PRODUCTION OF FEEDSTOCK FOR BIOFUEL ON MARGINAL LANDS IN UKRAINE: ASSESSMENT AND PROSPECTS

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A low-cost innovative strategy of creating fast-growing plantations of energetic crops and trees on post-mining lands is offered. The marginal lands can be used to produce bio-feedstock rich in carbohydrate components, suitable for heating objects of municipal importance. Using soil amendments can increase the yield, a positive effect on the technosols' biological activity, and the thermal indexes of the biomass of herbaceous and woody plants. Sewage sludge and crop residue ash are among them.

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INTRODUCTION

Rapid depletion of natural resources and environmental degradation all over the world raise the issue of developing innovative technologies for biological land reclamation. Dnipropetrovsk province is located in the southeast of Ukraine. The region covers an area of 31,923 km^2 (5.3 % of the total territory of Ukraine). Up to 10 % of Ukrainian gross domestic product is produced here. Dnipropetrovsk province holds a wealth of mineral resources that have been mined from the end of XIX century. When Ukraine was a part of the former Soviet Union, heavy industries were founded in Dnipropetrovsk province and emphasis was put on the mining, metallurgical and chemical industries. Two of the metal ore reserves are among the largest in the world: iron ore in Krivyy Rog and manganese ore in the vicinity of the city of Nikopol (Kharytonov & Resio Espejo 2013). On smaller scale, uranium ore is also mined (Anisimova et al., 2009). The region has also black coal deposits, which are located in Western Donbas (Kharytonov & Kroik, 2011). These types of industries use enormous quantities of resources and energy and pollute the environment as a result of obsolete production technologies and lack of relevant waste treatment facilities.Long time energy problem in Ukraine were connected with high price on gas and other energy products imported from Russia. Moreover, this situation got worse after the war-like arm conflict started in 2014 year since part of Donetsk coal mining region became uncontrolled. Technosols are a new groups of "young "soils in the beginning of fertility formation elaborated from any deposits including postmining, marine dredged sediments, etc (Betancur – Corredor et al., 2020). Crops grown in less fertile soils is usually limited by plant-available nutrients. Meantime, the application of the combination of wastes and industrial byproducts to reclaim derelict lands has received increasing attention in many countries in recent decades (Séré et al., 2008).

Domestically produced energy is one part of an overall Ukrainian strategy to replace imported fossil fuels. The largest components of the potential are agricultural residues and energy crops. Currently a portion of the Ukrainian corn and soybeans is being processed as ethanol and biodiesel. Depending on the yield of major crops economically feasible potential is in the range of 25–35 million tons of fuel/year, which is 13–18 % of consumption of primary fuels in Ukraine. Available potential of biomass for energy production in Ukraine is used for wood biomass and sunflower husk. The potential of woody biomass (firewood for heating, the remainder of the wood felling and waste generated in enterprises) already reaches 98 %, and sunflower husks – 59 %. Straw is utilized by only 1 %.

The demand for food from these crops, which are usually grown on good soils, is predicted to double by 2050 as worldwide population increases. Even using "waste" products, such as corn cobs and stover feedstock, for cellulosic conversion to produce ethanol is not without problems. Removing corn residues from agricultural lands could accelerate soil erosion that exceeds the acceptable limits, resulting in environmental consequences. Moreover, farmers have expressed concerns about the removal of organic matter, nutrients, and soil cover that may greatly impact ecosystems as a result of harvesting of crop residues and soil quality decline.

Using our prime land to grow crops for the production of ethanol, biodiesel or bioenergy feedstock is not a logical choice (Islam & Weil, 2000). The potential of marginal lands for growing second generation crops as biofuel has received increased attention in recent years (Blanco-Canqui, 2016). Marginal land such as idle, degraded, under-utilized, reclaimed stripe- or abandoned mine-lands, low quality pasture fields, and brushy, underutilized, and abandoned lands are still relatively low priced and can be the "solution" to growing crops as feedstock for bioenergy and high-value bio-based products in Ukraine.

The area of lands disturbed by mining development and industrial landfills is about 200,000 hectares, located in several areas with deposits of manganese, iron, non-ferrous metals, uranium ores and coal. Extraction and processing of minerals at the mining regions led to the formation of a significant area of reclaimed land and man-made deserts. Marginal lands such as quarry and mine tailings, low-productivity pastures and meadows, abandoned low-value lands have good potential for growing energy plants as raw materials for biofuel and bio-goods.

The marginal lands can be considered as an essential resource for the supply of bio-raw material rich in carbohydrate components, suitable for heating objects of municipal importance and for the production of bio-fiber, bio-plastics and biochar. Fast-growing crops and trees (miscanthus, switchgrass, sorghum, poplar, willow, paulownia) may be the first choice for cultivation in such areas. However, obtaining high yields of raw materials on marginal lands requires improving the physical and chemical properties of the soil. If it is provided using traditional fertilizers and lime, it can significantly increase the total costs. The use of some municipal and agri-waste as non-traditional fertilizers creates an additional reserve in increasing the yield of energy crops on marginal lands. Sewage sludge, biocompost, ash, and biochar (as products of biomass burning of energy crops and waste from agribusiness enterprises in boilers and pyrolysis furnaces) are among them. The use of such soil amendments can increase the yield, and have a positive effect on the biological and physicochemical properties of the soil profile. Therefore, the development of economic and energy-efficient solutions for the combined use of municipal and agricultural waste nutrients as an organo-mineral fertilizer can become an alternative to the use of conventional fertilizers for the production of energy and bioproducts on marginal lands in the mining regions of Ukraine. The use of bio-based by-products is a reliable method of waste management and ensures the recycling of nutrients for the growth of energy crops and trees, which is in line with the European circular economy policy.

1. CURRENT TRENDS IN THE DEVELOPMENT OF BIOFUEL PRODUCTION IN UKRAINE AND THE WORLD

The development of biofuel production at the intersection of agriculture and energy is the most important trend of applied developments in recent years. The industrialized economies of North America and Europe have been actively pursuing policies to support biofuel industries to achieve energy security, develop a substitute for fossil fuels, and support the rural economy since the 1990s. In addition, growing concern about climate change has led to interest in biofuels as a possible means of mitigating greenhouse gas emissions (Field et al., 2008; Gelfand et al., 2011; Chu and Majumdar, 2012). Raw materials in countries with a developed biofuel industry are taken from among the most important agricultural crops (corn in the USA, rapeseed in the EU, sugar cane in Brazil and oil palm in Malaysia and Indonesia). The choice of final biofuel product (ethanol in the USA and Brazil, biodiesel in the EU) is usually related to the cultivation of several dominant crops (sugarcane, cassava, palm oil, sweet sorghum, jatropha). However, there is growing interest in studying energy crops such as switchgrass, miscanthus, and short-rotation tree crops (Elbehri et al., 2013).

The most common biofuels are ethanol and biodiesel. Bioethanol is the most widely used liquid biofuel in the world. Global production of bioethanol (about 97 %) reached 28 billion gallons in 2010, with the United States (corn) and Brazil (sugarcane) leading the world, producing 23 billion gallons and together accounting for 90 % of total global production. Other bioethanol producing countries include China, Canada, Australia, and Thailand, and European Union countries (Germany, Spain, France, Sweden, Italy, and Poland). By 2012, ethanol production absorbed more than 50 % of the sugarcane crop in Brazil and 37 % of the coarse grain crop in the United States. The European Union, USA, Argentina, Brazil, Malaysia, Indonesia, Singapore and China dominate the biodiesel markets. The European Union is the largest producer and consumer of biodiesel, accounting for 80 % of global production (Pahl, 2005; de Vries et al., 2010; Saunders et al., 2011).

The structure of Ukraine's fuel balance is close to the world's: solid fuel (coal) makes up one third of all fuel, the hydrocarbon part (oil, gas) – two thirds. Ukraine can cover only 20 % of its needs in natural gas and 10 % in oil at the expense of its explored own resources. Every year, the production of certain types of fuel decreases, while the demand for them increases. The consumption of the main energy carriers has increased in recent years, which is associated with an increase in the production capacity of industrial enterprises (Heletukha and Zheleznaya, 2006). Decisions on environmental protection adopted by international organizations and national governments require new technical solutions to increase the efficiency of fuel burning and reduce emissions of combustion products. For more than 100 years of industrial development, success in the improvement of heat power stations has been evaluated on the results of fuel efficiency, increased power, and operational reliability.

One of the main directions of energy policy implementation in the country is the formation of a fuel and energy balance (FEB), which would correspond to Ukraine's own reserves of fuel and energy resources (FER) and world trends in the use of energy carriers. The second problem of FER is outdated technologies and equipment on which Ukrainian industry is based. In Ukraine, 89 kg of conventional fuel is used for one dollar of production. This is 3–5 times more than in developed countries. At the same time, dependence on fuel supplies from other countries has been 60 % in recent years. Reducing the level of energy dependence is primarily influenced by measures to reduce the share of total imports of renewable energy sources, as well as improving their use. Therefore, it is necessary to carefully consider and take into account the state of the world energy market, world energy as a whole, the prospects for their development and the role of Ukraine in the global world market. According to the comprehensive state energy conservation program of Ukraine, the energy resources of renewable energy sources (RES) total 78.2 million ton of condition fuel (cf)/year (Heletukha et al., 2005). The share of bioenergy is 21.2 million t.c.f./year (27 % of the total contribution of RES).

Due to its geographical location, Ukraine has a moderate potential for wind, hydro and solar resources. Agriculture is much more developed. As a result, agriculture produces a significant amount of organic biomass waste. This is a prerequisite for the production of various forms of biofuel. In general, the energy potential of bioenergy resources (agricultural and forestry waste, peat) in Ukraine is equivalent to 21 billion cubic meters of natural gas. Thus, by 2030, biomass is able to provide about 10 % of Ukraine's total need for primary energy (today it is 220 million tons of conventional fuel). The development of this component of the balance will allow in the future to redistribute the ratio of consumption of various types of energy, so that to increase the specific weight of non-traditional energy carriers, in particular, biofuel, and will be accompanied by a significant decrease in the consumption of solid fuel, gas and oil. Such a prospect has been proven in relation to the use of pyrolysis gas as an additive to natural gas. It is obvious that replacing traditional fuels with biological ones has a certain interest, both from an economic and a technological point of view.

1.1. Thermal energy aspects of biofuel use

The great demand for the energy use of biomass is connected not only with economic prerequisites, but also with the desire to reduce greenhouse gas emissions during the burning of fossil fuels. At the same time, the utilization of biomass waste is an equally urgent environmental task. The use of biomass as a fuel is one of the few real alternatives to reducing the greenhouse effect, since plant waste is neutral in relation to the CO_2 balance in the atmosphere. The same amount of CO_2 absorbed during the growth of plants is released during the burning of biomass. The use of oil, coal, and gas to obtain energy leads to an increase in the concentration of CO_2 in the atmosphere, since carbon that has accumulated in these energy carriers for many years is burned. It should be noted that methane is considered second only to carbon dioxide in the degree of influence on global warming. The concentration of methane in the atmosphere increases annually by 0.5 %, carbon dioxide by 0.4 %, and nitrogen oxide by 0.25 % (Mandyl, 2007). Biomass can be used as a solid fuel or processed into a liquid or gaseous state.

Lumpy wood processing waste can be used as solid fuel. However, it is unprofitable to transport large pieces of waste outside the enterprisedue to the great difficulty of storage and loading and unloading operations even for short distances. Therefore, it is advisable to process lumpy waste into chips on site and send this chip to appropriate specialized enterprises for use as raw material. Lumpy waste should be processed into chips in order to use them not only as technological raw materials, but also as fuel (using traditional boilers).

Waste (wood chips) with a size from 25 to 100 mm burns most efficiently and intensively (Levin, 1980). Depending on the purpose and the requirements, technological and fuel wood chips are distinguished. The main equipment during the production of technological wood chips are chipping machines. Briquetting of loose wood is performed by pressing with or without binders. Briquetting without binders is more widely used. Loose wood after briquetting decreases in volume several times, becomes transportable and convenient in circulation.

Briquetting of bulk waste increases the calorific value of sawdust and shavings. Briquettes are used as factory fuel and for supply to the local population. Sawdust briquetting increases the productivity of boilers in hydrolysis production when these boilers are loaded not with pine sawdust, but with sawdust briquettes. More powerful presses are required for wood chip briquetting than sawdust briquetting. Practically, only sawdust is suitable for briquetting. The moisture content of sawdust before briquetting should be no higher than 12–15 % and no lower than 8–9 % (Fengel and Wegener, 1996).

Pelletization of wood waste is the production of fuel pellets from any wood waste produced in the process of mechanical processing of wood. The advantages of this method of processing include the rational use of wood waste, the production of high-calorie environmentally friendly fuel, an increase in the efficiency factor (EF), the possibility of introducing a system of mechanization and automation of combustion devices thanks to the use of pellets, and increasing the stability of combustion processes. Wood waste granulation technology includes: collection of waste, grinding, drying and direct granulation. The essence of granulation consists in the sequential processing of dry finely dispersed bulk raw materials with moisture, temperature and pressure. Agricultural granulators can be used as the main equipment for granulation.

In unconventional energy, a special place is occupied by the processing of biomass by methane fermentation with the production of biogas containing about 70 % methane, and sterile organic fertilizers. Utilization of biomass in agriculture is extremely important, as a large amount of fuel is consumed for various technological needs. Therefore, the need for high-quality fertilizers is constantly growing. Biogas is a mixture of methane and carbon dioxide, which is formed in the process of anaerobic fermentation in special methane reactors, arranged and controlled in such a way as to ensure maximum release of methane. The energy obtained during the burning of biogas can reach 60–90 % (Heletukha and Matveev, 2008).

The advantage of the biomass processing process is that its waste contains significantly fewer pathogenic microorganisms than the raw material. Obtaining biogas is economically justified and is preferable when processing a constant flow of waste (runoff from livestock farms, slaughterhouses, plant waste, etc.). Economy is that there is no need for preliminary collection of waste, organization and management of its supply. At the same time, it is known how much and when waste will be received. Biogas production is possible in installations of various scales. It is especially effective to do this at agro-industrial complexes, since there is an opportunity to implement a complete waste-free cycle.

Biofuel (bioethanol, biodiesel) or resins, pyrofuel and oils are classified as liquid fuels produced from biomass. Fuel ethanol is a high-octane, oxygen-containing fuel component that is obtained during the fermentation of sugar. Sugar is usually obtained from sugar crops by hydrolysis of grain starch or by hydrolysis of lignocellulosic materials such as straw, grass and wood. The main process involves the enzymatic hydrolysis of starch and sugar contained in the grain and the fermentation of the sugar into ethanol by yeast. A weak solution of ethanol is distilled and dehydrated to obtain anhydrous ethanol, which is suitable for mixing with gasoline in cars.

Biodiesel fuel is a type of fuel obtained by trans-esterification of vegetable oil and can be mixed with or used as a substitute for diesel fuel in engines.

It is known that rape contains a lot of fats, which provide high heat of combustion. That is why rapeseed is one of the main types of raw materials for obtaining biodiesel. Rapeseed oil ranks fourth in the world (9.7 %) after soybean oil (29.7 %), palm oil (13.1 %) and sunflower oil (12.3 %). There are several ways to use canola for biodiesel production. The use of waste from agricultural enterprises as a raw material for fuel production has great economic appeal. Large areas of land, additional equipment for processing into liquid fuel, high energy costs for its production, which are proportional to the energy potential of the obtained product, are necessary for the cultivation of raw industrial crops. On the ecological side, it can help mitigate the problem of climate change, help maintain healthy forest conditions through better management. Therefore, the main attention is paid to the development of technologies for the production of fuel gas from the waste of biomass processing enterprises with a high heat of combustion.

1.2. Analysis of biomass processing methods

Biomass utilization technologies are at the beginning of their development in Ukraine and have good prospects for commercialization in the near future, especially in light of the sharp increase in the cost of natural gas. Ukraine consumes biomass mainly in the form of wood fuel – about 1 million tons of conventional fuel (c.f.)/year for the traditional burning of wood for heating private houses, as well as in more than 1,000 boilers installed at forestry and woodworking enterprises branches. It is obvious that the process of widespread introduction of bioenergy technologies should begin with the commissioning of modern boilers for burning wood, straw and peat waste, as well as the construction of mini-electric power stations using biogas from solid waste (solid household waste) landfills.

Other technologies for energy production from biomass (biogas from manure, liquid fuels, energy crops) are no less important and will be prioritized in the near future, but they still need to pass the demonstration stage to confirm the competitiveness of their economic indicators. It is the biomass boilers and mini-power plants on biogas from solid waste that can quickly replace natural gas for the production of heat and electricity with the lowest investment costs and the shortest payback periods of the projects.

Based on the existing potential of wood, straw, peat, and solid waste, the following technologies will be introduced in the next 10 years: wood-fired heating boilers (1–10 MWt) – 500 units; industrial wood-fired boilers (0.1–5 MWt) – 500 units; household wood boilers (10–50 kWh) – 53 thousand units; farm boilers on straw (0.1–1 MWt) – 16 thousand units; straw heating boiler houses (1–10 MWt) – 1,400 units; heating boiler rooms on peat (0.5–1 MWt) – 1000 units; projects on the collection and utilization of biogas from solid waste landfills are recognized as justified and expedient.

The main technologies of thermochemical processing of biomass are direct combustion, gasification and pyrolysis.

1.2.1. Overview of modern biomass gasification technologies

Thermochemical gasification is a process of partial oxidation of bio-raw materials containing coal, with the production of a gaseous energy carrier – generator gas. The resulting gas consists of carbon monoxide, hydrogen, methane, carbon dioxide, a small amount of higher-order hydrocarbon compounds such as methane and ethane, and contains water vapor; nitrogen (by air blowing), various impurities of resin and ash. Air, oxygen, steam or a mixture of these substances can be used as an oxidizer during gasification. The maximum temperature is 800–1300 °C.

Low-calorie gas is a generator gas produced during air gasification with a higher heat of combustion of 4–6 MJ/m. This gas can be burned in boilers, after cleaning – in gas engines or turbines. By the way, this gas is not suitable for pipeline transportation due to its low energy density. Medium-calorific gas is gas produced during gasification using oxygen (10–12 MJ/kg). It is suitable for limited pipeline transportation and for use as synthesis gas for the purpose of obtaining methanol and gasoline.

By means of steam gasification, an average calorific gas with a heat of combustion of 5–12 MJ/kg can be obtained, this is a two-stage process, which is implemented in two fluidized bed reactors. Air gasification is currently the most widely used. At the same time, all costs and difficulties associated with the production and use of oxygen, as well as with the need for two reactors during steam gasification, are excluded (Heletukha et al., 1997; Geletukha and Zheleznaya, 1998).

According to the type of raw material and the method of introduction of the oxidizing agent, the main technologies can be divided into gasification: in a dense bed with downward gas movement (DGM), in a dense bed with upward gas movement (UGM), in a dense layer with transverse gas movement, in a fluidized bed (FB), in the circulating layer, in the flow; in two fluidized bed reactors.

DGM gasification is simple, reliable and proven for relatively dry wood branches and chips with a moisture content of up to 30 % and an ash content of less than 3–5 %, which contain a small number of small biomass particles. Particle size limitations lead to an upper gasifier capacity limit of about 500 kg/h or 500 kV. The resin content in this gas is 50–500 mg/m^3 (Sergeev et al., 2003; Sergeev, 2007).

Gasifiers with UGM can work stably with raw material moisture up to 55 %. The requirements for the fractional composition of raw materials are less strict than in the gasifier with DGM. The disadvantage of this technology is the high content of resins (about 20 % of all pyrolysis products) in the produced gas. Therefore, for use as a fuel, this gas needs significant purification or must be used in the immediate vicinity of the gas generator.

Gasifiers with transverse gas movement in operation are similar to gasifiers with DGM in many respects. Gasifiers of this design were not widely used.

Gasification in FB is characterized by high heat and mass transfer rates and good mixing of the solid phase, which ensures high reaction rates and a constant bed temperature. The raw material particles should have a relatively small size compared to the particles in the dense layer. Therefore, additional grinding is necessary. Ash is captured and removed from the exhaust gases in the cleaning system. The working temperature during biomass gasification is 800–850 °C. In most cases, the degree of carbon conversion reaches 100 %. The CS gasifier produces gas with a resin content of 5–10 g/nm, which is between the levels of resin content in gases produced from UGM and DGM (Sergeev, 2009).

Gasification in the stream is carried out at higher temperatures of 1200–1500 °C. Consequently, the generator gas has low tar concentrations. However, great problems are created in the selection of materials and ash melting. Gasification in two fluidized bed reactors is used to obtain gas with a higher calorific value than in a single FB gasifier with air blast. Gas quality is unsatisfactory from the point of view of resin content. Combustion of generator gas obtained from biomass significantly reduces the content of harmful impurities in combustion products. It is obvious that this will certainly affect the ecological situation in the respective regions.

1.2.2. Gasification of biomass by the catalytic method

Carbohydrates of biomass contain a lot of oxygen and moisture. It is known that much less water vapor is required in the gasification process than during the gasification of fossil coal. The reaction of oxidative gasification of plant biomass is carried out in an autothermal mode by adding oxygen or air. Recently, there has been an increased interest in the research of catalytic gasification of biomass. It was found that alkaline catalysts (sodium, potassium carbonates, etc.) significantly increase the yield of synthesis gas during the gasification of biomass with water vapor in the temperature range of 550–750 °C. Sodium and potassium carbonates are also effective catalysts for charcoal gasification with carbon dioxide. Salts of transition metals, although they show high activity at the initial stage of the reaction, are deactivated during the process. Different methods of catalytic gasification of biomass are used.

