified liquid contains soluble salts and ammonium nitrogen. During evaporation of the mixture, crystals of an organo-mineral product form; subsequent granulation produces granules of a specified size, ensuring the convenience of mechanized application and reducing dust formation.

The M.F. Sydorenko Melitopol Horticultural

Research Station of the Institute of Horticulture, National Academy of Agrarian Sciences (2021) conducted a comprehensive analysis of the fertilizer (Product No. 1), produced at the pilot-scale facility of Svit Budivel LLC (Siverskodonetsk, Ukraine). The test report (Table 3) shows that the tested product is a high-ash, granulated organo-mineral fertilizer with low moisture content (7.9–10.0%) and a high organic matter content (45.1–46.3%). It is characterized by a highly alkaline reaction of the medium due to elevated hydrocarbonate levels, a high salt concentration (5.62–7.75%), and the presence of toxic alkaline salts, especially sodium and magnesium carbonates. The water-soluble forms of nitrogen, phosphorus, and potassium are low (0.08–0.61%), but total nitrogen and phosphorus are high, resulting in a prolonged fertilizer effect from the gradual breakdown of organic matter. The substrate can be applied as an organo-mineral fertilizer, growing overall application need 1–1.5 t/ha (equivalent to 25–35 t/ha of conventional manure) during the initial soil cultivation not later than in 1.5–2 months before sowing. It can also improve soil blends for greenhouses under similar conditions of application. Consequently, Product No. 1 may be suitable for occasional application to acidic, unsalted soils at low dosage rates.

It is clear that the relatively low nitrogen (0.05% NH_4^+ in the liquid) and potassium contents do not allow for the production of a fertilizer with a sufficiently balanced nutrient content. Therefore, to increase the mineral nitrogen content by 10–20 wt.%, enrichment with urea was planned at an optimal mass ratio of organic concentrate to urea (1.3–3.6):1 [8]. Thus, a batch of fertilizer with an increased nitrogen content for field testing was produced according to the basic technological scheme shown in Fig. 2.

Table 1

Elemental composition of solid organic waste (XRF analysis)

Component	Content, wt. %
CaO	26.14±0.05
SiO ₂	24.80±0.09
MgO	21.17±0.05
Fe ₂ O ₃ (as Fe)	12.80±0.03
Al ₂ O ₃	4.10±0.06
P ₂ O ₅	3.83±0.04
Na ₂ O	0.1
TiO ₂	0.3
MnO	0.52
K ₂ O	<0.07
Other components	<6.17

Table 2
Composition and properties of the clarified liquid from soda production

Property	Value
Appearance	A colorless, transparent liquid
Density, g/cm ³	1.135±0.005
pH	8.85±0.35
Mineral salt content in the residue after calcination, %	23.85±0.65
Contents (Ca+Mg)Cl ₂ , wt. %	13.7±0.4
Contents NaCl, wt. %	6.25±0.15
Contents SO ₄ ²⁻ , wt. % (expressed as Na ₂ SO ₄)	3.23±0.02
Contents CO ₃ ²⁻ , wt. % (expressed as Na ₂ CO ₃)	0.595±0.015
Contents NH ₄ ⁺ , wt. %	0.0515±0.0005

To test this fertilizer composition, a typical experimental soil plot in the region was selected, characterized by signs of fertility degradation, deficiency in macro- and micronutrients, with moderate salinity. An agrochemical analysis of the soil was conducted before and after the application of 1.5 t/ha of fertilizer, 2.5 months later (Table 4) by the accredited laboratory of UkrChemAnalysis LLC (Kyiv).