Gasification of mechanical mixtures of plant biomass and catalyst is characterized by technical simplicity, but is less effective compared to other methods of catalytic gasification due to the limited contact surface of the heterogeneous catalyst with solid raw materials. The exception is mechanical mixtures based on catalysts capable of melting or catching fire at process temperatures. The developed contact surface is achieved by forming highly dispersed catalyst particles in the porous structure of the biomass. For example, the pyrolysis of poplar wood with the introduction of K, Ca, Mg, Co, Ni cations by ion exchange is used to introduce catalysts into the composition of charcoal. In the gasification of CO_2 charcoal at a temperature of 800 °C, the catalysts are placed in the order of activity in the order of Co > Ca > Ni > Mg-K-Na > Cu.

The cobalt catalyst subjected to pyrolysis at a temperature of 600 °C, containing metallic cobalt particles in a charcoal matrix, exhibits the highest activity. When using the method of wood gasification, based on the steam cracking of volatile substances in wood in a fixed layer of aluminum-nickel catalyst, the yield of gaseous products increases from 50 to 90 % compared to the non-catalytic process. The high ratio of $H_{2:}CO$ (1.96) makes it possible to use synthesis gas for the production of methanol without the stage of conversion with steam (Williams and Nugranad, 1998).

The processes of oxidative gasification of chopped plant biomass in the pseudo-oxidic layer of the oxidation catalyst are promising. That is why it is possible to create combined biomass processing processes with the simultaneous production of fuel gas or synthesis gas, as well as porous carbon materials. However, oxidative gasification is characterized by a number of disadvantages: a small yield of the final product (40 %), the possibility of the destruction of hemicellulose into non-fermentable products, and the low quality of the by-product lignin which is difficult to dispose of.

1.2.3. Modern technologies of anaerobic fermentation

Anaerobic processing and reference fermentation refer to the biological method of biomass processing. In the process of anaerobic processing or rotting (fermentation method), organic substances are decomposed into CO_2 and CH_4. The process of anaerobic processing of organic waste takes place in the absence of oxygen, with the participation of various groups of bacteria (acetonobutanal fermentation), as a result of which, under the action of microorganisms, acetic acid, butyric acid, ethanol, butanol, isopropanol, as well as carbon dioxide and hydrogen are formed. However, technological processes that require the use of concentrated acids to accelerate hydrolysis occur at the same time. In this connection, there is a need to use additional special construction materials. Also, the cost of obtaining a fermentation product is currently still very high, and the processes developed on their basis are not very productive.

Fermentation of waste is a process of decomposition of organic substances with the formation of methane and carbon dioxide as a result of the vital activity of a complex complex of microorganisms in anaerobic conditions. At the first stage of the process, high-molecular compounds (carbohydrates, fats, proteins) are broken down into low-molecular organic compounds.

At the second stage, with the participation of acid-forming bacteria, their decomposition occurs with the formation of organic acids and their salts, as well as carbon dioxide (CO_2), hydrogen (H_2), hydrogen sulfide (H_2S) and ammonia (NH_3) alcohols. The final bacterial transformation of organic substances into two main components (carbon dioxide and methane) is carried out at the third stage.

The main influence on this process taking place in special biological reactors (methane tanks) is provided by the certain conditions. The first is the lack of oxygen, since methane-forming bacteria need an absolutely anaerobic environment for their vital activity. The second condition is maintaining a certain temperature. The biological process works best in the temperature range of 30–37°C. Good results also come from the implementation of the so-called thermophilic process, which takes place at 55–60 °C (Matveev, 2004). The third condition is maintenance of the specified pH value in the range of 6.5–8.5. The fourth is the preservation of certain ratios of gases in raw materials. The optimal ratio of carbon and nitrogen (C/N) should be within 16/19. In addition to the carbon-nitrogen balance, the presence of trace elements such as iron, molybdenum, nickel, cobalt and selenium is necessary for the implementation of a sustainable and effective process of anaerobic fermentation of raw materials. The final products of anaerobic fermentation are 60–70 % methane in biogas, 30–40 % carbon dioxide, 0–3 % hydrogen sulfide, hydrogen impurities, ammonia, nitrogen oxides.

The amount of biogas from various agricultural wastes, residues and mixtures depends on the amount of substrate, the conditions of the process, the bacterial composition in the reactor, etc.

In Ukraine, even small farms can implement simple and fairly effective anaerobic fermentation systems. The most profitable are large biogas plants (with a volume of methane tank of at least 800 m^3). Such systems can be built in our country on cattle farms with a herd of 600 or more, on pig farms with a herd of 6,000 or more, on poultry farms with a herd of 200,000 or more, at sugar, dairy, distillery and other food industry enterprises. It is at large biogas plants that it is possible to organize the mechanization and automation of the process, which means to optimize its parameters and ensure a round-the-clock stable supply of biogas to the cogeneration plant that produces electrical and thermal energy. The cost of imported equipment necessary for the construction of anaerobic digestion systems is high for our consumers. But if the installations are fully or partially equipped with equipment made in Ukraine, the price can be significantly reduced and, accordingly, the payback period is shortened.

Biogas with a high methane content can be obtained using anaerobic fermentation technologies of agricultural and organic household waste. However, its production, based on local resources of raw materials, is usually not large. In addition, anaerobic digestion is a batch process, and the composition of the resulting gas is difficult to control.

1.2.4. Biomass waste burning technologies

Direct combustion is one of the applied methods of processing wood biomass, wood waste, straw, municipal solid waste, dry manure, etc. The main chemical elements of wood chips are, % (mass) of dry matter: carbon – 50, oxygen – about 40, hydrogen – 5.7. Nitrogen concentration is less than 1 %, chlorine and sulfur – less than 0.1 %, ash content – about 1 %. The heat of combustion at a humidity of 40 % corresponds to 10.5 MJ/kg (Heletukha and Zheleznaya, 2007, 2008).

Wood biomass as a fuel is divided into several groups according to its origin: fuel wood specially harvested in the forest, logging waste, wood processing waste etc. Wood chips can be obtained from business wood, from trees felled during thinning of young plantations, from logging waste (twigs, branches). The group of woodworking waste includes wood waste after industrial wood processing (bark, sawdust, shavings etc.). Recently, specially grown fast-growing plants (willow, poplar and paulownia) are also being used to obtain wood fuel.

The moisture content of wood and bark varies widely from 2 to 75 % (Zhovtomir and Nedovesov, 2002). This is explained not only by the presence of water in the biomass structure, but also by the influence of the season, the place of growth, as well as the methods of wood storage and transportation. The heat of combustion decreases with increasing humidity. Wood biomass burning technologies include: burning in a vortex (cyclonic) furnace, burning of atomized raw materials in a burner, burning on a grate; burning of pulverized wood fuel, burning in a gas generator furnace; combustion in a fluidized bed, combustion in a circulating bed (Heletukha and Zheleznaya, 2007, 2008).

Combustion in vortex furnaces is used for sunflower, buckwheat or rice husk biomass particles up to 10–12 mm in size. The vortex method has quite high technological and environmental (in terms of CO) indicators of the furnace process, the possibility of implementation in furnaces of gas-oil boilers with small volumes (Aniskin et al., 2004).

Combustion in vortex burners is used for very small and dry wood waste (moisture up to 20 %). For example, sawdust can be burned in a vortex burner. The advantages of this technology: boiler power is used more efficiently; high boiler efficiency is ensured. It is possible also to burn gas or fuel oil together with biomass. This method requires preliminary grinding and drying of raw materials. So, it is associated with high costs. Therefore, combustion in vortex burners is economically unprofitable (Beloselskyi and Khmelevskaya, 2004).

Direct combustion takes place in furnaces with horizontal, conical, inclined or movable grates. This method is used in water-heating boilers and furnaces of low power (less than 20 MW) for burning wood fuel, including those with high humidity: lumpy and long waste, chips, bark, sawdust, fuel briquettes and pellets, etc. Tubular burners with screw feed are also used for automated burning of shredded waste.

Combustion in a fluidized circulating bed allows achieving greater efficiency and economy due to almost 100 % combustion of fuel with a lower level of emissions of combustion waste compared to direct combustion. This method is used in commercial or municipal heat power stations in the power range from 5 to 600 MW to obtain electrical and thermal energy.

Combustion of gases in the secondary combustion chamber (gas generator furnace) is a two-stage process. At the first stage, the fuel is fed by an auger onto an inclined grate in the primary chamber, where it is heated to a temperature at which the gasification process takes place. Overheated and mixed with secondary air, wood gas burns in the secondary chamber with almost no residue. Waste gases are used in the boiler to generate electricity.

The power range of combustion systems of this kind is from 150 kW to 30 MW. The disadvantage is the high cost.

Combustion of pulverized fuel is carried out with the help of special burners designed for burning wood dust. The entire process, from the initial wood waste, grinding it into dust with moisture content of about 8 %, to feeding and burning the dust, is fully automated. Obtaining energy using only wood dust is used quite rarely. This fuel is usually used in boiler houses or thermal power plants operating on pulverized coal or peat. The disadvantage is also the high cost of complete equipment for burning wood dust. For straw burning, farm straw boilers with a capacity of 1 MW are used. They are divided into boilers of periodic action and boilers with automatic loading of raw materials. Most of the intermittent farm boilers are designed for burning medium and large straw briquettes.

In order to improve the conditions of the combustion process and reduce the emission of particles in the combustion products, the flow rate of the air blast is regulated gradually changing from the upper to the lower section of the boiler. By gradually moving the area of air supply, you can achieve uniform burning of straw briquettes. To ensure thorough mixing of combustion products, air must be supplied in the direction opposite to the exit of flue gases from the boiler furnace (horizontally from the same end of the furnace where the flue gas exit is located, or vertically from top to bottom from under the tubes through which combustion products exit). The moisture content of the straw should not exceed 15–18 %, the efficiency of the batch boiler is about 75 %, and the level of CO content in the combustion products is less than 0.5 % (Suadicani et al., 1993).

Boilers with automatic loading differ in that the installation includes a dosing device that automatically and continuously feeds straw into the boiler. There are dosing devices for whole straw briquettes, chopped straw and straw pellets.

Using straw for direct burning is one way to reduce CO_2 emissions into the atmosphere. Straw, like biomass in general, is a CO_2-neutral fuel, that is, the consumption of carbon dioxide from the atmosphere during the growth of cereal crops corresponds to the emission of CO_2 into the atmosphere during the burning of straw. Taking into account the additional emissions of carbon dioxide that occur during the collection, transportation and preparation of straw for burning, the reduction of CO_2 emissions under the conditions of replacing the coal burned in the boiler with straw is about 90 %.

However, it is difficult to use straw as a fuel both at the stages of collection, transportation and storage, and at the stage of direct burning. This is due to the heterogeneity of the product, relatively high humidity, low volumetric energy content, rather low melting point of ash and high chlorine content, amount of straw and coal. Levels differ in energy content by approximately 10–20 times.

1.2.5. Technologies of pyrolysis

Pyrolysis is an effective method of thermochemical processing of plant biomass, industrial and household waste along with direct burning and gasification. This technology makes it possible to obtain high-quality, environmentally safe solid, liquid and gaseous fuel from almost any raw material (including polymers of artificial origin) containing organic components, since the use of relatively low temperatures means that a small amount of pollutants enters the atmosphere.

Technologies of pyrolysis and fast pyrolysis are the most common. Pyrolysis is associated with the thermal decomposition of organic compounds without air access. The products of pyrolysis are liquid fuel, which was named “bio-petroleum”, and gaseous fuel-pyrolysis gas. The most heat-resistant components of plant biomass, the basis of which is the lignin polymer, remain in a solid state. In terms of physical properties, lignin is close to charcoal and can be used as fuel or as a raw material for the production of various materials.

Production of liquid fuel from lignocellulosic biomass, which can replace oil in various variants, is the main goal of fast pyrolysis. This is its task in contrast to slow pyrolysis, which is also used for biochar production (Yaashikaa et al., 2020).

Pyrolysis is a process of thermal decomposition of organic compounds without access to oxygen and occurs at relatively low temperatures of up to 800 °C, compared to the processes of gasification (800–1300 °C) and combustion (900–2000 °C). Modern biomass pyrolysis technologies can be divided according to the following features: heating rates (fast and slow pyrolysis) and the environment in which pyrolysis occurs (vacuum, hydropyrolysis, methane pyrolysis), by the type of layer (in a fluidized bed, in a fixed bed, in a suspended bed, in a stream of hot air).

In the process of pyrolysis, a gaseous phase is released from solid biomass and gaseous, liquid and solid fuel can be obtained for obtaining heat, electricity, etc. Liquid pyrolysis products have a heat of combustion of 20–25 MJ/kg and consist of a complex mixture of highly oxidized hydrocarbons with a water content of up to 20 % (wt.). Unprocessed pyrofuel is a thick black resinous liquid, the output of which can reach up to 80 % of the dry raw material mass (with rapid low-temperature pyrolysis). The solid products of pyrolysis are a carbonaceous substance with a heat of combustion of 30 MJ/kg, the output of which reaches 30-35 % of the mass of dry raw materials during carbonization and slow pyrolysis.

Gaseous products of pyrolysis are usually medium-calorific gas with a heat of combustion of 15–22 MJ/m^3, and under conditions of partial gasification, low-caloric gas $Q = 4 - 8$ MJ/m^3. The yield of gaseous fuel can reach 70 % of the mass of dry raw materials under the conditions of high-temperature fast pyrolysis. The gas composition depends on the raw materials and process parameters. Calorific value increases if hot gas is used. This gas is used in the pyrolysis process to maintain the temperature of the process and to dry the raw materials.

Several hundred chemical components were found in the composition of pyrolysis products. More and more attention is paid to the regeneration of individual chemical compounds (levoglucosan and hydroxyacetaldehyde) or their families (polyphenols) from pyrolysis products. The higher value of individual chemical products compared to fuel could make it profitable to extract these products even at their small concentrations.

Fast pyrolysis has established itself as a thermochemical biomass conversion technology with significant potential, especially for high yields of liquid fuels and chemical products. This type of pyrolysis is used to obtain the maximum amount of either gas or liquid according to the set process temperature. Low-temperature fast pyrolysis allows maximizing the proportion of liquid product. Fast pyrolysis is the main thermochemical method of direct production of liquid from biomass and waste. Pyrolysis technologies, aimed at obtaining a high yield of pyrofuel, which is easier and cheaper to transport than biomass itself, have the greatest perspective for obtaining energy from biomass. Pyrofuel has a high energy density (28 GJ/m^3) compared to the raw material (2 GJ/m^3) for straw and 8 GJ/m^3 for wood chips (Nekrasov, 1992).

Deterioration of the quality of pyrofuel can occur at temperatures above 100 °C, which adversely affect the physical properties of the liquid (viscosity increase, phase separation, deposition of bituminous sediment due to polymerization). Water, methanol or ethanol is added to reduce the viscosity of the pyrofuel. The quality of the fuel also deteriorates during contact with air, but at a lower rate than when the temperature increases. The quality of pyrofuel obtained by pyrolysis of biomass may not be sufficient for its commercial use (in engines). The main characteristic that worsens the quality of pyrofuel is high oxygen content – 25–40 %. Improvement of the quality of liquid pyrolysis products is based on traditional hydrogenation or on zeolite technology aimed at reducing oxygen in the fuel (Sharma et al., 1993). Hydrogenation is carried out in the vapor or liquid phase, passing hydrogen through a liquid mixed with a catalyst. Processing of pyrofuel allows reducing the oxygen content to 2.2–3 % with the tetralin catalyst and to 4.7 % without the catalyst. Zeolite cracking is based on the use of synthetic zeolite (aqueous aluminosilicates of sodium and calcium). When the quality of wood and rice husk pyrolysis products is improved by zeolite cracking, a small yield of pyrofuel occurs (it will increase if cracking is carried out in the presence of water vapor). None of the technologies for improving the quality of pyrofuel have yet received reliable data on the mass balance in the considered processes and on the operation of installations at a commercial level (Bridgwater, 2002). Fast pyrolysis technologies are taking the first steps in Ukraine. Biomass waste from agricultural production (straw, corn stalks and cobs, sunflower stalks and husks and other biomass waste from agricultural production) form the basis of the biomass potential in Ukraine. Pyrolysis of biomass waste from agricultural production is practically the only possible technology for use in transport installations, since direct combustion and gasification technologies do not have a consumer for production heat and generator gas directly in the places of biomass collection (growing). The use of transport units will also significantly reduce the cost of energy produced from biomass due to the absence of capital and operating costs for briquetting, storage and drying of biomass.

Fast pyrolysis of plant materials, for example wood or nut shells, at temperatures of 800–900 °C leads to the formation of 10 % of solid charcoal and turns 60 % of the raw material into gas, which contains a large amount of hydrogen and carbon monoxide.

At this time, traditional pyrolysis is considered the most attractive type. The use of relatively low temperatures means that a small amount of pollutants enter the atmosphere compared to incineration. This circumstance gives an ecological advantage in the processing of some types of waste.

1.3. Raw material base of Ukraine

Biofuel feedstocks can be divided into 4 broad categories: 1) highly efficient feedstocks (palm oil, sugar cane); 2) raw materials with moderate efficiency (corn, soybeen, rapeseed, sugar beet); 3) raw materials (sweet sorghum, jatropha); and 4) special energy crops (switchgrass, miscanthus, tree plantations of fast-growing short-rotation crops, algae etc).

Agricultural waste is the main source of biomass in Ukraine. The main types of crop production waste in the agro-industrial complex, which are used for the production of solid, liquid or gaseous biofuels, are straw, chaff and husks of grain and cereal crops, husks, stems and leaves of agricultural plants, corn cobs and corn husks, bonfire of flax and other plant materials (Schreider, 2013).

Crop production waste and special energy plant resources are raw materials for the production of solid fuel: fuel pellets or briquettes. According to their characteristics, fuel pellets compete with natural gas, and in terms of environmental indicators, they surpass all other types of fuel.

Perennial grasses can be grown on marginal lands due to its ability to withstand diverse conditions, C4 photosynthetic pathway, greater nutrient and water-use efficiency, high yields, and low maintenance life cycle compared to agronomic crops (Berdahla et al., 2005; Heaton et al., 2008; Pimentel et al., 2008; Cheng, 2010). These grasses are very fast-growing (harvesting rotation is 1year) which tend to protect against soil erosion and can be commercially grown on land that is not rough to be planted and harvested by machinery. Established stands have root productivity commensurate with shoot production, making them a valuable soil carbon sequestration tool (Dohleman et al, 2009).

Marginal lands are often associated with low fertility, acidity, or heavy metal toxicities (Raut et al. 2010). Growing perennial grasses on marginal lands will require nutrient inputs or soil amendments (e.g. lime application) that, if provided using traditional fertilizer and lime sources, will add substantially to overall costs as well as require large amounts of energy (i.e. C inputs) for production and transportation. It makes sense to investigate the use of what are often called "waste nutrients" that are locally or regionally available to promote high yields of biofeedstock crops (Islam & Weil, 2000). Commercial recycling of nutrients can also contribute to the overall economic activity of a region.

Biosolids is a nutrient-rich wastewater product that can improve and maintain productivity of marginal lands. As biosolids application will not be associated with food crops or livestock, there would be minimal risk of food contamination. As municipalities nationwide face growing populations (meaning more waste), they are pleased with any opportunity to recycle biosolids in a positive, environmentally friendly, and productive way. Similarly, electricity-producing utilities face a similar problem from SO_2 emissions when burning high sulfur (S) coal.

The Ukrainian energy industry is in transition to use second generation trees/crops biomass as biofuel and bio-based materials. Currently, we have established two model experiments with second generation energy crops on reclaimed mine-lands, one in the Nikopol manganese ore basin and the other one in the Western Donbass Coal deposit.

The use of raw materials in the construction industry is also promising. For example, building blocks are made from pressed straw. Rye, flax or wheat straw is well suited for these purposes. The use of hay and reeds is also possible. Straw is pressed mechanically or manually on special presses. The compressed block is tied with a metal wire or nylon cord. Advantages of straw blocks: low cost (a straw block is about 1,000 times cheaper than a brick), good thermal conductivity and sound insulation (the thermal conductivity of straw is 4 times lower than wood and 7 times lower than bricks). This leads to a reduction in the cost of heating buildings), availability of materials, durability (retains properties for up to 100–150 years), low weight (buildings made of straw blocks do not need a heavy foundation, and for construction – lifting mechanisms), low labor costs. Disadvantages include high flammability and fire hazard. Construction requires careful observance of technologies and fire safety measures. The straw must be dry, and the blocks must be tightly pressed.

Plant raw materials are also promising in the production of various biopolymers. It is known that the annual production of polymers in the world as packaging materials is about 130 million tons. The terms of decomposition of polymer packaging are tens and hundreds of years. In connection with the aggravation of the ecological situation, the production of bio-degradable packaging from natural biopolymers is becoming widespread.

The most common biopolymers include polymers of lactic acid – polylactate. Raw materials for their production are corn, sweet sorghum and reed waste, etc. Lactic acid polymers are obtained by fermentation of vegetable carbohydrates – hydrolyzates of sucrose and starch. Polylactates have good physical and mechanical properties: high rigidity, transparency, gloss, preservation of the shape of the product after crumpling or twisting (50 % higher compared to traditional plastics), amenable to processing on traditional extrusion and blowing equipment, highly ecological (emissions of CO_2 into the atmosphere with calculation per 1 ton of biopolymer is 25–30 % less compared to linear low-density polyethylene), energy consumption during the production of biopolymers is 20–30 % lower compared to synthetic plastics.

The basis of another class of biopolymers is starch obtained from the waste of grain crops, potatoes and corn. In compost, this type of biopolymers decomposes in less than 12 weeks, which meets European standards.

Biopolymers polyhydroxyoxanoates (PA) belong to the class of aliphatic polyesters based on hydroxycarboxylic acids. These are polyester compounds produced by various microorganisms. For example, poly-3-hydroxybutyrate is a natural energy storage product of bacteria and seaweed in the cell cytoplasm.

PGA biopolymers are completely degradable. They are close in their properties to ordinary polymers. Mixtures of polymers, of which one component is synthetic and the other natural, are also used. The natural component provides the composition with the effect of biodegradation, the synthetic one – the necessary complex of operational and consumer properties. The polymer matrix is polyethylene and polypropylene waste with a processing temperature not higher than 120–230 °C to exclude thermal destruction of the filler. Plant waste can also be used as a filler: sunflower husk, rice husk, buckwheat husk, millet husk, potato pulp, corn pulp, beet pulp, etc.

Taking into account the current situation in the biomass market, it is expected that in the near future there will be companies specializing in the supply of biomass to the final consumer. As a result, it is possible to introduce a system of long-term contracts and a wider use of agricultural waste for the production of energy and biomaterials. The feasibility of creating new technologies is determined by favorable environmental conditions for the use of renewable energy sources and the availability of an industrial base.

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2. ECOLOGICAL ASSESSMENT OF THE POST-MINING LANDS

2.1. General characteristics of research areas

The research was conducted in the north and south of the Dnipropetrovsk province in the conditions of the Pavlograd research center and the Pokrov education and research station for land reclamation of the Dnipro State Agrarian and Economic University. The physical and geographical features of the study area are typical for the steppe zone of the southeast of Ukraine (Horb, 2006; Horb and Moroz, 2009). The main climatic features are the lack of precipitation with a sufficient amount of heat and light during the growing season of plants. The flat nature of the territory creates conditions for the unimpeded penetration of air masses with different properties. Intensive cross-latitude air exchange caused by cyclonic activity is observed in winter. Despite the relatively low frequency of arctic invasions (15 %), they play a significant role in the temperature regime, because the lowest air temperatures are associated with them. The temperature drop in the case of such invasions occurs quickly and can reach 20–25 °C per day (Pavlov and Peremetchyk, 2000). The frequency of tropical air in the Dnipropetrovsk province is also insignificant and is within 14–15 %. More often, the air of moderate latitudes is located over the region (70 %). The average annual air temperature varies within +7+9 °C. The coldest month is January, the average daily temperature of which is –5–7 °C, and the warmest is July with a temperature of +2+24 °C. An increase in the average monthly air temperature by 1–1.5 °C has been observed in recent years (Fig. 2.1).

On average, the activity of various winds in Dnipropetrovsk province is almost the same throughout the year. Winds from the southeast and northwest quarters (14–15 %) are dominant. The average annual wind speed in the region is 10 m/s. The duration of wind at a speed of 15 m/s (in different areas of the region varies from 10 to 25 days. The snow cover is not stable.

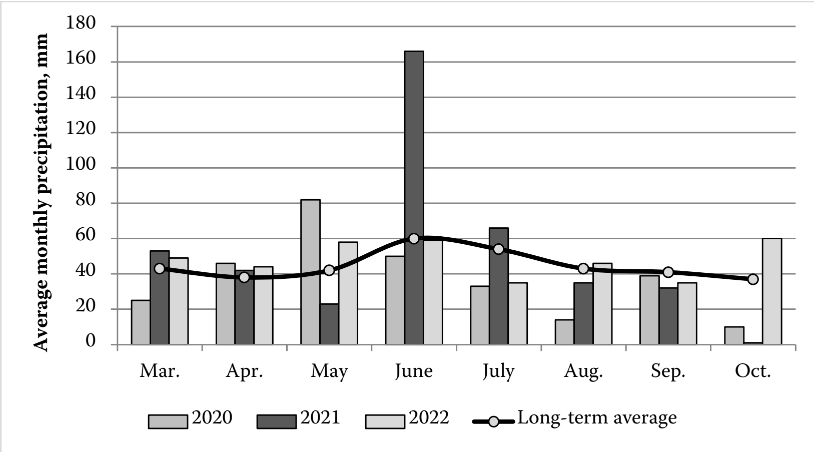

Fig. 2.1. Dynamics of the average monthly temperature for three years, °C

The duration of winter is 3–3.5 months. Frequent thaws, fogs, and ice are a feature of this period. Spring is short. Weather conditions are characterized by sharp variability. Strong gusty winds are observed, mainly from the south-west direction. They are sometimes accompanied by dust storms. The summer is moderately warm, sometimes hot, often dry, begins in the first decade of May, and ends in the third decade of September. North-western currents prevail during this period. The duration of the autumn season is determined by the period when the average daily air temperature drops from +15 °C to 0 °C. Atmospheric processes in autumn are similar to those in spring, but develop in the reverse order. During this period, south-west and north-west winds prevail.

Frosts are noted at the beginning and at the end of the warm season, with the exception of June-August. The duration of the frost-free period is about 120 days (Horb, 2006).

The steppe zone of Ukraine is characterized by rather arid conditions. The average annual precipitation usually does not exceed 550–560 mm

(Fig. 2.2). Rainfall is not regular. They can have a torrential nature. Droughts often occur during the growing season The uneven nature of precipitation is one of the unfavorable factors for plants.

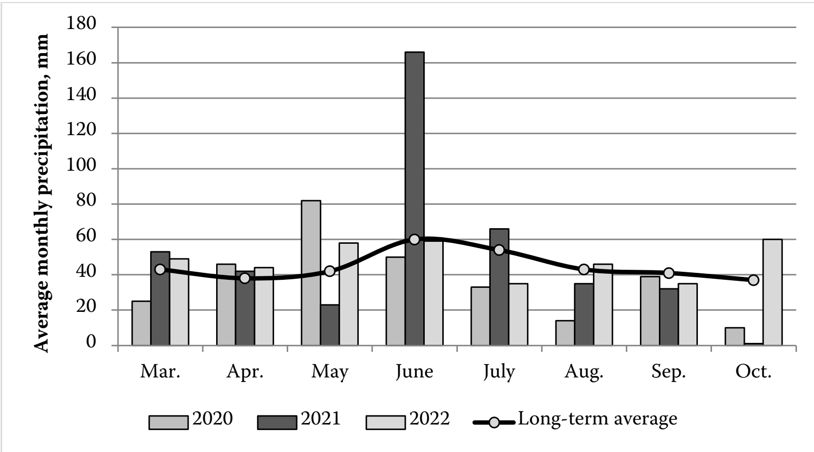

Fig. 2.2. Dynamics of average monthly precipitation over three years, mm

Dnipropetrovsk province is located within the Eastern European platform. Its relief belongs to two types of landscapes: watershed-beam and valley-terrace. Soil-forming rocks are anthropogenic sediments dominated by loess. The texture of the loess changes from heavy loam in the conditions of the watershed plateau to light loam in the direction of the river valleys. A large amount of calcium carbonates is characteristic of loess. Calcium carbonate fixes the organic mass, which is why black soils are widespread on loess. They were formed on ancient river terraces, at watersheds on sandy-clay parent rocks under the influence of meadow and steppe vegetation (Tsvetkova et al., 2016; Bozhko, 2014).

In the Right Bank and in the northern part of the Left Bank, where the influence of loess is observed, leached black soils are widespread. In the south of the region, there are typical thick and ordinary black soils. The territory of the city of Dnipro is located on the border between the distribution zone of ordinary low-strength black soils and ordinary medium-strength black soils. Along the valley of the Dnipro River on both sides, in a strip of up to 30 km, there are black soils with a lighter soil texture: sandy, light loam and medium loam. In the conditions of impermacid moisture, black forest soils are formed (Belova, 1997; Bogovyn et al., 2003). Gray forest soils are widespread in the northern regions. Dark chestnut soils in the Dnipropetrovsk province are located south of the Orel and Samara rivers (Tsvetkova et al., 2016). Soils in the region can be divided into 4 groups. These are natural undisturbed, anthropogenic-surface-transformed natural soils, anthropogenic-deep-transformed and man-made surface soil formations (Mirzak, 2001; Kobets et al., 2013). Natural soils preserve the normal occurrence of natural soil horizons and are concentrated in urban forest and park areas. Anthropogenic surface-transformed natural soils contain a diagnostic horizon < 50 cm thick and the lower part of the profile. Anthropogenically-deeply-transformed soils form a group of properly urban soils, where the diagnostic horizon has a thickness of > 50 cm. Surface soil formations are bulk, mixed, alluvial formations, completely created by man (artificially created soil-like formations). Anthropogenically disturbed soils are often contaminated with heavy metals or other pollutants (Hrygorenko et al., 2009; Kroik et al., 2010; Kharytonov and Shupranova, 2012). Thus, the land cover of urban areas is formed under the combined influence of zonal-climatic and environment-changing anthropogenic factors.

From a botanical and geographical point of view, the research region is located within the subzone of multigrass-sedge steppes. The influence of the subzone on the taxonomic composition of the vegetation is very great. The main life form of the vegetation of the steppes is represented by narrow-leaved, dense-grass grasses: furrowed sedge, combed sedge, common bearded sedge, Lessing's gorse, hairy, feathery. Various grasses are represented by alfalfa, fennel, sedge, viper, clover, etc. Poorly diverse grass steppes are located in the zone of southern black soils and dark-chestnut soils. Dense grasses dominate here. Dicotyledonous xerophytes such as soft yarrow, curly pyrethrum, woolly bramble are found as admixtures.

2.2. The main processes of reclamation of disturbed lands during mineral extraction

Mining activities can cause drastic disturbances in soil properties, which adversely affect the nutrient cycling and soil environment. The suitability of rocks taken up to the day surface as a result of open mining for biological reclamation is determined by their physical, chemical and biological properties (Legwaila et al, 2015). Destruction and grinding of the soil structure at the initial technological stage is due to the use of a rotary complex (Vondráčková et al., 2017). This process leads to an increase in the content of small particles of different quality rocks and black soil. As a result, the water characteristics of the substrates also change. The study of physical properties of reclaimed land depends on the specific indexes of substrates, the method of their formation and biological development. The technology of creating model two and multilayers lyzymeter and field experiments determines the differentiation of the density, porosity, aeration borehole, humidity state along the artificial reclamation profile. In the process of open-pit mining, the hydrological regime of not only waste dumps, but also the environment is violated (Kuter, 2013). The availability of moisture to plants is largely due to its movement in specific ground conditions. Water characteristics depend on the soil texture. Water in the soil is in continuous motion: it accumulates and is consumed, turns from one form to another, and is used by plants. As a result of the functioning of the root systems of plants and various physiological groups of microorganisms, enzymes accumulate, which are accumulated by the organo-mineral part of edaphotops. These functional manifestations are the ecological basis that contributes to the restoration of ecosystems and are an integral part of the ecological rehabilitation of used land (Sheoran et al., 2010). The correlation analysis shows that soil organic carbon contents in aggregate fraction of 0.25~0.5 mm were correlated with aggregate distribution and enzyme activities (Yin et al., 2016). The non-top -soiled areas, even after 6, 7 and 8 years, appeared to have lower enzyme activities than the younger top soiled areas or the undisturbed soil. The effects of top-soiling and reclamation age on dehydrogenase, nitrogenase, phosphatase, arylsulphatase, amylase, cellulase, invertase and urease activities were evaluated on three reclaimed non-top-soiled and five reclaimed topsoiled areas and compared with an undisturbed reference soil (Fresquez et al., 1987). Optimization of the properties of model structures of technosols in the process of long-term biological reclamation and use is slow. After all, enzymes significantly affect the biochemical processes, and subsequently the level of culture of the microorganisms. The main objective is to study water-physical, nutrition regimes and oxidizing-reducing conditions the phytomeliorated rocks of Nikopol manganese ore mining basin.

The land cover undergoes significant damage in the process of extracting minerals, especially in open pits. The technological processes of open field development are accompanied by disturbance of the soil cover, changes in hydrogeological and hydrological regimes, the formation of man-made relief, and other qualitative changes that worsen the environment. As a result, the territories remaining after the extraction of mineral raw materials are usually wastelands with areas of bare land, loose piles of disturbed soil, and large volumes of rock dumps brought to the surface (Masyuk, 1974; Sheoran et al., 2010; Menendez & Loredo, 2018). Given that high-quality ores are exhausted, and the content of useful components in them decreases, the share of waste and empty rocks is constantly increasing. Most of the mining waste enters into an active interaction with the environment (lithosphere, atmosphere, hydrosphere and biosphere). During storage, all mining waste is subject to changes caused by both internal physico-chemical processes and the influence of external conditions. As a result, new ecologically hazardous substances can be formed in the places where these wastes are stored, and when they enter the biosphere, they can cause a great threat to the biota (Boruvka et al., 2005; Navarro et al., 2008).

Land restoration is a complex of engineering, mining, reclamation, biological, sanitary-hygienic, and other measures aimed at returning territories disturbed by industry to various uses: agricultural, forestry, recreation areas, etc. It is known that reclamation works take place in several stages. The main ones are the stages of mining and biological (forestry and agricultural) reclamation (Kuter, 2013). Mining reclamation is rightfully considered the most mass-intensive and energy-intensive stage (Dryzhenko, 1985). This is due to the movement and stacking of large masses of rocks and the humus layer of soil removed before development in a certain order.

The most difficult are the works related to increasing the fertility of the top layer of dumps, improving its hydrophysical properties (Legwaila et al., 2015). The possibility of migration of acid solutions to the surface of the dump is not excluded if the lower layers consist of particularly toxic rocks. The ultimate goal of the mining stage of reclamation is to create an underlying layer of overburden of the necessary strength on disturbed lands, and to apply a humus layer of soil or potentially fertile rocks suitable for biological reclamation to its surface. It is most expedient to carry out the mining stage of reclamation in one cycle with the development of minerals to include it in the technological process of production.

The biological stage of reclamation, which is carried out after the complete completion of mining, involves the restoration and formation of the soil cover, the accumulation of humus and nutrients. This process is facilitated by the sowing of perennial leguminous and cereal grasses or their mixtures, which create favorable ecological and biochemical conditions for soil genesis (Eterevskaya, 1974; Demidov et al., 2013). Phytostabilization and phytoextraction methods are successfully used for detoxification and removal of toxic metals from landfills. The introduction of various ameliorants and chelates contributes to a more intensive absorption of heavy metals by plants from technozems (Wong, 2003; Le et al., 2017).

During the open mining of minerals, rocks of past geological eras are brought to the earth's surface. They are subjected to further intensive weathering due to the interaction of the surface layers of the litho-, hydro- and atmosphere. Reclamation processes have been going on for several decades. Meanwhile, technogenic edaphotopes formed during this period differ significantly from zonal soils in terms of fertility, physical, physicochemical, agrochemical, and other ecologically important indicators.

Important edaphic characteristics of the substrates used in the construction of technosols are their agrophysical properties, both in an undisturbed state and at various stages of reclamation works. The physical properties and regimes of technosols receive the greatest transformations as a result of the interaction of climatic and biological factors. The substantiation of such a diagnosis of the regimes of various technosols is possible only with a thorough study at various stages of their biological development.

2.3. Physico-chemical and biological testing of phytomeliorated mining rocks of the Pokrov land reclamation station

The terrain of this area is mainly flat. Within the plains of the Lower Dnieper, three levels of terraces are found with extreme clarity, which can be traced over considerable distances. The third terrace of the Dnipro can be traced in its hollow part, and further down the Dnipro, it stretches in fragments to the Tomakivka River, and south of Nikopol it has a continuous distribution. Here the terrace also enters the Chortomlyk and Bazavluk river valleys. In the area between the villages of Kapulivka and Pokrovske, the terrace forms a wide platform, the edge of which rests on the slope of the watershed of the rivers Chortomlyk-Bazavluk. In the southern direction, the terrain gradually decreases to the valley of the Bazavluk River.

The highest points of the terrain are located in the north and northwest of the manganese ore mining pits, where they reach +60 m

The main soils are southern black soils. They contain an average of 3–4 % humus. The thickness of the upper humus horizon is 30–35 cm, the humus profile 62–74 cm. This structure of the soil profile when setting aside areas for mining development determines the depth of preventive removal of the upper layer with a thickness of 50 to 60 cm. Lower horizons with a content of less than 1 % humus are impractical use for land reclamation. Due to the decrease in the humus content, the water resistance of structural aggregates is noticeably reduced, as a result of which the upper horizon is more scattered and prone to siltation and compaction.

It was noted that the arable layer of southern black soil contains easily hydrolyzed nitrogen 6.2–8.8, mobile phosphorus 10–12, exchangeable potassium 14.8–24.6 mg in 100 g of soil. The sum of absorbed bases (Ca^{2+} + Mg^{2+}) is 32.8–34.5 mg-equiv./100g of soil. The acidity values of the investigated technosols vary from 7.3 to 7.9. In the area of manganese ore mining, there are also eroded soils, which, in contrast to full-profile soils, are characterized by a lower strength of the soil profile, a low content of humus, exchangeable cations, and worse physical and agrochemical properties.

Precambrian crystalline rocks, sedimentary deposits of the Neogene, Paleogene and Quaternary ages take part in the geological structure of the

Nikopol manganese ore basin. The stratigraphy of the Nikopol manganese ore basin is shown in Table 2.3.1.

Table 2.3.1

Rock deposits stratigraphy

Age	Depth, m	Name of substrate
Q	0–7	Black soil, loess-like loam
N_2SQ	7–12	Red-brown loam and clay
N_1Srm_{2+3}	12–47	Grey-green clay
N_1Srm_{1+2}	47–63	Sand-clay deposits
Pg_1ch_3	63–71	Green montmorillonite clay
Pg_1ch_3	>71	Manganese ore

Q – quaternary; N_2 – Pliocene, upper (late) Neogene; N_1 – Miocene, lower (early) Neogene; Srm_1 – lower Sarmat; Srm_2 – middle Sarmat; Srm_3 – upper Sarmat; Pg_3 – Oligocene, upper Palaeogene.

Accepted conventional meanings for the substrata as following: SBS – southern black soil; LLL – loess-like loam; RBL – red-brown loam; RBC – red-brown clay; GGC – green-grey clay; GMC – green montmorillonite clay; AAS – ancient-fluvial sand; DGSC – dark-grey schist clay.

The manganese ore layer is associated with Paleogene sediments. The Lower Sarmatian, which lies at the top of the Paleogene, is widespread and consists of loams that pass downwards into medium- and coarse-grained sands (Fig. 2.3.1).

Middle Sarmatian was formed by two horizons: a horizon of dark gray and black clays and a horizon of limestones. Upper Sarmatian consists of marly clays. They are dense, sometimes cracked. Red-brown clays lie on the upper layer of the Sarmatian. They are dense, contain calcareous concretions and gypsum crystals. Post-Pliocene, Pleistocene and Holocene Quaternary sediments are placed above the red-brown clays. The lower part of the Quaternary period (post-Pliocene) contains ancient alluvial sands and clays (on the terraces), as well as red-brown loams (on the watershed). Post-Pliocene sediments are covered by a continuous cover of carbonate, macroporous loess-like loams and loess

Fig. 2.3.1. Panorama of the upper stratigraphic layer of rocks deposit

of Pleistocene age. The latter occupy the entire territory of watersheds up to 15–20 meters thick.

The soil mass was taken off, piled up and heaped onto the land after the rock has been replaced (Fig. 2.3.2).

Substrates formed in this way can be attributed to the category of technosol. Technosol are soils dominated or strongly influenced by human-made materials and correspond to soils whose properties and pedogenesis are dominated by technical origin. Their parental material is made of all kind of materials made or exposed by human activity that otherwise would not occur at the Earth's surface.

Fig. 2.3.2. Land reclamation process and soil storage in the day surface

On the basis of the described climatic conditions, soils and vegetation, two conclusions can be drawn: a) relatively fertile soils with humus reserves of 170–210 t/ha were formed in the territory of the Nikopol manganese ore basin; b) lack of water is a condition that limits the possibility of plant vegetation. Therefore, the selection of agricultural crops for reclaimed land should be carried out taking into account their relation to moisture. Plants should, as a rule, be located in the interval between xerophytes and mesophytes, that is, include xerophytes, xeromesophytes, mesoxerophytes and mesophytes.

Previous DSAEU research (Tarika and Zabaluyev, 2000) has shown that the initial 10–12 years of biological reclamation should use a cycle of alfalfa followed by sainfoin (or vice versa), and that subsequent cycles should use a grass-legume mix (Fig. 2.3.3).

The forecast of the duration of the formation of the moisture reserve in the case of artificial water aquiclude was performed for the conditions of the Northern Steppe of Ukraine, taking into account the difference between

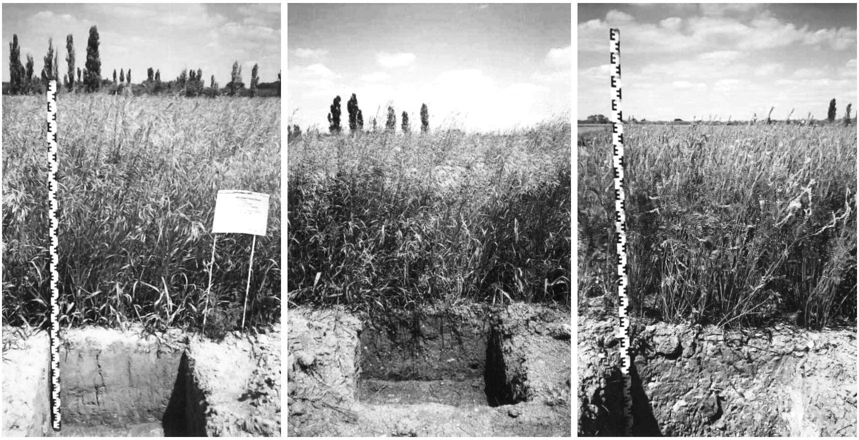

Fig. 2.3.3. Artificial Profiles of Rocks after Long-Term Plant Melioration

precipitation and evaporation. The change in the groundwater level is indicated as Δh (Kharytonov et al., 2013):

$$\Delta h = \frac{\varepsilon \cdot t}{\mu}, m / year,$$

where ε – infiltration nutrition in natural conditions;
t – time, days;
μ – coefficient of lack of soil saturation in the aeration zone.