Agrochemical analysis revealed that the positive effects of Product No. 2 (including increases in nitrogen by +45 mg/kg, phosphorus by +6 mg/kg, and the

presence of trace elements Zn, Cu, Co, Mo, B) are countered by significant drawbacks in the formulation caused by the use of clarified soda production liquid: a sharp rise in pH, chloride content, and salinity. At the same time, studies have confirmed the value of solid organic waste as a source of micronutrients (in chelated form due to organic acids) and organic matter. The use of clarified liquid from soda production as a liquid component in the technology is appropriate for producing soil conditioners for acidic soils ($\text{pH} < 6.0$), as the presence of calcium, magnesium, and carbonates helps neutralize acidity.

To create a versatile agrochemical product that prevents salinization and maintains a consistent composition, the decision was made to stop using clarified liquid. This choice guided the strategy to refine the technology further and develop a complete fertilizer (Product No. 3) with a neutral pH and low salinity. Removing the clarified liquid decreases overall salinity by a factor of 8–10 (to 0.7–0.8%), sulfate content by a factor of 15–20 (to 5–6 mg-eq/100 g), chlorides by 3–5 times (to 2–4 mg-eq/100 g), and results in a neutral pH (6.5–7.5). Taking the proposed modification into account, a trial batch of this fertilizer was produced (Fig. 3).

The effectiveness of Product No. 3 (organic waste+water+urea) was tested under field conditions at the «Minko» farm (Bilenke village, Zaporizhzhia oblast, 2021) on «Vypel» corn and «Zhemchuzhina» pumpkin crops. Fertilizer was applied at rates of 200 kg per 0.2-hectare plot for corn and 120 kg per 0.12-hectare plot for pumpkin; it was incorporated during plowing to depths of 5–8 cm for corn and 12–15 cm for pumpkin, respectively. The test results are presented in Table 5.

The data collected statistically confirmed the fertilizer's effectiveness and safety. The modified composition reduces the risk of secondary salinization while preserving the product's high agrochemical value. The yield increase for corn (+6%, $p < 0.05$) and pumpkin (+16–20%, $p < 0.01$) at a low application rate demonstrates the fertilizer's acceptable effectiveness and supports its commercialization.

Despite Product No. 3 having high efficacy, its agrochemical composition features a strong deficiency of potassium (K_2O 0.05%), with only 0.3% nitrogen

Table 3

Physical and chemical properties of the fertilizer (Product No. 1)

Property	Value
General properties	
pH of the aqueous extract	8.98–9.01
Total salts, %	5.62–7.75
Humidity, %	7.9–10.0
Ash content, %	53.7–54.9
Nutrient content	
Total nitrogen, %	1.10–1.41
Ammonium nitrogen, %	0.0002–0.004
Nitrate nitrogen, %	0.45–0.61
Total phosphorus (P_2O_5), %	0.46–0.47
Mobile phosphorus, %	0.008–0.009
Total potassium (K_2O), %	0.05
Mobile potassium, %	0.01
Organic matter, %	45.1–46.3
Water extract (mg-eq/100 g)	
CO_3^{2-}	4.32–4.40
HCO_3^-	6.91–11.44
Cl^-	6.04–10.56
SO_4^{2-}	73.08–99.20
Ca^{2+}	10.79–11.00
Mg^{2+}	75.53–110.0
Na^+	3.83–4.39
K^+	0.20–0.21
Trace elements in mobile forms (mg/kg)	
Zinc	22.1–24.3
Iron	53.2–82.1
Manganese	97.1–99.4
Copper	3.7–5.7
Cobalt	0.03

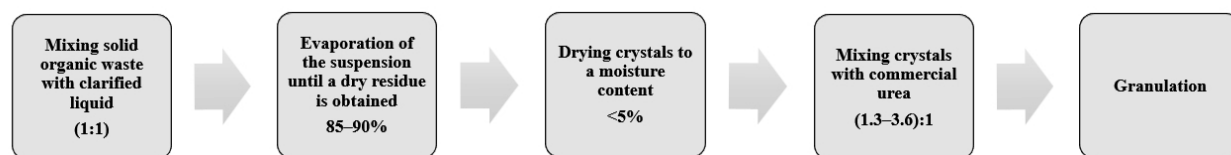


Fig. 2. Flowchart of the production process for granular organo-mineral fertilizer (Product No. 2)