Moisture transpiration velocity (V) formula was applied for comparison of the components of rain precipitation and moisture losses due to evaporation and vegetation transpiration in agroecosystem:

$$V = \frac{P - (E + T)}{1000 \cdot D},$$

where *P* is rain precipitation, *mm*,
E – evaporation, *mm*,
T – transpiration (moisture transfer with crops harvest),
D – the amount of days in a year.

Moisture transpiration with crops harvest was calculated by multiplying annual crops harvest to water absorption ratio. The results of calculations of the ground water rise time to the day surface for profiles with a water aquiclude at three land reclamation stations of DSAEU are shown in the table 2.3.2.

Table 2.3.2

Calculations of the time of formation of reserve moisture in reclamation profiles with artificial clay aquiclude

Site	Profile	Depth, cm	t, year
Vylnogyrsk	30 cm LLL	30	1.3
	10 cm Sand + 30 cm LLL	40	4.2
	30 sand + 40 LLL + 50 BS	120	13.4
	50 LLL + 50 BS	100	5.1
Pokrov	50 LLL + 50 BS	100	5.1
Pavlograd	50 LLL + 50 BS	100	6.6

Notes: LLL – loess-like loam; BS – black soil; t – time of formation of the reserve moisture, years

It should be noted that the rock materials ability for using as a water aquiclude depends on the specific geological conditions of mineral deposit exploration in each case. Red-brown clay can be used in Volnogorsk and Pavlograd mining regions, gray-green and green free carbonated clay – in Pokrov city. It is necessary to provide the creation of artificial drainage in order to avoid any risk of swamping during reclamation profile forming with a water aquiclude. Restoration of disturbed land means the creation of a flat terrain with slopes of the earth's surface, from 0°30 seconds to 1.5°, the organization of runoff and removal of precipitation. This is a guarantee of restoration of disturbed lands due to the process of forming a reclaimed layer with a capacity of 1.0–1.2 m, using the rocks most suitable for crops cultivation. Loess-like and red-brown loams with 34–44 % silt content meet these conditions. Meanwhile, red-brown loams in natural conditions are water-containing rocks of the upper waters and lie above water-resistant red-brown clays. This is why they are often salted. Therefore, a more susceptible way is to use them in a mixture with loess like loam. The process of land reclamation in the conditions of the steppe zone of Ukraine makes sense if the special measures for drainage management to avoid runoff and precipitation removal were provided. The use of an artificial water barrier can be considered as a low-cost water saving technology. Incorporation of artificial drainage is a necessary measure to protect the mine workings from the rise of groundwater and drip irrigation application.

2.4. Forecast of ground water level dynamics taking into account natural lateral spreading for reclaimed dump without drainage with irrigation

The forecast of the dynamics of the ground water level (taking into account the natural lateral spreading) was carried out for a reclaimed dump with a width of 100 m and a length of 200 m. The hydrodynamic scheme "rectangular irrigation section in an unlimited reservoir" can be applied in this case (Fig. 2.4.1).

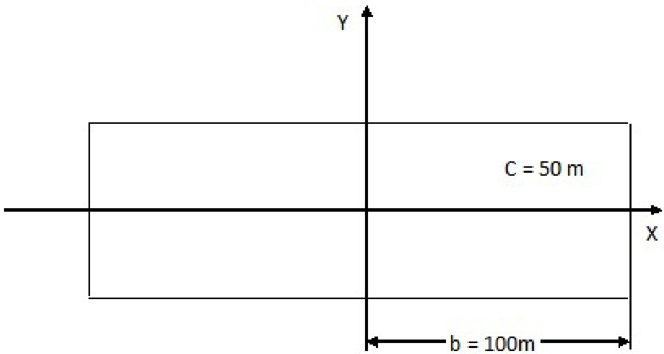

Fig. 2.4.1. Scheme "rectangular irrigation plot in an unlimited layer"

This scheme solution is as follows:

$$z = 0,25\frac{\varepsilon \cdot t}{\mu}\left[I(\eta_{,x} m_1) - I(\eta_x, m_2) - I(\xi_x, m_3) + I(\xi_x, m_4) \right],$$

where z – increase in water level under the influence of infiltration. Value of coefficient m according to formula, the following:

$$m_1 = \frac{y+c}{x+b} = 0.5\,;\ m_2 = \frac{y-c}{x+b} = -0.5\,;\ m_3 = \frac{y+c}{x-b} = -0.5\,;\ m_4 = \frac{y-c}{x-b} = 0.5\,.$$

Value of coefficient η_x and ζ_x the following:

$$\eta_x = \frac{x+b}{2\sqrt{at}} = 0.64\,;\ \zeta_x = \frac{x-b}{2\sqrt{at}} = -0.64\,.$$

Initial data: C = 50 m, b = 100 m; t = 365 days.

Detailed function was compiled according to the calculated data. We used the numerical values of the function when $m \leq 1$.

The calculation was performed for the maximum elevation point with coordinates: x = 0, y = 0. Calculation example:

$$I(\eta_x, m_1) = I(0.64:0.5) = 0.461\,,$$

$$z = 0.25\frac{\varepsilon \cdot t}{\mu}\left[I(\eta_{,x} m_1) - I(\eta_x, m_2) - I(\xi_x, m_3) + I(\xi_x, m_4)\right] =$$

$$= \frac{0.25 \cdot 1.64 \cdot 10^{-4} \cdot 365}{0.03} \cdot 0.461 \cdot 4 = 0.922\,m\,.$$

So, the rise of groundwater will be 0.922 м.

The level of underground outflow of irrigation water outside the zone of formation of the initial “hump” (Fig. 2.4.2) for time t can be represented by the equation:

$$z = 0.25\frac{\varepsilon \cdot L^2}{T}\ [F\ (x_1^1, y_1, \tau) + F(x_1^{11}, y_1, \tau) - F(x_2^1, y_1, \tau) - F(x_2^{11}, y_1, \tau) -$$
$$F(x_1^1, y_2, \tau) - F(x_1^{11}, y_2, \tau) + F(x_2^1, y_2, \tau) + F(x_2^{11}, y_2, \tau)]$$

Initial data. Plot dimensions: width – 100 m, length – 200 m

$$b_1 = 0\,;\ b_2 = L\,, b_1 < x < b_2\,;\ b_1 < x < L\,;\ -c < y < c\,,$$

$$L = 100;\ C = 90;\ X = 50;\ Y = 0;\ b_2 = L,\ b_1 = 0.$$

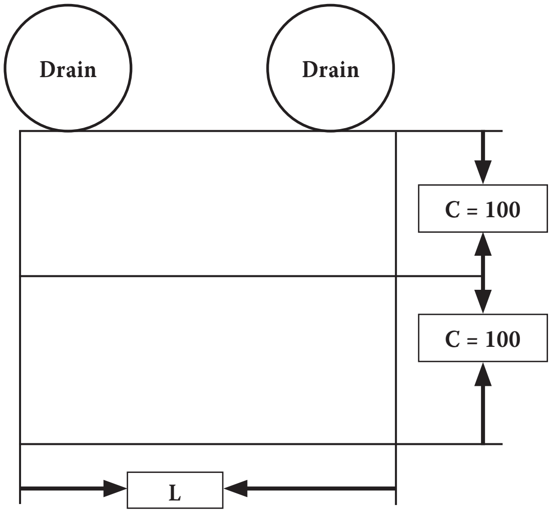

Fig. 2.4.2. Scheme of underground outflow of irrigation water outside the site

The solution of the infiltration rectangular section in a formation-strip with boundaries of the 1st kind was used to assess the level of ground water, modified for the proposed scheme of reclamation of rock dumps with irrigation against the background of horizontal drainage. The solution has the form:

$$z = 0,25\frac{\varepsilon \cdot L^2}{T}\,[F\ (x_1^1, y_1, \tau) + F(x_1^{11}, y_1, \tau) - F(x_2^1, y_1, \tau) - F(x_2^{11}, y_1, \tau) -$$
$$-F(x_1^1, y_2, \tau) - F(x_1^{11}, y_2, \tau) + F(x_2^1, y_2, \tau) + F(x_2^{11}, y_2, \tau)],$$

where $F\,(x, y, z)$ – the tabulated function.

Value of coefficient x_1^1, x_1^{11}, x_2^1 and x_2^{11} according to formula (3), the following:

$$x_1^1 = \frac{x + b_1}{L} = 0,5\,;\ x_1^{11} = \frac{x - b_1}{L} = 0,5\,;\ x_2^1 = \frac{x + b_2}{L} = 1,5 \text{ та } x_2^{11} = \frac{x - 100}{100} = -0,5\,.$$

The following sequence of calculations using the formula (5) is as follows:

$$\tau = \frac{a \cdot t}{L^2};\ T = 2{,}2;\ A = \frac{k_1 \cdot m_1}{\mu_1} + \frac{k_{2.} \cdot m_2}{\mu_2} = 16{,}7;\ t = 1 \text{ year};$$

$$\tau = \frac{a \cdot t}{L^2} = \frac{16{,}7 \cdot 365}{10000} = 0{,}61;\ y_1 = \frac{0 + L}{100} = 1{,}0;\ y_2 = \frac{y - L}{L} = -1{,}0;$$

$$F(x_1^1, y_1, \tau) = F(0{,}5;1{,}0;0{,}61) = 0{,}0605;\ F(x_1^{11}, y_1, \tau) = F(0{,}5;1{,}0;0{,}61) = 0{,}0605,$$

$$F(x_2^1, y_1, \tau) = F(1{,}5;1{,}0;0{,}61) = 0{,}015;\ F(x_2^{11}, y_1, \tau) = F(-0{,}5;1{,}0;0{,}61) = -0{,}06,$$

$$F(x_1^1, y_2, \tau) = F(0{,}5;-1{,}0;0{,}61) = 0{,}06;\ F(x_1^{11}, y_2, \tau) = F(0{,}5;-1{,}0;0{,}61) = -0{,}06,$$

$$F(x_2^1, y_2, \tau) = F(1{,}5;-1{,}0;0{,}61) = -0{,}015;\ F(x_2^{11}, y_2, \tau) = F(-0{,}5;-1{,}0;0{,}61) = 0{,}015,$$

So, the rise of ground water against the background of drainage is determined after the calculations as follows:

$$z = 0{,}25 \frac{\varepsilon \cdot L^2}{T} [F\ (x_1^1, y_1, \tau) + F(x_1^{11}, y_1, \tau) - F(x_2^1, y_1, \tau) -$$

$$F(x_2^{11}, y_1, \tau) - F(x_1^1, y_2, \tau) - -F(x_1^{11}, y_2, \tau) + F(x_2^1, y_2, \tau) +$$

$$F(x_2^{11}, y_2, \tau)] = 0.25 \frac{1.64 \cdot 10^{-4} \cdot 10^4}{2.2} \cdot 0.286 = 0.05 m / year$$

The calculation is made for a period of one and ten years. Thus, for one year, the rise against the background of drainage will be 0.05 m, and for 10 years (stabilization time) z = 0.2 m.

Irrigation justification on the reclaimed heap of the Zaporyzhya quarry of the Pokrov mining enterprise of the Nikopol manganese deposit was performed for a site located on the territory of the reclaimed heap of Zaporyzhya quarry of the Nikopol manganese ore deposit. The planned area of 16 hectares was planted with alfalfa. The substrates brought to the surface of the day surface were represented by a mixture of overburden rocks with different degrees of predominance of loess like, red-brown loams and clays. Alfalfa irrigation at the experimental site was performed using a sprinkler. Water was supplied to the sprinkler by a pump through a pipeline. The irrigation rate was 400–500 m^3/ha. The dynamics of the ground water level for the new reclamation station without drainage with irrigation of 16 ha (width – 200 m, length – 800 m) was quantitatively characterized by the hydrodynamic scheme (Fig. 2.4.3) "rectangular irrigation section in an unlimited layer".

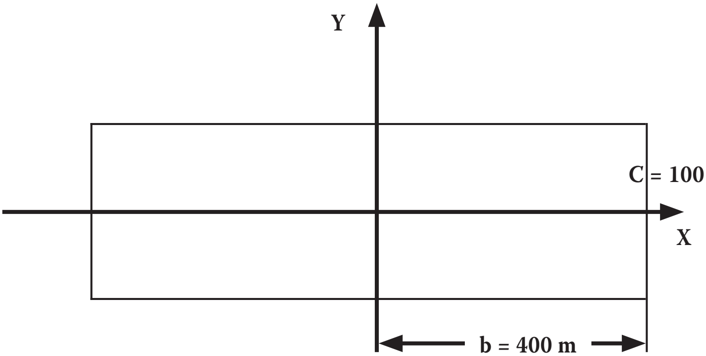

Fig. 2.4.3. Hydrodynamic scheme "rectangular irrigation section in an unlimited reservoir"

Calculation for the point (maximum rising) 0.0 (x = 0, y = 0) conducted according to the formula:

$$z = 0,25\frac{\varepsilon \cdot t}{\mu}\left[I(\eta_{,x} m_1) - I(\eta_x, m_2) - I(\xi_x, m_3) + I(\xi_x, m_4) \right].$$

Initial data: C = 100 m, b = 400 m; t = 365 days. Calculation of coefficients $m, \eta_x, and \xi_x$ according to formula, the following:

$$m_1 = \frac{y+c}{x+b} = \frac{0+100}{0+400} = 0.25\,;\; m_2 = \frac{y-c}{x+b} = \frac{0-100}{0+400} = -0.25\,;$$

$$m_3 = \frac{y+c}{x-b} = \frac{0+100}{0-400} = -0.25\,;\; m_4 = \frac{y-c}{x-b} = \frac{0-100}{0-400} = 0,25\,;$$

$$\eta_x = \frac{x+b}{2\sqrt{at}} = \frac{0+400}{2\sqrt{16,7\cdot 365}} = \frac{400}{2\cdot 78,07} = 2.56\,;\; \zeta_x = \frac{x-b}{2\sqrt{at}} = -0,64\frac{-400}{156,14} = -2.56\,.$$

Calculation example: $I(\eta_x, m_1) = I(2.56 : 0.25) = 0.71$;

$$z = 0.25\frac{\varepsilon \cdot t}{\mu}\left[I(\eta_{,x} m_1) - I(\eta_x, m_2) - I(\xi_x, m_3) + I(\xi_x, m_4)\right] =$$

$$= \frac{0.25 \cdot 1.64 \cdot 10^{-4} \cdot 365}{0.03} \cdot 0.71 \cdot 4 = 1.42m\ .$$

The results of determining the pH reaction, anionic-cationic composition of water from potential sources for irrigation (g/l) are shown in table 2.4.1. All analyzed water samples are evaluated as neutral and slightly alkaline according to the pH value. The waters of the quarry lake have a high level of mineralization.

Table 2.4.1

Assessment of the water chemical composition from potential irrigation sources

Source	pH	Salinity, g/l	g/l					
			HCO_3	Cl	SO_4	Ca	Mg	Na
Quarry lake	8.0	5.17	0.32	1.14	2.44	0.46	0.75	0.06
"Chortomlyk" lake	8.2	0.44	0.189	0.091	0.072	0.04	0.048	0.028
Well	8.1	1.26	0.708	0.161	0.134	0.06	0.159	0.066

Assessing the suitability of water from potential sources for irrigation by the SAR coefficient allowed us to assert that they belong to the first type (SAR = 0 – 10). It is possible to dilute the waters of the quarry lake with another source with a low level of salinity taking into account the requirements for the quality of irrigation water C ≤ 3 g/l.

Dumping of dumps on quarries is carried out by a walking excavator with a volume 10–15 m^3. Cones of deposited rocks have a non-uniform composition. Crushed rocks accumulate in the center and at the top of the cone. More lumpy rocks are poured along the perimeters. Heterogeneity and randomness in the composition of dump rocks is observed with this method of dumping. This creates real prerequisites for uneven subsidence of the base on the surface of the dumps, as well as local subsidence in their body.

In this regard, topographic and geodetic studies of intensive subsidence on reclaimed land were conducted. It was determined by 10 years observations after dumping. The amount of subsidence for individual points on the surface of the dumps is uneven and ranges from 0.3 to 1.88 m. The area of subsidence reaches 16 % of the total surface of the experimental site. It was obvious that the previously homogeneous land cover was deformed with depressions forming to provide situation for water accumulation. Analysis of heaps dumping with a walking excavator in places where studies of subsidence phenomena were conducted at the Zaporyzhya quarry showed that the technology of heaps forming causes the possibility of uneven subsidence. This technology heaps are cone-like ridge, where the rocks in the center of the cones are most densely spreaded (with a small coefficient friability), and on the periphery of cones – with the lowest density.

The crumbling coefficient was 1.2, and the residual coefficient in the body of the dumps was about 1.05. At the same time, the compaction coefficient during the dumping period reached 10 %. Calculations based on the established parameters showed that drawdowns can be about 5 % of the capacity of dumps. This corresponds to the size of the drawdown of 3–3.5 m for the entire period of subsidence of dumps. In recent years, the Pokrovsky mining and processing plant has improved the technology of forming dumps in order to reduce subsidence and reduce the time of their occurrence. Extraction of manganese ore in the conditions of technogenic landscapes was carried out on three types of quarry, depending on the mining and geological conditions and the use of overburden and dump equipment.

The first type – Zaporozhye, Shevchenko, North, Chkalovsky quarries. The second type – Bogdanovka, and the third type – Alexandria and Pokrov open pit quarries. Quarries of the first and second types had a depth up to 80 m, and the third type-with an opening capacity of up to 40 m. Heap reclamation after seven years of surface levelling was involved in studies of suitability for irrigation works. Geodetic survey of the surface of the new heap, intended for irrigation, was carried out one year after the beginning of the annual (for four years) irrigation of alfalfa. The average height of the planned heap was 64.3 m. The coefficient of variation, according to statistical processing of geodetic survey results (30 measurements of high-altitude marks of the dump surface) was 1.45 %. A comparison of the survey results, which was conducted a year later, did not reveal significant subsidence of the heap surface. The average height of the planned heap was 64.07 m. The coefficient of variation was 1.6 %. The heap surface was planned again and covered with a 50 cm of black soil after four years of alfalfa cultivation takin in account that 7 years period is sufficient for natural compaction of the soil stage and the end of the stage of stabilization of the dump surface. The use of drip irrigation technologies was made at the depth of wetting of the top and sub-top soil layer. These systems are promising for organizing irrigation on reclaimed heaps after the necessary stage of surface stabilization.

2.5. The study of the main water-physical properties of the black soil and rocks of the Nikopol manganese deposit

The study of the main water-physical properties of the black soil and rocks in the Nikopol manganese deposit was associated with the assessment of the soil texture (in particular, the content of silt and physical clay), the maximum hygroscopicity, and the content of clay minerals of rocks.

The content of silt and physical clay in the soil and rocks of the Nikopol manganese deposit is shown in figure 2.5.1.

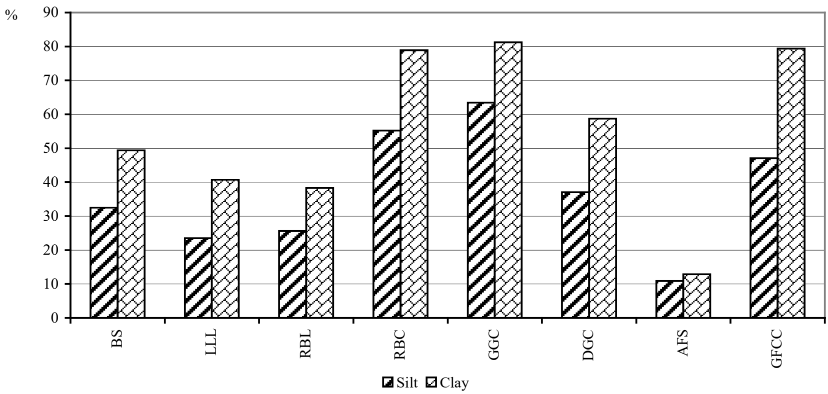

Fig. 2.5.1. The content of silt and physical clay in the soil and rocks of the Nikopol manganese deposit, %

The studied sedimentary deposits of the rock, with the exception of loess-like and red-brown loam (medium loam), ancient alluvial sand (sandy loam) and dark gray clay (heavy loam) are medium-loam. For the content of "physical clay", the soil mass of the black soil is light clay, and the loams and clays studied are medium and heavy clay. The stratum of ancient alluvial sand is characterized as sandy loam, while sand-clay deposits and iron ore slime are light clay. X-ray phase analysis of oriented preparations of clay minerals before and after treatment with ethylene glycol, as well as after firing at a temperature of 550 °C, allowed us to determine the qualitative and quantitative composition of clay minerals of the soil and rocks of the Nikopol manganese deposit (Table 2.5.1).