content, while for most agriculture crops an NPK balance is required of $N:K_2O$ ratio=1:(0.4–0.6). This imbalance limits the product's use, as potassium-loving crops (potatoes, sugar beets, vegetables, and fruit crops) require much higher potassium levels to reach their genetic yield potential. In addition, an excess of magnesium in the organic concentrate (Mg^{2+} 75–110 mg-eq/100 g) can displace potassium from the soil exchange complex, reducing its availability to plants even when it is present in the soil. Given its balanced nitrogen-potassium complex, thus allowing to expand the line of products and meet different agricultural production needs. Product No. 4 has been proposed. In addition, by adding potassium salt (KCl or K_2SO_4) to the mixture at 10% of its weight it is possible to achieve a K_2O content of about 6.3%, providing an NPK ratio of 14:2.3:6.3 suitable for meeting the agronomic needs of intensive agriculture and organic production as well as the cultivation on light soils poor in cation exchange capacity with potassium-deficient crops.

The production of organo-mineral fertilizers follows the process flow diagram shown in Fig. 4, with the mixing and evaporation units capable of operating in two modes.

Mode A (Products No. 1 and No. 2 with clarified

liquid): clarified liquid from soda production from tank No. 1a and solid organic waste (a mixture of C_4 – C_8 dicarboxylic acids) with a moisture content of 60–70% from tank No. 1c are dosed in a 1:1 ratio by weight and fed into a mixer-disperser No.1 with an anchor agitator, where a homogeneous suspension is formed during continuous mixing for 15–20 minutes. The suspension is pumped with metering pump No. 2 into the stirred vacuum dryer No. 3, where evaporation takes place at 80–100°C and vacuum of 0.1–0.2 bar for 2–3 h until moisture content reaches up to 12–13%. The slurry is also fed into fluidized-bed dryer No. 4, where at 120 to 140°C heat transfer fluid for a time of 15–20 min final moisture <5% is reached.

Mode B (Products No. 3 and No. 4 without clarified liquid): solid organic waste with a moisture content of 60–70% is fed from tank No. 1c into the mixer-disperser No. 1, where mechanical grinding takes place with the addition of 10% process water from tank No. 1b to ensure the required consistency. The ground wet material is fed through a bypass system into the fluidized bed dryer No. 4, where, at 120–140°C and 30–45 minutes of drying time, it reaches a moisture content of <5%. The subsequent stages are the same for both modes. The organic

Table 4

Soil agrochemical parameters before and after fertilizer application (Product No. 2)

Indicator	Unit	Value	
		Before applying	After applying
Macronutrients			
Nitrate nitrogen	mg/kg	10	75
Alkaline-hydrolyzed nitrogen	mg/kg	35	63
Mobile phosphorus	mg/kg	3	9
Mobile potassium	mg/kg	290 (according to Chirikov)	252 (according to Machigin)
Organic matter	%	2.17	2.85
Physical and chemical properties			
pH of the aqueous extract	–	7.1	9.6
pH of the brine extract	–	6.9	9.4
Total salinity	mg/100 g	2957	4428
Total salts	%	0.55	6.17
Microelements			
Zinc	mg/kg	0.000	0.151
Copper	mg/kg	0.000	0.444
Cobalt	mg/kg	0.000	0.492
Molybdenum	mg/kg	0.000	2.150
Bor	mg/kg	1.120	2.110
Water extractor			
Metabolizable calcium	mmol·eq/100 g	3.0	6.3
Magnesium metabolism	mmol·eq/100 g	0.00	2.37
Chloride	mmol·eq/100 g	1.30	142.40
Sulfates	mmol·eq/100 g	3.70	5.10

concentrate, cooled to 40–50°C, is transported by screw conveyor No. 5 to storage hopper No. 6, from where the concentrate, together with commercial granulated urea (2–4 mm fraction) and potassium salt (KCl or K₂SO₄, <1 mm fraction) from hoppers No. 6a and 6b, respectively, are metered by three weighing feeders No. 7a, 7b, 7c in a specified ratio depending on the Product: No. 1 – 100% concentrate; No. 2 and No. 3 – concentrate:urea=2:1; No. 4 – concentrate:urea:KCl=6:3:1 (with an accuracy