Table 2.5.1

Content of clay minerals in soil and rock substrates, %

Substrate	Clay mineral		
	Montmorillonite	Hydromica	Kaolinite
Black soil	9.1	14.2	9.1
Loess like loam	6.6	9.0	7.9
Red-brown clay	4.3	36.5	14.4
Grey-green clay	0.7	47.2	15.6
Dark-grey clay	1.6	30.8	4.7
Ancient fluvial sand	1.7	2.5	6.7
Green carbonate-free clay	31.4	11.8	3.9

It was determined that the predominant minerals in clay fraction of soil and rocks are hydromica, montmorillonite and kaolinite. Gray-green, green carbonate-free, red-brown and dark-grey clay are the most affluent with hydromica and montmorillonite. The redox state of the soil-plant system largely determines the growth and development of plants. It is an integral characteristic of the microbiological, biochemical, and physicochemical processes that take place. The results of studies of the redox potential (Eh), ion activity in the pot experiment, and data obtained after thermodynamic potentials calculations are shown in table 2.5.2.

Table 2.5.2

Ion activity and calculations of thermodynamic parameters of black soil and rocks

Substrate	pH	Eh, *mv*	rH_2	pCa	pK	pNO_3	pH-0,5pCa	pK-0,5pCa	pH-pK
Black soil	7.12	523	32.2	2.8	2.35	3.0	5.72	0.95	4.77
Loess like loam	8.2	475	32.8	2.7	4.3	2.95	6.85	2.95	3.9
Red-brown clay	7.7	507	32.9	2.5	3.2	2.9	6.45	1.95	4.5
Grey-green clay	8.4	499	34.0	2.9	3.4	2.5	6.95	1.95	5.0

The black soil was characterized by highest value of Eh, and the lowest index has got loess like loam. The loess like loam has a more alkaline reaction of the water phase (by 1.08 pH units) in comparison with the black soil. The Eh fluctuations in the studied soil and rocks were in the range of 475–523 *mv*. The rH_2 indicates the predominance of oxidative or reducing processes in the greater or lesser side of the number 27. The rH_2 value for all soil and rock samples is greater than 27. Oxidative processes in rocks brought to the surface were predominant. The best conditions for potash nutrition are marked by black soil, red-brown and gray-green clay in accordance with the calculations of potash potential for pH-pK index. Grey-green clay is also determined to be a more favorable substrate for passing the processes of mineralization of organic matter of root residues, since the activity of pNO_3 ions here was 2.5. The study of the distribution of Eh in the profiles of pre-formed rocks revealed its highest value at a depth of 20 cm in red-brown and gray-green clay, and for loess like loam at a depth of 30 cm (Table 2.5.3). The highest activity of calcium and potassium is distinguished by the upper 20-centimeter layer of all three studied rocks.

Thus, data on Eh and ion activity can be used to assess the redox state of rocks. Studies of the redox state of reclaimed land at the Pokrov land reclamation station revealed the advantage of oxidative processes, which was reflected in the change in ion mobility. Parameters of soil substrates

Table 2.5.3

The activity of the ions along the profile of plant meliorated rocks

Substrate	H, cm	Eh, mv	pCa	pK	pK-0,5 pCa
Loess like loam	10	487	2.15	3.0	2.5
	20	501	2.7	5.05	3.7
	30	512	3.0	4.45	2.95
Red-brown clay	10	485	0.77	4.15	3.77
	20	508	1.7	3.85	3.0
	30	502	1.5	4.5	3.75
Grey-green clay	10	526	0.8	2.35	1.95
	20	540	0.83	3.8	3.39
	30	520	1.25	4.0	3.39

and plant meliorated for 5 years rocks in the pot experiments on the level of potential nitrogen fixation are shown in Table 2.5.4. All rocks had a low level of potential nitrogen fixation (20–100 times less than in black soil) even after five years of their phytomelioration.

Table 2.5.4

Potential nitrogen fixation of black soil and rocks after five years of plant melioration (nm C_2H_4 / day)

Substrata	Potential nitrogen fixation
Black soil	68.8 ± 17.5
Loess like loam	3.2 ± 0.77
Red-brown loam	2.5 ± 0.84
Red-brown clay	1.2 ± 0.15
Grey-green clay	1.1 ± 0.001
Green carbonate-free clay	0.7 ± 0.13

Studies to determine the nitrogen content in the vegetative mass of barley, peas and corn grown during the application of “artificial” crop rotation on black soil and rocks in a five-year pot experiment were conducted to assess the adaptive potential of crops (Table. 2.5.5).

Table 2.5.5

The nitrogen content in the vegetative mass of barley, peas and maize grown on plant meliorated substrata, g/kg

Substrata	Barley	Pea	Maize
Black soil	9.0 ± 0.1	25.4 ± 0.55	5.1 ± 0.2
Loess like loam	8.98 ± 0.1	23.1 ± 0.7	5.1 ± 0.3
Red-brown loam	9.3 ± 0.17	22.37 ± 1.5	4.9 ± 0.06
Red-brown clay	9.2 ± 0.19	28.0 ± 1.0	4.9 ± 0.05
Grey-green clay	9.6 ± 0.36	24.0 ± 0.49	5.3 ± 0.09
Dark-grey clay	10.8 ± 0.17	23.8 ± 0.72	5.2 ± 0.09
Ancient fluvial sand	9.4 ± 0.18	25.5 ± 1.4	5.3 ± 0.17
Green carbonate-free clay	9.8 ± 0.37	26.2 ± 1.3	4.9 ± 0.03

The calculated data on the mineral elements uptake with plants that were grown in three variants of the initial application of fertilizers (control, RC, manure) in the first five years of the experiment are shown in Table 2.5.6. The macronutrients uptake with alfalfa, barley, peas and corn biomass on gray-green and green carbonate-free clays was equal or even higher than the corresponding indicators at the black soil.

Table 2.5.6

Nutrition elements uptake from plant biomass for 5 years (g)

Substrata	Control		P + K		Manure	
	Ca/Mg	P/K	Ca/Mg	P/K	Ca/Mg	P/K
Black soil	$\frac{0.91}{0.19}$	$\frac{0.35}{1.11}$	$\frac{1.68}{0.38}$	$\frac{0.60}{1.72}$	$\frac{2.4}{0.46}$	$\frac{0.64}{1.85}$
Loess like loam	$\frac{0.23}{0.06}$	$\frac{0.10}{0.35}$	$\frac{0.61}{0.12}$	$\frac{0.15}{0.64}$	$\frac{0.92}{0.22}$	$\frac{0.27}{0.82}$
Red-brown clay	$\frac{0.18}{0.05}$	$\frac{0.10}{0.31}$	$\frac{1.68}{0.73}$	$\frac{0.32}{1.71}$	$\frac{1.45}{0.68}$	$\frac{0.28}{1.75}$
Grey-green clay	$\frac{1.03}{0.66}$	$\frac{0.28}{1.62}$	$\frac{1.05}{0.76}$	$\frac{0.38}{2.39}$	$\frac{1.13}{0.89}$	$\frac{0.42}{2.83}$
Green carbonate-free clay	$\frac{0.63}{0.23}$	$\frac{0.19}{1.61}$	$\frac{0.80}{0.63}$	$\frac{0.37}{2.64}$	$\frac{0.84}{0.52}$	$\frac{0.44}{2.73}$

The highest degree of ecological and biological compliance during two years alfalfa and peas growing in pot experiment is distinguished for green carbonate-free and grey-green clay. Plant meliorated rock substrates were analyzed for the content of humic acids and fulvic acids after five years of crops growing in a long-term pot experiment (Fig. 2.5.2).

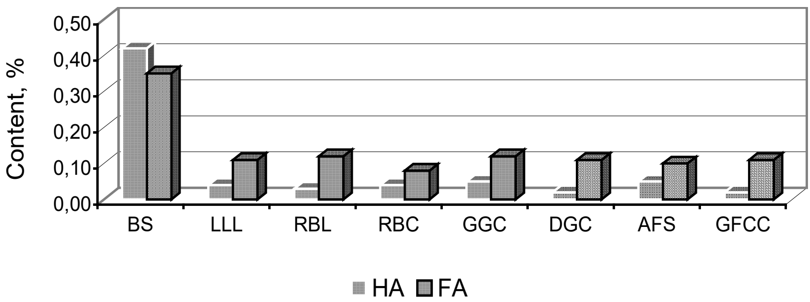

Fig. 2.5.2. Concentration of humic and fulvic acids in black soil and rocks after five years of plant melioration, %

The obtained data allowed us to estimate the potential reserves of organic matter in plant meliorated substrates. Differences in the humus composition of plant meliorated rocks are marked by 4–6 times lower content of fulvic acids compared to black soil. The level of humic acids in rocks differs from that of black soil at least to 10 times. The advantage of fulvate humus in the analyzed substrates is associated with a low ratio of humic and fulvic acids (0.2–0.5), which is 2.5–6 times less than black soil.

Other approaches application for substrata organic substance composition evaluation (gel chromatography, potentiometer titration with 0,1N$KMnO_4$, etc) gave an opportunity to reveal the formation of the humic fractions with a high movability and low molecular weight (Table 2.5.7 and Fig. 2.5.3). Thus it was approved additionally that plant melioration of rocks with perennial legumes grasses lead to improvement their fertility.

After a long 20-year phytomelioration, the rocks were analyzed again for humus, organic carbon, nitrogen, and phosphorus. The data obtained allow us to estimate the growth rate of the amount of humus and nutrients in the plant meliorated substrates of soil and rocks (Fig. 2.5.4 and 2.5.5). The 20-year presence of rocks under the influence of plants contributed to an increase in the amount of humus (5–8 times). The results of analytical studies of soil and rock samples selected in four typical profiles at the Pokrovsky hospital for reclamation of disturbed lands 20 years after the start of stationary studies made it possible to confirm the leading role of plant melioration.

Table 2.5.7

The Rocks Oxidation-Reduction Buffer Capacity after long–term melioration by plants (mv)

Substrate	Titration stages					
	0	1	2	3	4	5
LLL	195	506	523	532	535	538
LLL after first phytomeliorative stage	193	427	459	479	489	496
LLL after first phytomeliorative stage	198	380	448	469	478	479
GGC	175	494	512	520	527	531
GGC after first phytomeliorative stage	215	384	452	471	483	489
GGC after first phytomeliorative stage	198	376	430	452	462	481
BS	213	303	328	348	374	404

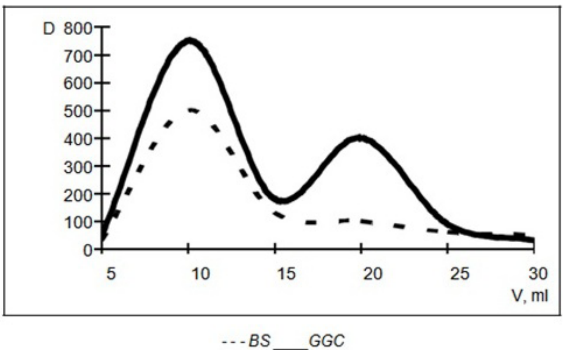

Fig. 2.5.3. Gel-chromatogramma of humic acid extracted of black soil and grey green clay

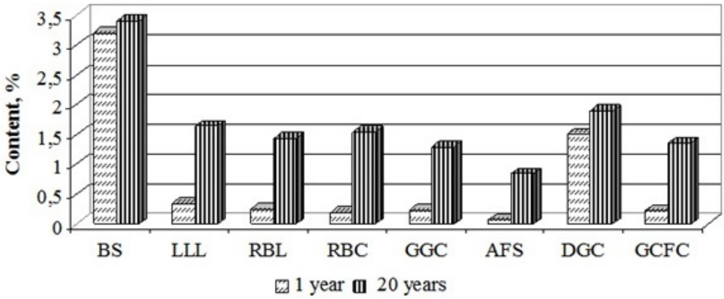

Fig. 2.5.4. Changes in humus content in soil and rocks after 20 years of plant melioration

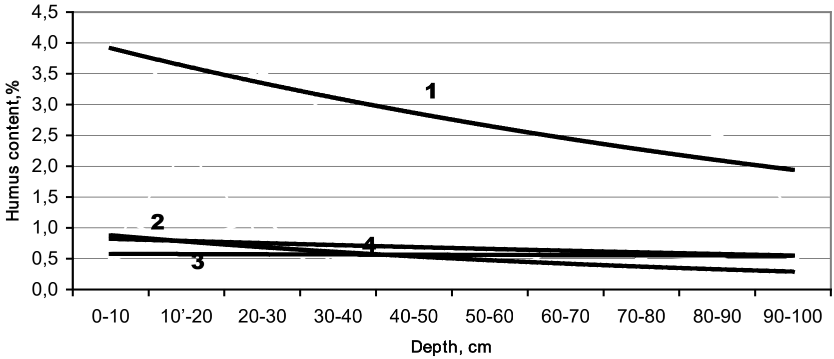

Fig. 2.5.5. The humus profile distribution in the soil and plant meliorated rocks:
1-black soil; 2- loess like loam; 3-red brown clay; 4-grey green clay

In particular, analyses of the humus content showed that the upper layer of plant meliorated rocks, and especially loess like loam, took more influence during the soil formation process. Rock samples that have been under the natural long-growing pioneer phytocenosis for more than 25 years, were selected in layers (0–5, 5–10, 10–20, 20–40 cm) to study the organic matter formation along profile of reclaimed land. The results of the “active” and “passive” humus determination are shown in Figure 2.5.6.

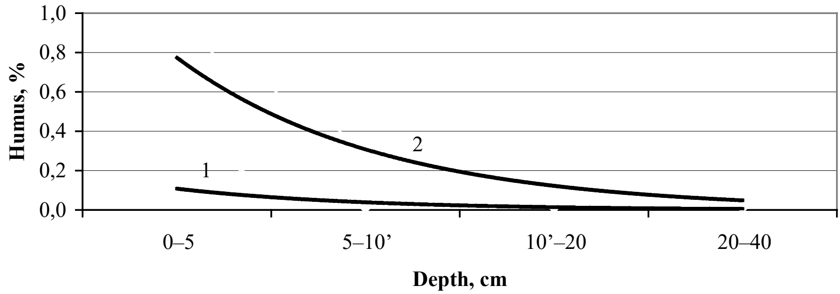

Fig. 2.5.6. Layer-by-layer distribution of “active” (1) and “passive” (2) humus fractions in a mixture of plant meliorated rocks

Calculations show that the content of “active” humus in the layer of 0–5 cm of plant meliorated rocks is at the level of 25 % of the total. However, its level is reduced to traces in the lower layers. It is known that at the first stages of reclaimed land development, newly taken to the day surface rocks have low microbiological activity, which results in slow mineralization rates. Therefore, the value of “active” humus can be included in the list of parameters for the formation of fertility of plant meliorated rocks.

The results of long-term of pot experiment also confirmed that the rocks phytomelioration over two decades significantly increased the total content of nitrogen and phosphorus in the substrates (Fig. 2.5.7).

The nitrogen content increased almost on all rocks and on ancient alluvial sand by 14 times. The increase in the level of total phosphorus ranged from 28–68 %. The study of the phosphates fractional composition in top and subtop soil and plant meliorated rocks can help to clarify the results obtained regarding changes in phosphorus (Fig. 2.5.8).

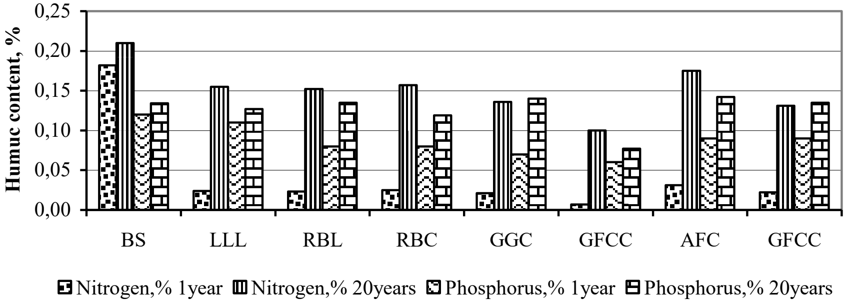

Fig. 2.5.7. Changes in total nitrogen and phosphorus in soil and rocks after 20 years of phytomelioration

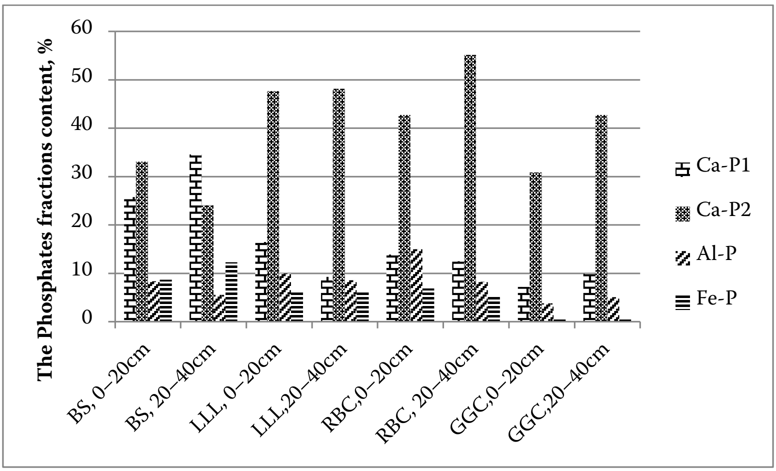

Fig. 2.5.8. The phosphorus fractions composition in top and subtop of soil and plant meliorated rocks

This research has shown that different forms of phosphates are present in the soil mass and rock substrates: dissimilar calcium phosphates, aluminum and iron phosphates. The largest numbers of water-soluble and fragile related calcium phosphates (CA-P_1 fraction) are found in the black soil. The content of available forms of phosphorus in rocks is 2–5 times less. However, the percentage of the near-term phosphate reserve (CA-P_2 fraction) is more pronounced in rock substrates. Al-P and Fe-P fractions content are less in several times comparative to Ca-P fractions. Therefore, it is possible to count on the transition of phosphorus compounds from a brittle to an easily accessible form due to the processes of weathering of rocks and, in particular, the action of a biological factor (phytomelioration, etc.).

The results of estimation of the phosphorus potential buffer capacity changes in soil and rocks are shown in Table 2.5.8.

Table 2.5.8

Potential buffer capacity of soil and rocks in relation to phosphorus

Substrate	Plant melioration stage (1pms)	Q/I
Black soil	One plant melioration stage	0.025
Loess like loam	Quarry board	0.06
Loess like loam	One plant melioration stage	0.04
Red brown clay	Two plant melioration stages	0.04
Grey green clay	One plant melioration stage	0.04

The results confirmed the effect of phytomelioration on the ability of rocks to absorb phosphorus compounds. Loess like loam plant melioration led to a decrease in the Q/I ratio to 0.04 even after one stage of plant melioration. The study of the rocks ability to absorb phosphorus allowed us to find that their biotic capacity increases under the influence of plant melioration.

Differences in the buffer capacity of plant meliorated rocks to the absorption of phosphorus to a certain extent associated with the pH level of the soil solution and the ratio of clay minerals. The results of estimating the direct potash reserve in soil and rocks are shown in Figures 2.5.9 and 2.5.10. The concentration of potassium in the water extract is almost ten times less than in the ammonium-acetate extract. A comparative assessment showed that the potassium content in extracts from gray-green and dark-gray clays is 3-10 times higher than in other substrates.

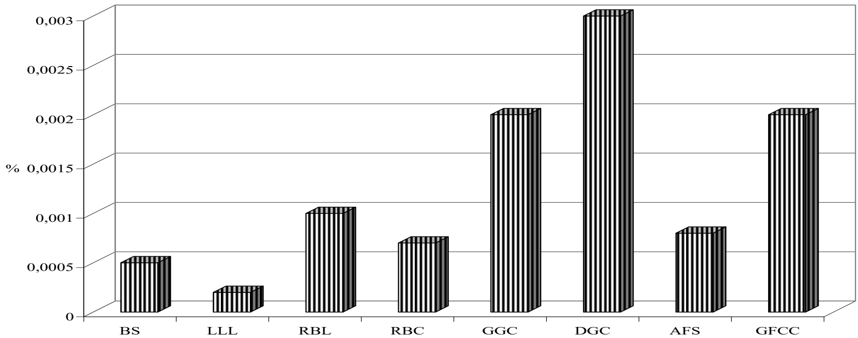

Fig. 2.5.9. Potassium content in aqueous extract of black soil and rocks, %

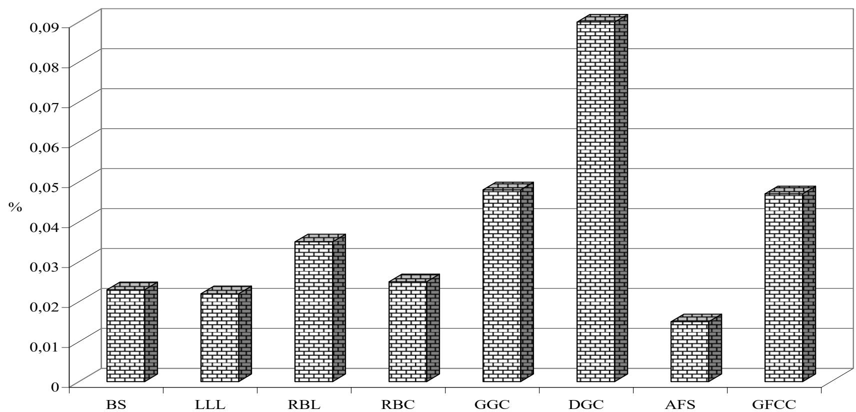

Fig. 2.5.10. Potassium content in buffer extract of black soil and rocks, %

Analysis of the initial information on the content of nutrients allowed us to draw some conclusions. The studied substrates have a low supply of nutrients, especially nitrogen, and partly phosphorus. Due to the fact that in loamy and clay soils, compared with sandy and sandy loam, the humification processes are more intensive, the studied rocks are more suitable as substrates for the accumulation of organic matter due to the thawing of the root remains of plants. Thus, the physical, chemical and biological properties of rock substrates determine both the potential and effective fertility of plant meliorated rocks.

The estimation of easily accessible (AAB pH 4.8) and hard-to-reach (1N HCl) reserves of phytomeliorated substrates in relation to heavy metals is given in Table 2.5.9. The increased concentration of manganese in dark gray clay limits the prospect of using this substrate during creating of reclaimed land. Meanwhile, the content of trace elements in the remaining weathered rocks did not exceed the indicators of the black soil. The highest degree of microelements balance was fixed loess like and red-brown loam, red-brown and gray-green clay. Elongated plant melioration leads to an increase in the share of available reserve of trace elements in these substrates during the process of biological weathering of rocks. The level of trace elements in weathered rocks did not exceed the indicators of black soil even after 14 years of their phytomelioration.

Table 2.5.9

The content of trace elements in black soil and rocks, mg/kg (numerator-AAB pH 4.8, denominator-1N HCl)

Soil	Fe	Mn	Zn	Cu	Ni	Cr
BS	5.0±0.5	140±3.2	16.0±1.3	1.96±0.4	1.8±0.3	1.0±0.04
	1747±7.2	535±7.5	62.0±8.2	8.3±0.4	8.4±0.4	3.0±0.2
LLL	5.0±0.5	70±3.9	10.0±1.1	2.5±0.04	3.6±0.6	2.0±0.1
	1283±7.1	343±7.2	81.0±8.1	6.6±0.2	7.9±0.5	3.1±0.2
RBL	4.3±0.2	62±3.44	11.3±2.2	2.8±0.2	3.8±0.2	2.2±0,1
	1243±3.3	348±7.5	28.3±2,4	6.8±0,2	8.43±0.1	3.0±0.2
RBC	4.0±0.2	68±3.0	9.5±1.8	2.3±0.2	3.2±0.2	1.9±0.1
	1848±18.4	467±7.0	35.0±3.6	8.57±0.3	11.3±0.3	3.8±0.1
GGC	4.4±0.1	51±3.4	5.9±1.7	2.2±0.3	2.7±0.15	1.4±0.2
	1082±43.0	155±5.1	16.3±3.0	7.3±0.7	4.0±0.32	3.5±0.3
DGC	11.2±2.1	206±9.0	8.7±1.1	2.2±0.2	5.8±0.8	1.3±0.1
	2005±51.6	2053±80.1	35.8±4.4	8.22±0.6	9.2±1.3	3.0±0.3
GLC	4.7±0.5	50±2.2	11.7±0.6	2.1±0.3	1.5±0.2	1.3±0.02
	1330±14.7	291±4.6	37.2±1.9	7.9±0.2	3.5±0.5	3.3±0.5

Trace elements spectrum was studied to assess the species differences in their concentration in the vegetative mass of plants, when growing barley, peas and alfalfa in the pot experiments with black soil and three phytomeliorated rocks. The results of these studies are shown in Figures 2.5.11 and 2.5.12.

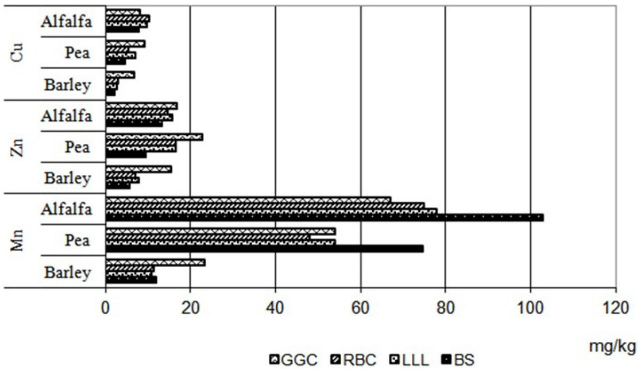

Fig. 2.5.11. Mn, Zn, Cu content in aboveground crop biomass

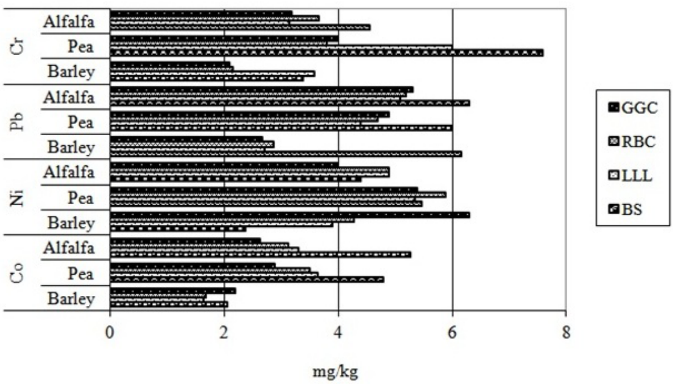

Fig. 2.5.12. Co, Ni, Pb, Cr content in aboveground crop biomass

It was found that the content of trace elements in the aboveground mass of barley, peas and alfalfa grown on three phytomeliorated rocks (loess-like loam, red-brown and gray-green clay) it is comparable to the data obtained when growing these plants on black soil.

The next couple of data were obtained in the soil laboratories at the DSAEU and Department of Ecology, Botany and Plant Physiology, University of Córdoba, Spain. Comparing the pH values in the selected samples of the bulk soil layer and phytomeliorated rocks over 40 years, we can see that the weathering process contributed to the normalization of the water extraction reaction of technosols (Fig. 2.5.13).

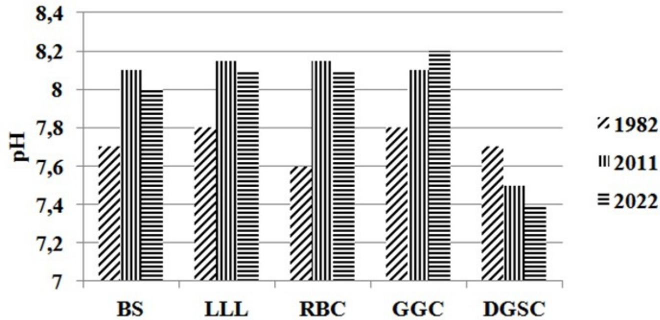

Fig. 2.5.13. Changes in pH in phytomeliorated rocks and soil

Meanwhile, there is a trend of a complete decrease in pH for dark gray schist clay.

Electrical conductivity is justified by another important parameter for conducting a spatial survey of the salinity of the arable layer of technosols (Fig. 2.5.14).

Test samples of the bulk soil layer, loess-like loam, red-brown and gray-green clay had fairly close electrical conductivity indicators, which are in the range of 119–137 μS/cm. At the same time, the dark gray shale clay had the highest electrical conductivity of 176 μ/S.

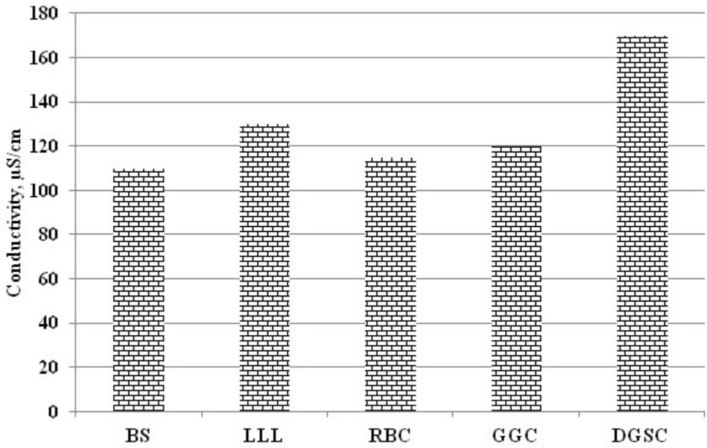

Fig. 2.5.14. The conductivity content in the black soil and technosols

The content of humus in phyto-reclaimed rocks does not exceed 1.2 % (Fig. 2.5.15). This is up to 3 times less than black soil.

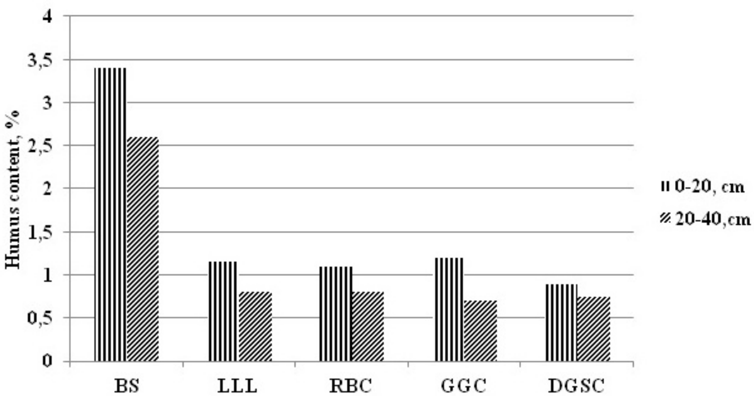

Fig. 2.5.15. Humus content in two layers of black soil and phytomeliorated rocks

It is known that cereal crops are the most protected from the accumulation of an increased amount of trace elements due to Caspari belt. The formation of the Caspari strip leads to the absorption of increased harmful heavy metals by the root mass (Ilyin, 1985). This mechanism ensures the preservation of the seed as a generative organ. Based on this information, attention was paid to the concentration of trace elements in the root system of winter wheat grown on various man-made substrates (Table 2.5.10).

Table 2.5.10

The content of trace elements in the root mass of winter wheat grown on post-mining rocks, mg/kg

Soil	Co	Ni	Pb	Mn	Zn	Cu	Fe	Cr
BS	8.4	10.0	11.0	100	15.0	6.6	4600	18.8
LLL	6.8	6.2	12.0	105	15.0	5.2	3300	10.2
RBC	4.2	6.8	9.3	45	27.2	6.2	1320	6.4
DGSC	7.8	6.4	11.6	154	19.0	7.2	4600	14.6

The lowest content of manganese and iron in root samples (2–3 times less) was noted in wheat grown on red-brown clay. The highest level of manganese absorption by the root system of winter wheat was recorded on dark gray clay.

2.6. The impact of VAM fungy and bacterial fertilizer effect on the yield of crops in the pot and field experiment

The limitations of the crop's yield can be explained by abiotic, biotic, and anthropogenic factors occurrence. As usual marginal lands define as soils that have physical and chemical problems or are uncultivated or adversely affected by climatic conditions. Following this definition erodible, compacted, saline, acid, contaminated, or sandy soils, reclaimed mine soils, urban marginal sites, and abandoned or degraded croplands fit this term (Blanco-Canqui 2016). However, it is necessary to raise agricultural productivity without enhancing the environmental footprint (Di Benedetto et al., 2017). Seed inoculation has been considered a precise and cost-effective method to deliver microbial inoculants (Ehsanfar & Modarres-Sanavy, 2005; O'Callaghan, 2016), with the potential for large-scale bio-fertilizers application to improve crops associative nitrogen fixation in the root zone, and soil phosphorus mobilization. *Rhizobium radiobacter* (syn. *Agrobacterium tumefaciens*, syn. *"Agrobacterium fabrum"*) is an endofungal bacterium that induces growth promotion and systemic resistance in cereal crops, including wheat (Guo et al, 2017). Recently, biological seed coating with PGPM was proposed as an alternative to conventional seed treatment (such as fertilizer and protection products) to mitigate biotic and abiotic stresses. (Ma, 2019). The seed coating process involves covering seeds with a small number of exogenous materials to deliver beneficial microbes to crops (Rocha et al., 2019). The improved growth, yield, and nutrient uptake in wheat plants demonstrated the potential of mycorrhizal inoculation to reduce the effects of drought stress on wheat grown under field conditions in semiarid areas (Al-Karaki et al., 2004). The arbuscular mycorrhiza symbiosis with crop roots increased with rising soil temperatures in the spring, in time to enhance late-sea-son P accumulation and grain production (Mohammad et al, 1998). Field AMF inoculation increased aboveground biomass, grain yield, harvest index, aboveground biomass P concentration, and content, straw P content, aboveground biomass N concentration and content, grain N content, and grain Zn concentration (Pellegrino et al., 2015).

The main reclamation objective included the cultivation of field grain and energy crops. The scheme for reclamation of disturbed land was based on the study of the effectiveness of capping the mine dumps with different layers of black-soil mass both with and without a shielding layer of loess-like loam. The following artificial models (trials) of technogenic edaphotops were used to look into the peculiarity of upward migration of heavy metals from the coal mine dump: mine rock (MR) + 30 cm of the bulk layer of black soil (30BS); MR + 50BS; MR + 50BS; MR + 50 cm of the loess-like loam (50LLL) + 30BS; MR + 50LLL + 50BS; MR + 50LLL + 70BS. The pH GIS maps were created in the ArcMap 9.3.1 application of ESRI's ArcGIS Desktop GIS software, using SAS Planet version 141212.8406. Interpolation methods were used to build GIS maps in the ArcMap software component and to assume intermediate values of raster points based on the available discrete set of known values. Bacterial fertilizers *Agrobacterium radiobacter 20, Bacillus polymyxa KB* and two strains of *Glomus fasciculatus* were cultivated at the Institute of Agroecology and Nature Management UAAS. Winter wheat variety Albatros Odesky was taken as the object of field experiments.

Additional steps to improve phytomeliorated rocks fertility have been done in several pot and field experiments. In particular it was fixed that soybean treated by mycorrhizal VA-fungies could use phosphorus of hard soluble combinations (Fig. 2.6.1). Root-substrate Mix without VAM and Glomus mosscae Isolate 5 impact was more available for montmorillonite clay using. The fields experiments to check winter wheat seeds treatment with different biological preparations were conducted at the land reclamation station in the Nikopol Manganese Basin.The rocks substrata were presented the loamy soil and clays which were took up to the day surface after manganese ore mining.These rocks were involved in that experiment after long term plant meliuoration.

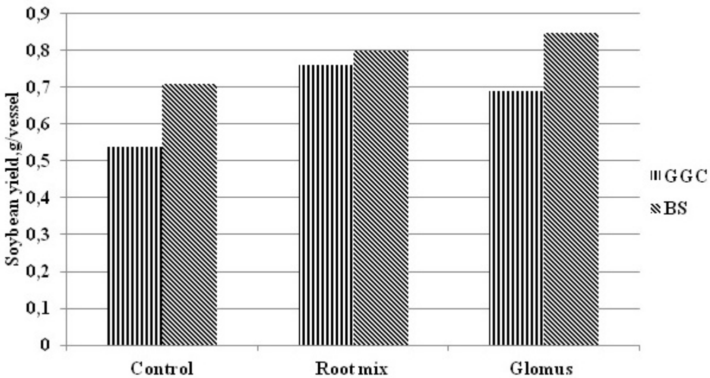

Fig. 2.6.1.VAM fungi effect after soil, rock treatment for soybean yield, g/vessel

The data on winter wheat experiment are presented in the Table 2.6.1. It is clear that long-term plant melioration allow opening the bacterial fertiliser's efficiency.

Table 2.6.1

Bacterial fertilizers application at the phytomeliorated rocks

Bio-fertilizer	Loess like loam	Red brown clay	Grey green clay
Control	2.64	3.52	2.61
Agrobacterium Radiobacter	3.07	3.76	2.96
Bacillus sp.	2.92	4.01	3.19
Agrobacterium Radiobacter 204	3.34	3.90	2.50
Alcaligenes paradoxus 207	3.44	3.69	2.41
Flavobacterium	2.53	3.14	2.42

2.7. Assessment of the suitability of reclaimed land for production of apple fruits

The results of long-term field experiment with apple trees grafted on a low-growth M9 rootstock were analyzed both on growth and productivity indicators over four decades. Long-term observations allowed us to establish the duration of five age periods: I) the period of growth and fruiting bearing is 3 years, II) fruiting is 6 years, III) fruiting and desiccation is 9 years, IV) desiccation, fruiting and growth is 7 years, V) desiccation, growth and fruiting is18 years. The field trials included soil with and without fertilizers: 1) LLL, 2) BS(50 %) + LLL(50 %), 3) BS, 4) BS + NPK, 5) BS + NPK + manure, 6) BS + manure and 7) BS + NPK + manure. Apple trees began to bear fruit after four years of growth (Fig. 2.7.1).

The maximum yield was obtained from 12-year-old trees and ranged from 20.35 to 28.2 t /ha. Average yield of apple fruits in the first three periods ranged from 7.68 (and the variant with a forest-like loam) to 9.1 t/ha (the third trial is black soil mass). High productivity of apple trees was observed for first two decades, and then sharply decreased.

Heavy metals distribution along two main soil profiles filled with the black soil and loess like loam shown in the Fig. 2.7.2 and Fig. 2.7.3.

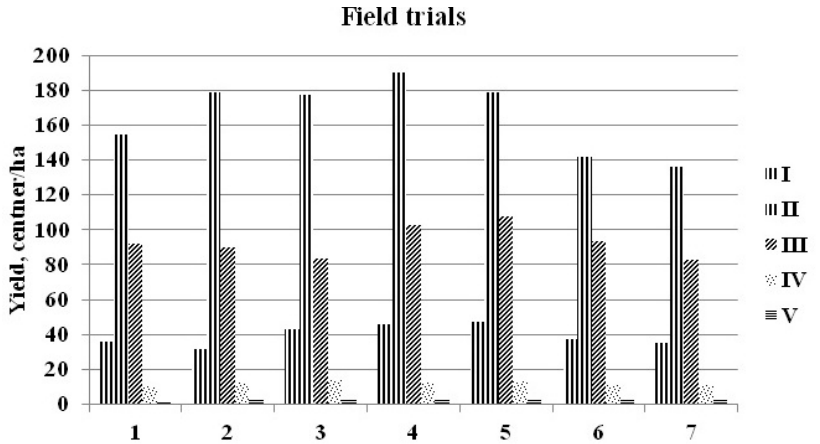

Fig. 2.7.1. Long-term dynamic of apple tree yield depending on the age period, t/ha

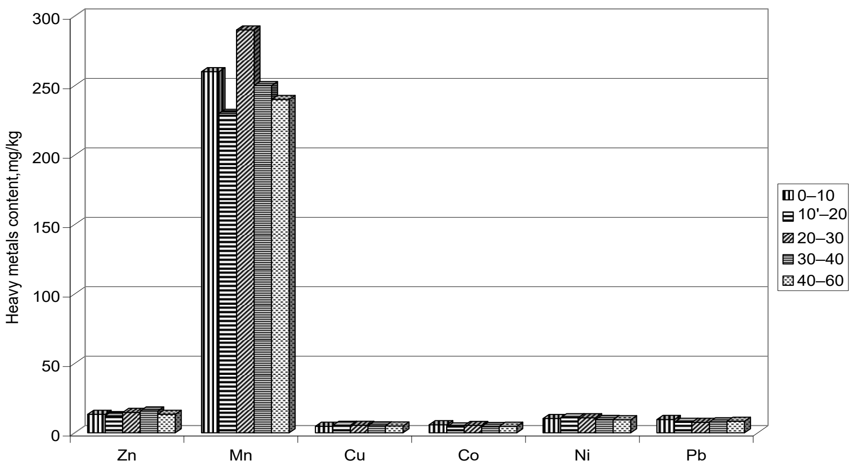

Fig. 2.7.2. Heavy metals distribution in the black soil profile

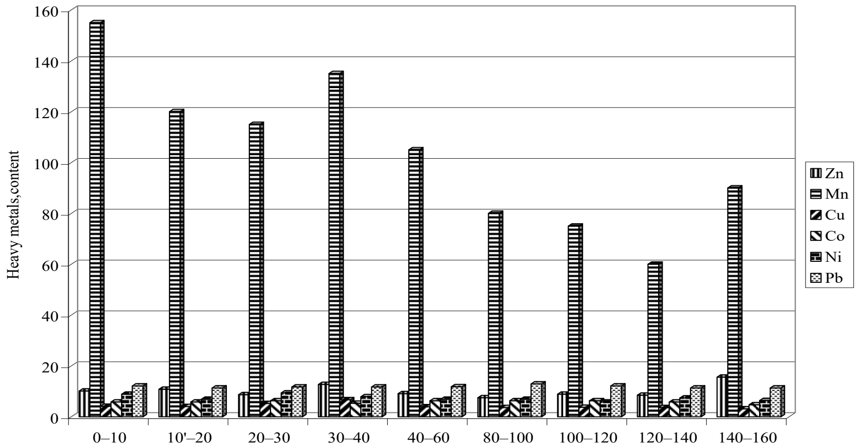

Fig. 2.7.3. Heavy metals distribution in the loess like loam profile

Comparison of the results revealed some differences in the distribution of heavy metals. The content of manganese in the profile of the loess like loam ranged from 60 to 160 mg/kg and was 2–4 times less than the data for the black soil. The distribution of the other elements in the profile was almost identical.

The results of assessing the content of heavy metals in apple fruits in different trials of the experiment are shown in Table 2.7.1.

Comparative analysis of the data shows that the content of heavy metals in apples does not exceed maximum permissible concentrations (MPC) regarding Ukrainian standards. The increased content of biological forms of iron in fruits was found in the trials BS, BS + NPK and BS + NPK + manure. Meanwhile, this is half the maximum permissible concentrations (50 mg/kg). The concentration of copper in the fruit varied from 2.18 to 2.71 mg/kg and did not exceed MPC 5.0 mg/kg. The amount of zinc in the apple fruit was in the range of 2.06–2.92 mg/kg. The highest content of manganese was fixed in the fruit samples in the BS + NPK + manure trial.