Fig. 3. Appearance of the granular organic-mineral fertilizer (Product No. 3)

of $\pm 1.5\%$) and fed into the blade-type dry component mixer No. 8 with a mixing time of 8–10 min. The homogeneous mixture enters the humidifier No. 9, a horizontal unit equipped with a ribbon-paddle mixer (80–120 rpm), where 8–10% water (based on the mixture's mass) is sprayed through nozzles during intensive mixing for 3–5 minutes to achieve a moisture content of 10–12% and prepare the mixture for agglomeration; at the same time, a fine fraction from the recirculation stream is added, which serves as the nuclei for granule formation. The moistened mixture is fed into the drum granulator No. 10, where, at a rotation speed of 4–12 rpm and a residence time of 10–20 minutes, agglomeration occurs via the rolling method, resulting in spherical granules with a diameter of 5–6 mm. The formed granules are fed into the drum dryer No. 11, where, upon being blown with hot air at a temperature of 80–90°C for 30–45 minutes, a moisture content of 2–3% is achieved while simultaneously cooling to 60–70°C; the dried granules enter a counter-current cooler No. 12, where they are cooled to a temperature of 30–35°C for 15–20 minutes, after which they are directed to a two-deck vibrating screen No. 13 for classification into fractions: fines (<4 mm, returned to mixing), marketable fraction (5–6 mm, yield 85–90%), and oversize (>7 mm, directed to the crusher No. 14). Fine particles and crushed oversize material are combined and returned to the humidifier No. 9. The marketable fraction is packaged into polypropylene bags weighing 1, 3, 5, 25, or 50 kg and stored in the finished goods warehouse; the yield of the marketable fraction is 88–92%. The compressive strength of the granules is 5–6 MPa, ensuring their resistance to

Table 5

Effect of fertilizer (Product No. 3) on crop yields (M $\pm$ SD)*

Indicator	On the control plot (without fertilizer)	On the experimental plot (with fertilizer)	Growth, %
"Vypel" Corn			
Plant height, cm	255 $\pm$ 13	270 $\pm$ 8	+5.9
Number of leaves, pcs.	16.5 $\pm$ 0.6	16.5 $\pm$ 0.6	–
Head length, cm	24.5 $\pm$ 0.6	25.5 $\pm$ 0.6	+4.1
Number of rows of grains, pcs.	17.0 $\pm$ 1.0	18.0 $\pm$ 1.0	+5.9
Grain yield, %	84.5 $\pm$ 0.5	86.0 $\pm$ 1.0	+1.8
Weight of 1,000 grains, g	285 $\pm$ 5	292 $\pm$ 3	+2.5
"Zhemchuzhna" Pumpkin			
Number of fruits per bush, pcs.	5.0 $\pm$ 1.0	6.0 $\pm$ 1.0	+20.0
Fetal length, cm	49 $\pm$ 2.0	50.5 $\pm$ 2.0	+3.1
Fetal weight, g	5500 $\pm$ 1080	6250 $\pm$ 950	+13.6**

Notes: * – M $\pm$ SD stands for mean $\pm$ standard deviation; differences between treatments are statistically significant at $p < 0.05$;

** – the difference is statistically significant at $p < 0.01$.

mechanical damage during transportation and storage. The line's capacity is 300 kg/hour of finished product.