Table 2.7.1

Heavy metal content in apple fruit, mg/kg

Trial	Co	Ni	Pb	Mn	Zn	Cu	Fe
Pit: length – 1.4 m; width – 1 m; depth – 0.7 m							
LLL	trace	trace	trace	3.18	2.06	2.71	15.0
BS(50 %) + LLL(50 %)	trace	trace	trace	3.10	2.33	2.47	15.0
BS	trace	trace	trace	3.18	2.08	2.47	21.25
BS + NPK	trace	trace	trace	3.41	2.62	2.18	22.75
BS + NPK + manure	trace	trace	trace	3.18	2.50	2.24	18.75
Pit: diameter – 0.8 m; depth – 1.0 m							
BS + manure	trace	trace	trace	2.83	1.67	2.59	15.0
BS + NPK + manure	trace	trace	trace	4.10	2.92	2.71	12.5

Note – loess like loam (LLL); the black soil (BS)

The amount of lead, nickel, and cobalt was found in trace amounts. The possibility of organic production of apple fruits on the studied trials with black soil enriched with manure was established. It is known that depending on the type of rootstock, fruit trees with weak, medium and strong growth rates are distinguished. The speed of growth determines the age of the garden. Fruit trees on dwarf rootstocks produce fruits up to 15–20 years. The life cycle of apple tree on MM106 rootstock is from 30 to 35 years. The garden was lauded on strong-growing rootstock can produce fruits up to 80–100 years. It is obvious that the age of the laid garden needs to be uprooted. A comparative assessment of the wood energetic value was conducted to see the prospects to use it as fuel briquettes. Wood samples were taken from two orchards planted on rootstocks with a weak (M9) and medium (MM106) growth rate. The wood age from the orchard laid on the M9 rootstock was 15 years. The age of wood from the garden laid on the rootstock MM106 was 40 years. The results of thermogravimetric assessment of biomass of wood samples of apple trees from two orchards with different types of rootstock are shown in figures 2.7.4–2.7.6. Three stages of wood combustion for samples different at the age can be distinguished according to the thermogravimetric analysis.

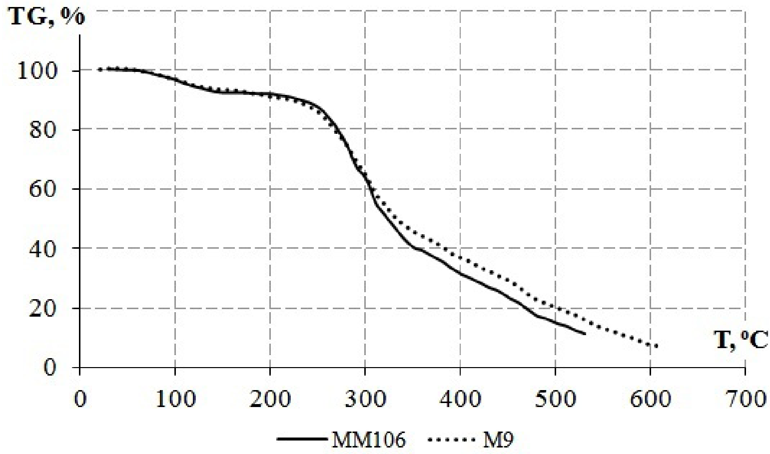

Fig. 2.7.4. Estimation of mass loss during heating

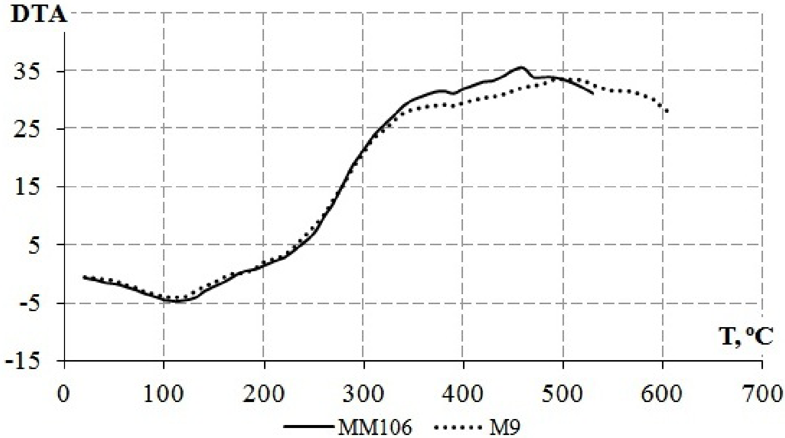

Fig. 2.7.5. Differential thermal analysis of biomass

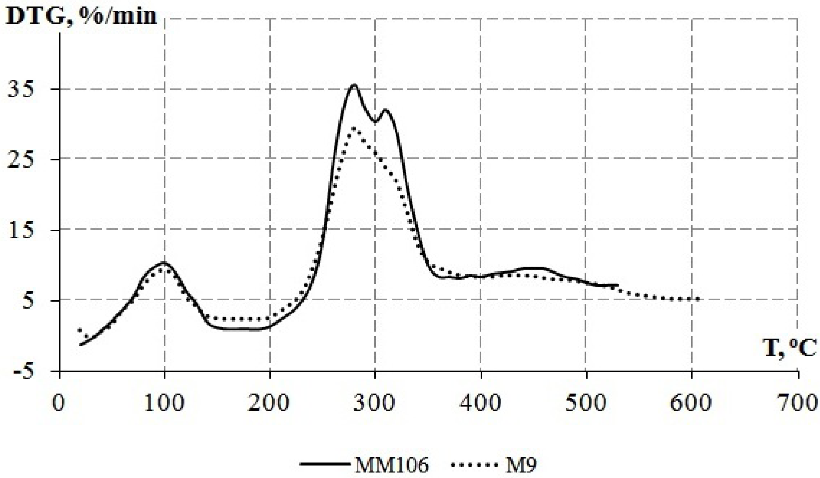

Fig. 2.7.6. Estimation of the rate of combustion of biomass during heating

The first stage takes place within the temperature range of 40–150 °C. The second stage continues in the temperature range of 200 °C–370 °C. This stage is characterized by the highest speed of combustion. The third stage takes place within the temperature range of 375 °C–550 °C. A higher DTG value was observed in the biomass sample no. 1 at the age of 40 years. So, the wood of apple fruit trees with an average growth rate (rootstock MM106) at the age of 40 years can be used with the best energy effect on fuel briquettes after uprooting the orchard.

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3. BIOFEEDSTOCK PRODUCTION ON THE RECLAIMED LANDS OF WESTERN DONBASS COAL MINING REGION

The need to restore the condition of the disturbed landscapes of Western Donbass is connected with the long-term development of coal in the floodplain of the Samara River. Pollution of surface and underground water is one of the main negative phenomena associated with coal mining. The source of pollution, along with mine waters coming from the beneficiation factory, are waste mine rock and coal beneficiation products. The development of coal seams by mines leads to the formation of deep cracks and intensive subsidence (up to 1 m, sometimes up to 3–7 m) on the surface of the floodplain. The drained area is filled with ground and surface water and turns into a wetland. This leads to deterioration of soil fertility, condition of floodplain meadows and forests. Work on reclamation of the Samara River floodplains in Western Donbas has been carried out for the last half century. Reclamation of the floodplain flooded areas is carried out using rocks from mine workings. In this regard, it is possible to release environmentally harmful substances from mine rocks at the level of their critical concentrations in soils and surface waters. Environmentally harmful substances found in mine dumps (sulfides, chlorides, etc.) change over time depending on physical and chemical conditions. The leaching of water-soluble salts from mine rocks can be considered as the initial stage of weathering. This process begins almost immediately after the mine rocks are dumped on the surface. With the passage of time, the removal of salts decreases. This trend of removal contributes to the improvement of the condition of waste rocks in case of their reclamation. The rate of removal of salts from the dump depends on several reasons. These include geomorphological conditions of deposition, texture and chemical composition of rocks. The rate of change in the chemical composition of rocks can be different. Such minerals as pyrite and marcasite are the main sources of sulfide oxidation to iron sulfate and sulfuric acid. Most mine dumps require measures to protect the upper layer from vertical migration of toxic salts before their land reclamation. High levels of exchangeable aluminum are considered to be the main limitation of plant growth.

3.1. Western Donbass coal mining region environmental problems

Western Donbass is a powerful coal-mining region. High rates of its industrial and economic development cause environment anthropogenic transformation in the area over 12 thousand hectares. Every year dumping sites is replenished by more than 4 millions of cubic meters of mine rock (Kharytonov 2007). In this regard using mine rocks for reclamation of subsided areas and building of dams is considered.

Coal mining wastes in Western Donbas (Dnipropetrovsk province) are shown in Figure 3.1.1.

Fig. 3.1.1. An example of the Western Donbass huge coal waste deposits

The wastes stored in tailings and heaps are subjected to continuous erosion processes and chemical reactions releasing soluble metal compounds easily uptaken by the biota. It is believed that the rate of metal removal depends on the filtering capacity of the waste, as well as the resistance of the waste to the weathering process. In the map (Fig. 3.1.2) part of the emplacement of the coal mine wastes in Western Donbas region is shown.

Fig. 3.1.2. Aerial map of the bigger coal mine emplacement at Western Donbas region

It has postulated that the rocks and mud of the coal tailings spread all over the Western Donbas district contain trace elements of the first class of hazard (Kharytonov and Kroik 2011). The greatest concentrations of metals correspond to the mine waste rocks and mud showing strong acidic reaction.

Coping with a large number of sites with serious environmental and health impacts is complicated. Often the liable owners are missing or not willing to charge or afford environmental remediation especially in countries with more flexible directives. In some cases the government is held accountable. But the huge financial liability attached to any systematic rehabilitation program represents a challenge that far exceeds the financial or organizational resources of any one regional actor. The situation is further aggravated by the lack of expertise required to take practical responsibility for dealing with sound reclamation of mine sites and the associated issues.

For many years, the creation of forest plantations in difficult soil and hydrological conditions was associated with anthropogenic subsidence in the areas of Western Donbass. The methods of forest restoration for lands disturbed by coal industry in the steppe zone of Ukraine were developed. Comprehensive study of forest ecosystems in etalon and reclaimed areas was conducted due to this. The forest restoration approaches were tested for anthropogenic landscapes resulting from: a) subsidence of the areas; b) changes in the hydrological regime or flooding; c) degradation of forest and agricultural land; d) degradation of soil and vegetation; e) emissions of saline mine water; f) intensive formation of industrial dumps; g) severe imbalance in food chain relations technogenesis. At the mine dump sites of the Wester Donabss in the technogenicaly negative forms of relief experimental-production forest restoration sites with a total area of 60 hectares were created.

During last 40 years biogeocenological comprehensive study on the development of methods of phytomelioration on disturbed lands was conducted. In particular, study was dedicated to defining of optimal design of remediation layer, finding promising types of forest plants and forestry measures to improve the stability and durability of ecosystems on land restored after anthropogenic degradation (Travleyev et al. 2005).

To evaluate the biogeocenlogic role and functional significance of plants in the process of restoration of disturbed lands, the physical and chemical properties of mine rocks and artificial soil of the remediation layer and their change during long-term remediation measures were monitored (Kharytonov 2007). It was established that mine dumps are mainly filled with debris of the lower coal beds which originate form shallow seas of the Carboniferous Period. Without implementation of any remediation measures, territories occupied with such dumps will remain vegetation free areas for many years and will be the source of chemical pollution. Due to specific landscapes features it looks like “industrial desert”. Lithological structure of the strata of rocks is quite variable – in some places more plastic rocks (clays, mudstones) dominate, in other fragile (sandstones, siltstones). In completely different hydrothermal conditions and atmosphere pressure and also under the impact of biological factors, rocks are rapidly eroded with generation of new chemical and biogenic products. These processes are accompanied with significant changes in rocks’ properties which cause expansion (ingrowth of trophy and aggregation, improvement of physical properties) or narrowing (self-consolidation of rocks redistribution of salts in the soil profiles, generation of sulfuric acid due to pyrite degradation, etc.). The process of mining rock oxidation (combustion) are intense rate due to physical and chemical weathering, under the exothermic reactions impact (Travleyev et al. 2005). The most common reactions are hydration, dehydration, hydrolysis, oxidation, dissolution and exchange. Pyrite in the interaction with oxygen and water is included in the following changes (Bilova et al. 2011):

$$2FeS_2 \text{ (pyrite)} + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4;$$
$$12FeSO_4 + 6H_2O + 3O_2 = 4Fe_2\,(SO_4)_3 + 4Fe(OH)_3;$$
$$2Fe_2(SO_4)_3 + 9H_2O = 2Fe_2O_3 \times 3H_2O \text{ (limonite)} + 6H_2SO_4.$$

The results of research have revealed three main factors of toxicity in acid sulfide minesoils of Western Donbass are following: exchangeable Al, water-soluble Mn and Na (Kostenko et al. 2012). The occurrence of these soil factors depends on the initial wastes' pyrite concentration, time since dumping, dumping technique, and relief. In the range of pH from 2.96 to 4.5, the mobile forms of Al suppress plant growth in the leached soils of depressions; the mobile forms of Al and Mn suppress plant growth in the slopes of hillocks; the mobile forms of Al, Mn, and Na suppress plant growth in the soils of recently dumped and compacted mine wastes. Therefore transition from initially favorable rocks (in terms of forest substrate) to bad and all way around is possible.

Many authors consider the evaluation of the state of assimilation apparatus of the trees as environmental monitoring tool, as it is directly connected to their environmental stabilization role preventing spreading of the pollutants in the environment (Dulama et al. 2012, Kabata-Pendias 2011; Nik et al. 2011; Pietrzykowski et al. 2014).

Flooding of the of the Samara River floodplaine territory was observed due to mine drainage and subsidence of the earth's surface. A multi-year plan was developed at PA "Pavlogradvugyllya" in the 80s of the last century to carry out restoration work in the area of coal mining in the Western Donbass. This plan provided for a balanced approach to environmental management, including the geomorphological features of the landscape in the floodplain of the Samara River. The results of the relief remote sensing upon completion of the reclamation of coal dumps are shown in figure 3.1.3. Analysis of landscape features has revealed additional prospects for the creation of feeding ponds for fish breeding as well.

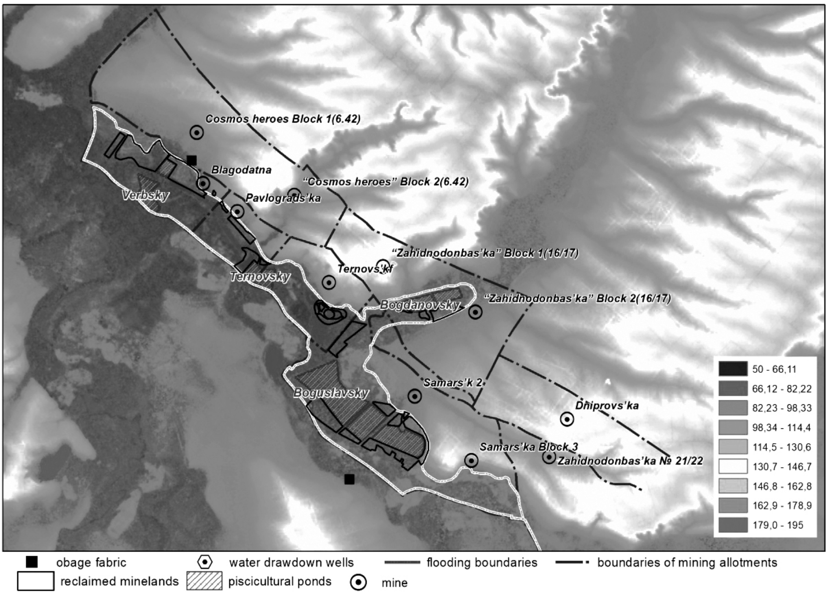


Fig. 3.1.3 Remote sensing of Samara River floodplain geomorphology

The results of calculations of the sodium adsorption rate (SAR) for the use of waste mine water accumulated in four beams and water from the Samara River for irrigation are shown in Figures 3.1.4 and 3.1.5.

The risk of soil salinization under the conditions of water use from the beam "Glynyana" and from the Samara River is estimated as insignificant, from the beam "Kosminna" as average. The SAR value of mine waters in "Taranova" and "Svidovok" beams corresponds to a high level of salinity.

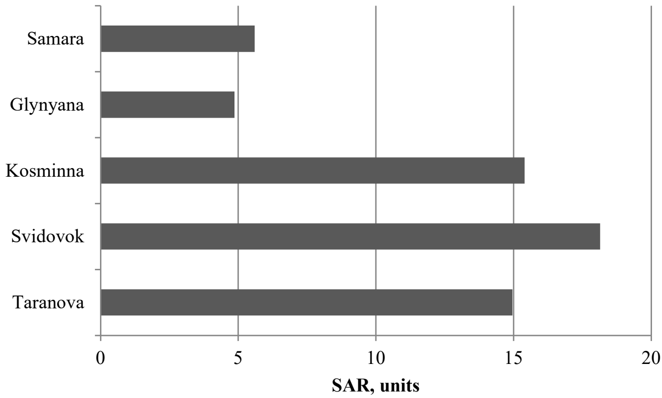


Fig. 3.1.4. The sodium adsorption rate for the mine water use of four ponds

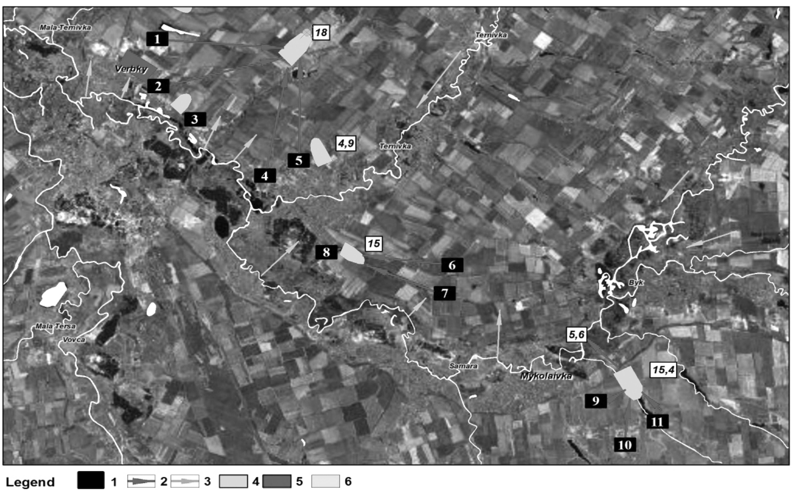


Fig. 3.1.5. SAR spatial distribution in the map of Samara river floodplain

Note as a comment to figure the following: the beam "Svidovok" accumulates wastewater from the mines "Heroes of Space" (1), "Blagodatna" (2), "Pavlogradska" (3), "Zakhydno-Donbasska" (4), "Ternovska"(5). Beam "Taranova" absorbs wastewater from the mines "Dniprovska"(6), named after "Stashkov" and "Samarska"(7). The mineralized waters of the "Stepova" (8), "Pershotravneva"(9) and "Yuvileyna"(10) mines flow into the "Kosminna"(11) beam.

Differences in the conditions of formation of mine waters determine the nature and degree of their impact on the environment. The waters of the central group of mines, due to high mineralization, cause salinization of soils and increased mineralization of surface and groundwater in places of their accumulation and by discharge routes. Mine waters of the eastern group have a relatively low mineralization, do not lead to a significant deterioration in groundwater quality and are used for irrigation of lands adjacent to storage ponds (Yevgrashkina et al., 2021). However, the drainage of the eastern group of mines led to the formation of a depression funnel on an area of 500 km^2 with a decrease in the center to 40 m in the Buchak horizon, which is used for water supply to settlements. The depression funnel has a radius of 8 km; the level decrease in the center is 15 m. The regime of the Sarmatian and Quaternary alluvial aquifers is disturbed. As a result, the conditions for water supply to settlements have worsened, and the conditions for feeding and unloading groundwater have changed over large areas. Artificial ponds built without waterproofing the bottoms, rock heaps, mine water discharge routes and other sources of pollution are actively involved in the zone of influence of mine drainage and deteriorate the quality of drinking water, the reserves of which are limited in the Western Donbass. The results of the assessment of the mineralization of water in the Samara River for the Verbki village based on the data from the 40 samplings (2–4 times per day) for the period 2007–2016, are shown in Figure 3.1.6. Thus, river waters belong to the 3rd class and are characterized as highly mineralized, sometimes unsuitable for irrigation.

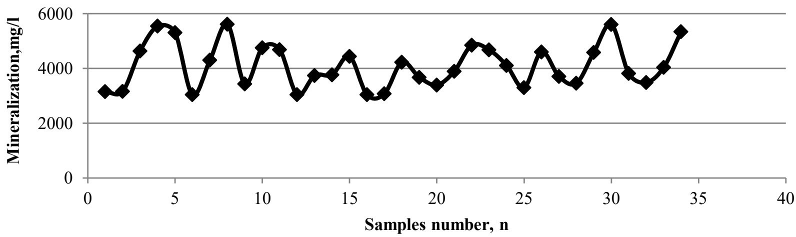
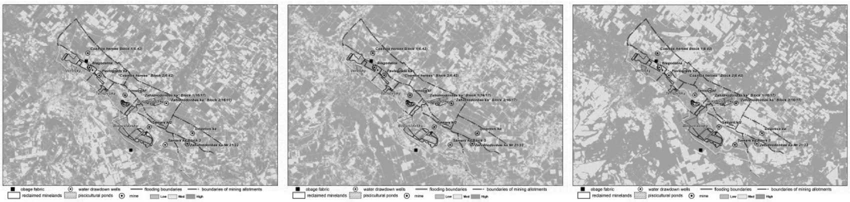


Fig. 3.1.6. Mineralization of water of the river Samara for the period 2007–2016

Part of the land was restored for arable land and pastures by the end of the last century. Their share was 66.8 and 10.2 %, respectively, and for the cultivation of forest crops 23 %. The assessment of the projective cover of the earth's surface by vegetation is possible due to the assessment of the spectral reflective features of the surface. Remote sensing of the area was carried out to estimate dynamic of the current state of the vegetation cover after reclamation of mine dumps in the floodplain zone of the Samara river from 2004 to 2020 (Fig. 3.1.7).