This technology enables the production of multiple products with varying agrochemical characteristics to meet customer demand and needs (Table 6). Products No. 2–4 with added urea are characterized by a high total nitrogen content (14–16 wt.%) with a moderate organic matter content (29–32 wt.%); whereas Product No. 1 without urea contains significantly more organic matter (48–50 wt.%) with a low nitrogen content (0.03–0.04 wt.%).

The analysis for heavy metals revealed that the Pb, Cd, Hg and As in all products meet but do not exceeding the maximum values i.e. MRC obtained for organic fertilizers (EU Regulation 2019/1009): Pb <5 mg/kg (MRC 120 mg/kg), Cd <0.5 mg/kg (MRC 3 mg/kg), Hg <0.1 mg/kg (MRC 1 mg/kg) Detectable levels of ^{137}Cs and ^{90}Sr were below the relevant detection limit; this confirms radiological safety in respect to these products.

Since the source of bound nitrogen in formulations 2–4 is added urea, their environmental and carbon footprint remains linked to the energy-

intensive process of producing ammonia from natural gas. Further research aimed at replacing urea with cheaper and more environmentally neutral sources of nitrogen (biological fixation [9,10], low-energy methods of N_2 fixation [11,12]) has the potential to reduce production costs, lower the carbon footprint of fertilizers, and improve their competitiveness in sustainable agriculture.

Conclusions

It has been established that solid waste from organic synthesis processes is a promising secondary raw material for producing organo-mineral compositions for agrochemical applications. Thermogravimetric analysis showed that its thermal transformations were multi-stage, with a total mass loss of approximately 42%, corresponding to dehydration, thermal decomposition of the organic component, and partial decarbonization of the mineral phase.

Calcium, magnesium, silicon, iron and phosphorus oxides were detected in significant concentrations using X-ray fluorescence analysis, confirming that the waste can be used as a component of organo-mineral fertilizers or soil conditioners.

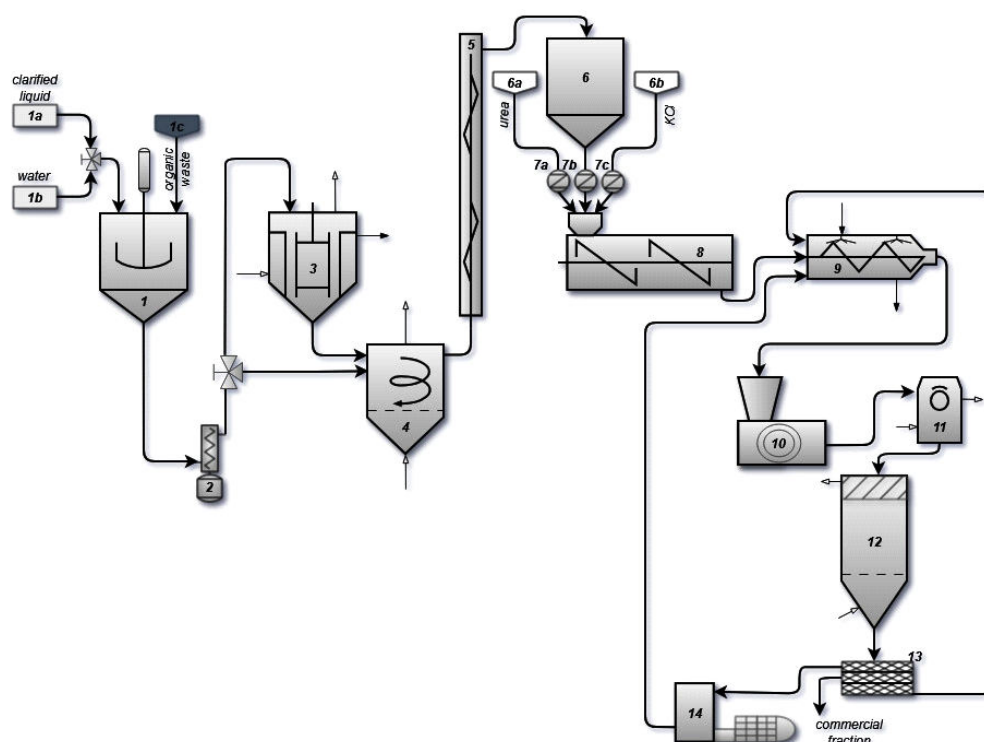


Fig. 4. Schematic flowchart of the process for producing organo-mineral fertilizers: 1 – mixer-disperser; 1a – clarified liquid tank; 1b – process water tank; 1c – solid organic waste tank; 2 – metering pump; 3 – vacuum dryer with agitation; 4 – fluidized bed dryer; 5 – conveyor; 6 – storage hopper; 6a, 6b – urea and potassium salt tanks; 7a, 7b, 7c – weighing feeders; 8 – dry component mixer; 9 – humidifier; 10 – drum granulator; 11 – drum granule dryer; 12 – cooler; 13 – vibrating screen; 14 – crusher

Based on the organic concentrate, several formulations of organo-mineral products have been developed by adding urea and a potassium salt to achieve a balanced nutrient content. A basic process flow diagram for the production of granular fertilizers has been proposed, including the stages of mixing, evaporation, drying, moistening, granulation, drying, and granule classification.

Field trials show the beneficial effect of developed fertilizer to yield and growth of corn and pumpkin,

confirming the agronomic advantages of using organic waste as material for organo-mineral fertilizers.

It has been proven that the addition of clarified soda production waste into the liquid part strongly increases soil salinity and alkalinity, which complicates their use. This liquid is absent from an alternative formulation that provides more stable agrochemistry properties and minimizes the incidence of secondary soil salinization.

The proposed technology for recovering and

Table 6

Comparative characteristics of agrochemical products based on solid organic waste

Indicator	Value			
	Product No. 1	Product No. 2	Product No. 3	Product No. 4
Ingredients				
Liquid for suspension	The clarified liquid	The clarified liquid	Process water	Process water
Urea enrichment	–	+	+	+
KCl enrichment	–	–	–	+
Agrochemical parameters (% of dry weight)				
N _{total}	1.25	15.4	15.3	13.8
P ₂ O _{5total}	0.47	2.0	2.6	2.3
K ₂ O _{total}	0.05	0.04	0.05	6.3
Ratio NPK	1.3:0.5:0.05	15.4:2:0.04	15.3:2.6:0.05	13.8:2.3:6.3
Organic matter	48	32	32	29
Total salts	20.1	13.4	<0.5	10.0
pH of the aqueous extract	8.5–9.0	8.5–9.0	7.0–7.5	7.0–7.5
Agronomic parameters				
Application rate, t/ha	1–1.5	1.0–1.5	1.5–2.5	2.0–3.0
Frequency of use	Once every 3-4 years	Once every 2-3 years	Every year	Every year
Interval until sowing, months	2	1.5–2.0	0.5–1.0	0.5–1.0
Classification and purpose				
Classification	Organic soil conditioner/soil restorer	Organo-mineral nitrogen fertilizer/soil bioactivator	Universal organo-mineral fertilizer (starter fertilizer)	Potassium-nitrogen complex fertilizer
Target soils	Acidic and degraded soils with low organic matter content, light sandy and sandy loam soils	Acidic soils, nitrogen-deficient soils, soils with sufficient natural potassium content (chernozems, dark gray forest soils)	Neutral and slightly acidic soils, gray forest soils, loamy soils, chernozems	Chernozems, light soils with potassium deficiency, sandy and sandy loam soils, intensive agricultural systems
Main effect	Increased humus content, improved soil structure, partial soil deacidification, stimulation of microbial activity	Stimulating vegetative growth, activation of soil microbiology, and partial deacidification	Stimulating root system development, ensures early plant growth, and enhances nitrogen and phosphorus uptake	Increased yield, improved fruit quality, drought and stress tolerance, and regulation of plant water balance

utilizing chemical industry waste as an alternative raw material for organic-mineral fertilizers enables the production of products with a wide range of agrochemical properties and represents a promising avenue for resource conservation, ecological restoration, and the implementation of circular economy principles.

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Received 09.04.2026

Revised 23.06.2026

Accepted 10.07.2026

Published 10.08.2026

ТЕХНОЛОГІЯ ВИРОБНИЦТВА ОРГАНО-МІНЕРАЛЬНИХ ДОБРІВ З ВІДХОДІВ ХІМІЧНОЇ ПРОМИСЛОВОСТІ

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У роботі досліджено можливість утилізації відходів виробництв органічного синтезу та содового виробництва з метою отримання орґано-мінеральних композицій агрохімічного призначення. Проведено термогравіметричний аналіз твердого органічного відходу, рентгенофлуоресцентне визначення його елементного складу, а також хімічний аналіз освітленої рідини содового виробництва. Встановлено багатостадійний характер термічних перетворень органічного відходу із сумарною втратою маси близько 42 мас.%, що зумовлено дегідратацією, термічним розкладом органічної складової та частковою декарбонізацією мінеральної фази. Показано, що відхід містить значні кількості сполук кальцію, магнію, заліза та фосфору, що визначає його потенціал як сировини для виробництва агрохімічної продукції. На основі органічного концентрату розроблено декілька композицій орґано-мінеральних добрив із додаванням карбаміду та калійної солі для регулювання співвідношення елементів живлення. Досліджено їх фізико-хімічні та агрохімічні характеристики, а також запропоновано принципову технологічну схему виробництва гранульованого продукту. Польові випробування на культурах кукурудзи та гарбуза показали позитивний вплив добрива на ріст рослин і показники продуктивності. Встановлено, що використання освітленої рідини содового виробництва у складі композицій призводить до значного підвищення засоленості та лужності ґрунту, що обмежує сферу їх застосування. Модифікована композиція без використання цієї рідини характеризується більш стабільними агрохімічними властивостями та зниженим ризиком вторинного засолення. Запропонована технологія дозволяє отримувати орґано-мінеральні добрива з регульованим складом і може бути використана для утилізації промислових відходів у рамках концепції циркулярної економіки.

Ключові слова: орґано-мінеральні добрива; альтернативна сировина, модифікація, агрохімічні показники, відновлення відходів.

PRODUCTION TECHNOLOGY FOR ORGANO-MINERAL FERTILIZERS FROM CHEMICAL INDUSTRY WASTE

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This study investigates the potential of using waste from organic synthesis and soda production to produce organo-mineral compositions for agrochemical applications. Thermogravimetric analysis of solid organic waste, X-ray fluorescence determination of its elemental composition, and chemical analysis of the clarified liquid from soda production were conducted. The multi-stage nature of the thermal transformations of the organic waste was identified, with an overall mass loss of about 42 wt.%, due to dehydration, thermal decomposition of the organic material, and partial decarbonization of the mineral phase. The results show that the waste contains significant amounts of calcium, magnesium, iron, and phosphorus compounds, which highlights its potential as a raw material for agrochemical production. Several formulations of organo-mineral fertilizers were developed from the organic concentrate by adding urea and potassium salt to adjust the nutrient ratio. Their physicochemical and agrochemical characteristics were studied, and a basic technological scheme for producing the granulated product was proposed. Field trials on corn and pumpkin crops showed the fertilizer's positive effects on plant growth and crop yield. The results show that incorporating clarified soda production liquid into these mixtures significantly raises soil salinity and alkalinity, thereby restricting their use. The modified composition, which does not use this liquid, exhibits more stable agrochemical properties and a lower risk of secondary salinization. The proposed technology enables the production of organo-mineral fertilizers with a controlled composition and can be used to utilize industrial waste within the circular economy framework.

Keywords: organo-mineral fertilizers; alternative raw materials; modification; agrochemical indicators; waste recovery.

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