2004 2013 2020

Fig. 3.1.7. Vegetation cover at the Samara River floodplain (2004–2020)

The presence of territories with a high level of projective cover near the mines of "Heroes of Space", "Pavlogradska" and "Samarska" indicates intensive natural overgrowing of mine dumps that have passed the stage of land reclamation. The rate of spontaneous growth of the land cover around the "Ternovska" and "Blagodatna" mines is estimated as average. The spontaneous growth rate of the three reclaimed areas of the "Zahydno Donbasska" mine varies from low to high.

3.2. Analysis of soil profiles of reclamation of post-mining lands

Rainfall, evaporation, rock weathering, saltwater intrusion, or chemical contamination can cause the salt source for soil salinization in abandoned and reclaimed lands.

The need for land reclamation in Ukraine's Western Donbass region is associated with the long-term underground coal development in the Samara River floodplain. The problems associated with environmental restoration after coal mining are relevant even for such developed countries as USA, Germany, UK and others (Chugh and Behum 2014; Bellenfant et al. 2013; Wiessner et al. 2013; Lottermoser 2010; Bian Zhengfu et al. 2010). However, the difference in the ratio of precipitation and evaporation can exclude the automatic application of known reclamation approaches and so requires the development of new technologies for application in Ukraine.

The problem of nature conservation in Western Donbass is very real since almost half of the coal reserves are deposited under Samara River floodplain and its tributaries. Among the negative impacts after coal mining, contamination of surface and groundwater bodies is the most significant. The main sources of such contamination (that is, besides the mine water from beneficiation plant) are the mine-tailing dumps and products resulting from coal dressing. The coal mining also results in the formation of deep fissures and intense subsidence on the floodplain surface (up to 1 m, and sometimes up to 3–7 m). The areas of subsidence are then filled with ground and surface water and turn into a waterlogged reservoirs, leading to subsidence at the surface and, eventually, to the flooding of large areas. The environmental state is aggravated by leaching toxic substances from waste rocks accumulated in slag heaps, which contaminates soils and groundwater (Yevgrashkina et al. 2009).

Reclamation of these floodplain areas has been carried out for almost 50 years using rocks from mine excavation. This may result in the extraction of environmentally hazardous substances at critical concentrations in soils and surface waters (Kostenko and Opanasenko 2005; Kharytonov et al. 2012). In that regard, environmentally harmful substances in mine dumps (such as sulfides and chlorides) vary over time, depending on the physical and chemical conditions (Kharytonov and Yevgrashkina 2009).

At the initial stage of weathering, leaching of water-soluble salts from mine-dump rocks is observed, a process that begins almost immediately after placing the mine rocks at surface level. With the passage of time, the rate of salt removal decreases, and such trends contribute to the improvement of the dumps in terms of their reclamation. The rate of salt removal depends on several factors, such as geomorphological conditions of excavation, the texture and chemical composition of mine rocks, and bioclimatic potential.

However, the rate of change in the chemical rock composition can be different, and the main source of harmful chemical influence is sulfides (such as pyrite, pyrrhotite, and marcasite) which, after oxidation, turn into iron sulfate and sulfuric acid (Kharytonov and Yevgrashkina 2009; Hayes et al. 2014; Huff 2014).

The main environmental challenge in developing the optimal scheme for land reclamation in Western Donbass is the prevention of upward salinization and consequent man-made contamination of overlying artificial surfaces which results from the rate of evaporation being greater than the infiltration rate from rainfall precipitation (Kharytonov 2007; Tarika and Zabaluev 2004; Konhke 1950). This imbalance is the most important factor in enhancing the weathering of potentially toxic rocks accumulated in mine dumps. An earlier assessment of the qualitative and quantitative composition of the anions and cations in aqueous extractions from soil and rock samples showed that the main unacceptable consequence is the gradual salinization of the artificial surface layers of reclaimed lands with sodium and magnesium chlorides and sulfates contained in coal dumps (Kharytonov and Kroik 2011; Bender 1983).

Thus, the majority of mine dumps require measures for protecting the upper layer from the accumulation of toxic salts resulting from their upward migration. For example, high levels of exchangeable aluminum are considered to be the main restriction for plant growth (Shengyin Wang et al. 2016; Silva 2012), and to neutralize this effect it is recommended that chemical ameliorants are applied so as to create geochemical barriers (José Roberto Pinto de Souza et al. 2000). In addition, several methods for land reclamation have been proposed, such as application of various calcium-containing substances (such as lime) (Nkongolo et al. 2016), fly coal ash (Malik and Thapliyal 2009; Zhenqi Hu et al. 2004), sludge from alumina processing (Kyncl 2008), increased amounts of organic matter (such as sewage sludge and compost) (Baran et al. 2015; Tamanini et al. 2008; Larney and Angers 2012) and mineral fertilizers (Sheoran et al. 2010), plus the imposition of a layer of carbonate rocks (Hoff and Kolff 2012).

Observations of the mine dumps in Western Donbass indicate the need to study the changes in physicochemical properties of the mine rocks, establish the rate of removal of the weathered rock material, and study the migration of toxic substances along the surface of the reclaimed land. Thus, experiments suggested a long-term study of the effectiveness of the two- and three-layer reclamation models as geochemical barriers for blocking the upward migration of toxic salts from the mine dumps.

Considering the above-mentioned issues, the goal of the presented study was to identify the regularity, or otherwise, of patterns in the leaching of soluble salts along the surfaces, and the dynamics of these processes over time, depending on the initial designs of the soil-like bodies at the reclaimed mine dumps.

The Pavlograd experimental station for the reclamation of disturbed lands in the Western Donbass (eastern Ukraine) is located in the area of the "Pavlogradska" mine (48°33'24'' N, 35°58'46'' E). The station was founded in 1976 in the floodplain of the Samara River in order to examine the best restoration measures.

The "Pavlogradska" mine was put into operation in 1968 with the project capacity of 1200 thousands ton per year. The project capacity was reached at 1977. Industrial field of the mine is located in the floodplain of Samara River in Dnipropetrovsk region.

The main reclamation objective included the cultivation of both field and orchard crops. The scheme for reclamation of disturbed land was based on the study of the effectiveness of capping the mine dumps with different layers of black-soil mass both with and without a shielding layer of loess – like loam.

The following models (trials) of technogenic edaphotops were used to look into the peculiarity of upward migration of toxic salts from the post-mining lands:

1. Mine rock (MR) + 30 cm of the bulk layer of black soil (30BS).
2. MR + 50BS.
3. MR + 50 cm of the loess-like loam (50LLL) + 30BS.
4. MR + 50LLL + 50BS.

Samples of the soil substrates were collected at 10 cm depth intervals until the dump material was reached. The pH, conductivity and dry residue values were determined in accordance with the State Standard 26423-85. Besides, concentrations of the following cations and anions were determined in accordance with commonly used techniques: bicarbonates, chlorides, sulfates, calcium, magnesium, sodium and potassium (the State Standards 26428-85, 26423-85, 26426-85, 26425-85, 29269-91).

Principal components analyses were applied in order to reveal the regularities of the upward salt migration along the overall surface of reclaimed coal mine dumps. In the presented study the following factors were considered as the predictors: the "type" of reclamation factor (factor levels: reclamation variants 1 (MR + 30BS), 2 (MR + 50BS), 3 (MR + 50LLL + 30BS) and 4 (MR + 50LLL + 50BS); the "time" factor (factor levels: 1987, 2003 and 2016 years of research); the "depth" of sampling factor represented by data from each 10 cm of the soil substrate profile until dump material (factor levels: data of the physical and chemical analysis of the concentrations in soil water extracts, namely pH, total salinity and concentrations of the bicarbonates, chlorides, sulfates, calcium, magnesium, sodium and potassium).

The principal component analyses revealed three main components whose Eigen values exceeded 1; in aggregate these account for 68.13 % of total variance (Table 3.2.1).

Table 3.2.1

Principal component analyses of the variation related to the mineralization of soil solution and chemistry of water extraction

Variable	Principal components		
	PC1	PC2	PC3
pH	0.86	–	–0.30
Dry residue, %	–0.97	–	–
HCO_3^-	–0.73	0.28	–0.29
Cl^-	–0.84	–	–0.24
SO_4^{2-}	–0.96	–0.12	–
Ca^{2+}	–0.95	–	0.13
Mg^{2+}	–0.91	–0.13	–
$Na^+ + K^+$	–0.89	–0.16	–0.19
% Total variance	47.01	10.73	10.39

Note: Statistically significant correlation coefficients are given for $p < 0.05$.

The principal component 1 (PC1) accounts for 47.01 % of total variance, and this component is characterized by statistically significant correlation coefficients with all features under consideration. The acidity index of soil extract is characterized by a positive coefficient of correlation, in contrast to the other indicators which are characterized by a negative coefficient. Thus, the PC1 reflects the level of total mineralization of the soil solution, indicating that the increase in mineralization is associated with a decrease in pH values.

The general linear model of the effect of the type of technogenic edaphotop, in combination with time and depth of sampling, provides an explanation for 92 % of the PC1 variability (Table 3.2.2).

Table 3.2.2

General linear model of effect of technogenic edaphotop type, in combination with time and depth of sampling on the PC1 value ($R^2 = 0{,}92$)

Predictors	Sum of squares	Degree of freedom	Mean Sum of squares	F-ratio	p-level
Intercept	739.94	1	739.94	1370.08	0.00
Type	396.11	3	132.04	244.48	0.00
Time	8.79	2	4.40	8.14	0.00
Depth	908.05	1	908.05	1681.37	0.00
Type*Time	7.41	6	1.23	2.29	0.04
Type*Depth	40.77	3	13.59	25.16	0.00
Time*Depth	15.01	2	7.50	13.90	0.00
Type*Time*Depth	12.08	6	2.01	3.73	0.00
Error	191.18	354	0.54	–	–

It should be noted that all studied predictors, and their combinations, proved to be statistically reliable predictors of the PC1. The highest value for variation of the PC1 is established for “type” of technogenic edaphotop and “depth” of sampling (Figure 3.2.1). Although “time” is a statistically reliable predictor, it plays an insignificant role in the PC1 variation. In general, predictor “time” can be described as one that changes insignificantly during the study period.

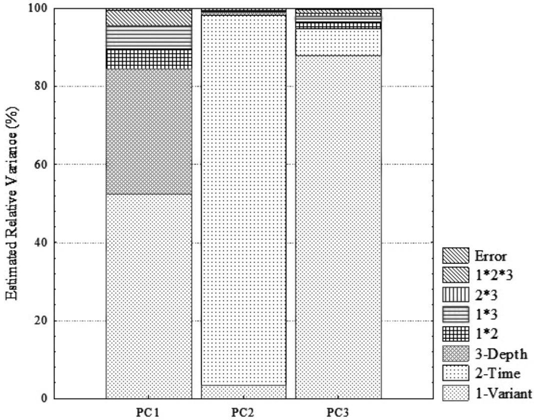


Fig. 3.2.1. Main elements of variations of PCs 1–3

The highest general level of mineralization is established in variant 1 (i.e. MR + 30BS), a level a little bit lower is specific for variant 2 (i.e. MR + 50BS), and the lowest level of mineralization is more representative for variants 3 and 4 (i.e. MR + 50LLL + 30BS and MR + 50LLL + 50BS respectively) (Figure 3.2.2).

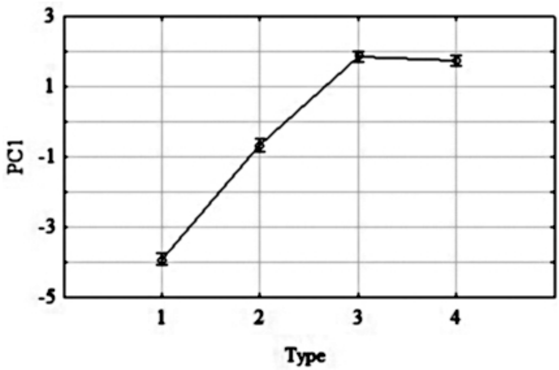


Fig. 3.2.2. Variation of PC1 depending on the type of technogenic edaphotop

Conditional notations: 1 – variant 1 (MR + 30BS), 2 – variant 2 (MR + 50BS), 3 – variant 3 (MR + 50LLL + 30mBS), 4 – variant 4 (MR + 50LLL + 50BS).

The profile distribution analysis of the PC1 values indicates the specificity of this feature depending on the type of technogenic edaphotop. Moreover, this index shows certain invariance over time (Figure 3.2.3).

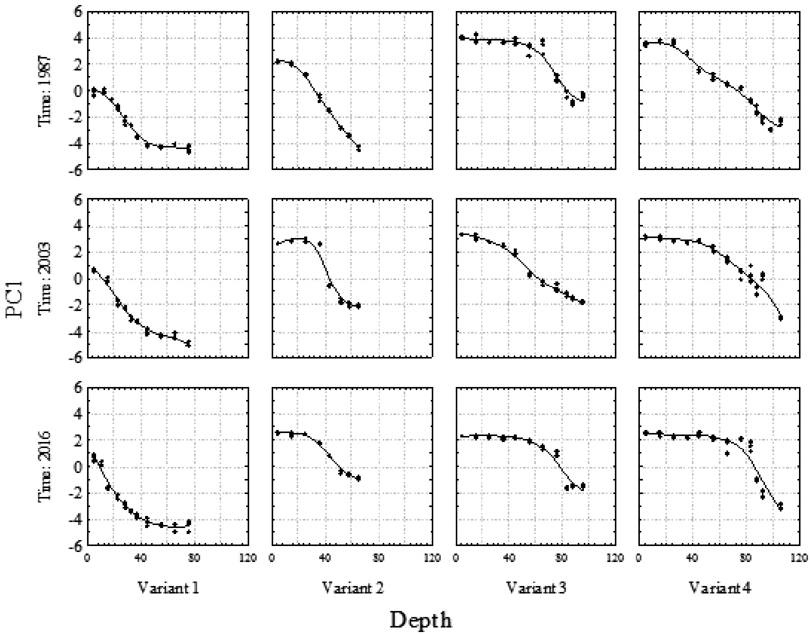


Fig. 3.2.3. Profile distribution of PC1 values depending on the type of technogenic edaphotop in different periods of the study

Thus, PC1 reflects the constitutional features of the profile distribution of the technogenic edaphotops properties. The general level of mineralization is sufficiently conservative feature, and its profile distribution is quite stably invariant over time. Similar behavior is observed for the distribution of general patterns of the water-soluble ions and pH.

The principal component 2 (PC2) describes 10.73 % of the total variability. It positively correlates with the concentration of the hydrocarbonate ion and negatively with the concentration of the sulfate, magnesium and monovalent ions. It should be noted that the variation of these ions occurs under conditions of stable pH and stable mineralization of the soil solution (Table 3.2.3.).

Table 3.2.3

General linear model of effects of technogenic edaphotop type in combination with time and depth of sampling on the PC2 value (R2 = 0,99)

Predictors	Sum of squares	Degree of freedom	Mean Sum of squares	F-ratio	p-level
Intercept	3.35	1	3.35	243.93	0.00
Type	3.55	3	1.18	86.27	0.00
Time	148.11	2	74.06	5396.96	0.00
Depth	4.17	1	4.17	304.11	0.00
Type*Time	0.28	6	0.05	3.38	0.00
Type*Depth	0.33	3	0.11	7.99	0.00
Time*Depth	1.30	2	0.65	47.29	0.00
Type*Time*Depth	0.25	6	0.04	3.05	0.01
Error	4.86	354	0.01	–	–

External factors provide an explanation for 99.14 % of the PC2 variation. All investigated predictors are statistically reliable, and the highest PC2 variation value is established for "time" (94.9 %). As shown in Figure 3.2.4 the PC2 value increases over time. The regression coefficient of depth has a negative sign (–0.10 ± 0.01), which indicates that the influence of the PC2 decreases with depth.

The peculiarities of the profile distribution variation of the PC2 values reflect the biogenic nature of this component, the value of which accumulates in time and attenuates with the depth of the soil layer (Figure 3.2.5). Thus, the PC2 reflects the trend of an increasing content of hydrocarbonates and a reduction of sulfates, magnesium, potassium and sodium in the aqueous solution of soil extractions. This trend can be linked to the effects of the biogenic factor. Probably, the increase in the content of hydrocarbonates may occur due to the metabolic activity of the microbiota, which leads to a certain desalinization of the soil profile.

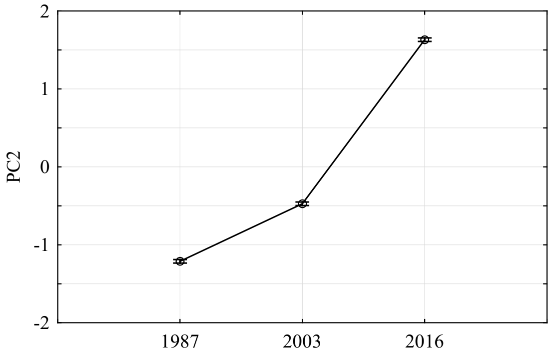


Fig. 3.2.4. Variation in PC2 over time

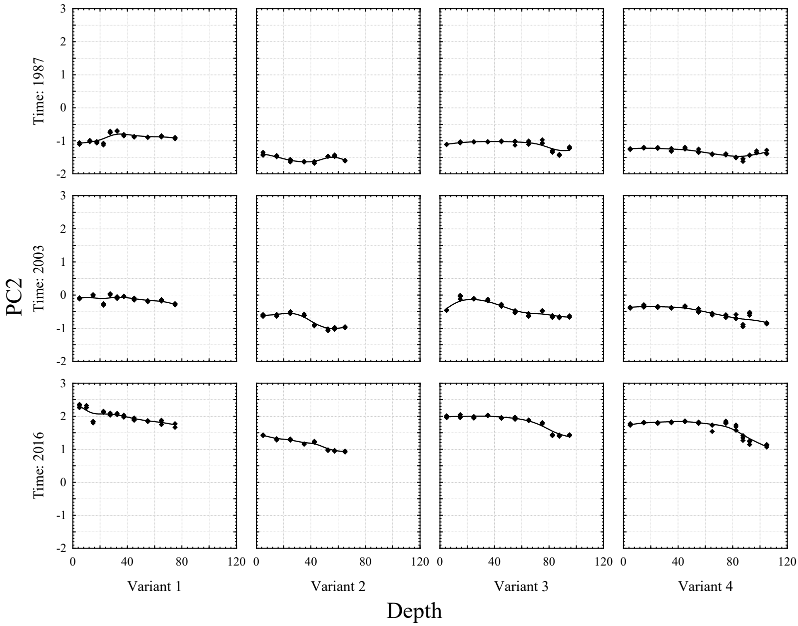


Fig. 3.2.5. Profile distribution of PC2 values depending on the type of technogenic edaphotop in different periods of the study

The principal component 3 (PC3) accounts for 10.39 % of the total variability. It correlates positively with the calcium content, and negatively with the pH value, as well as the content of hydrocarbonates, chlorines and monovalent ions. The general linear model of influence of the type of technogenic edaphotop, time, depth of sampling and their combination, explains 98 % of the PC3 variability (Table 3.2.4).

Table 3.2.4

General linear model of effect of technogenic edaphotop type in combination with time and depth of sampling on the PC3 value (R^2 = 0,98)

Predictors	Sum of squares	Degree of freedom	Mean Sum of squares	F-ratio	p-level
Intercept	1.42	1	1.42	38.95	0.00
Type	74.60	3	24.87	683.24	0.00
Time	6.80	2	3.40	93.40	0.00
Depth	0.49	1	0.49	13.47	0.00
Type*Time	1.09	6	0.18	5.01	0.00
Type*Depth	8.07	3	2.69	73.87	0.00
Time*Depth	2.51	2	1.26	34.55	0.00
Type*Time*Depth	1.67	6	0.28	7.65	0.00
Error	12.88	354	0.04	–	–

The most important factor in the PC3 variation is the type of technogenic edaphotop (i.e. 88.1 % of the PC3 variation depends on this predictor). The PC3 indicates a relatively high content of hydrocarbonates in the technogenic edaphotop with a layer of black soil 50 cm (variant 2), while in other types the higher content of hydrocarbonates, chlorines and monovalent ions is observed at a higher pH. In time, the PC3 values increase with a layer of black soil 50 cm. However, for other types the variation with respect to time is not evidence.

The PC3 indicates the specific features of the profile salts distribution in the variant 2 which were formed at the moment of laying the technogenic edaphotops and the processes of salts redistribution in this variant during the study period (Fig. 3.2.6). Variant 2 is characterized by a higher content of calcium ions and lower values of pH and HCO_3^-, Cl^- and $Na^+ + K^+$ concentrations. During the overall time of observation, the aligned distribution of the appointed indices tends towards those indicators, which are typical for other types of technogenic edaphotops mainly in the topsoil. The observed tendency of acquired characteristics is similar to other types of reclamation; this is in contrast to processes in the deeper layers where their dynamics slow down in the top soil of the profile in variant 2. However, the appointed features retain their stability over time.

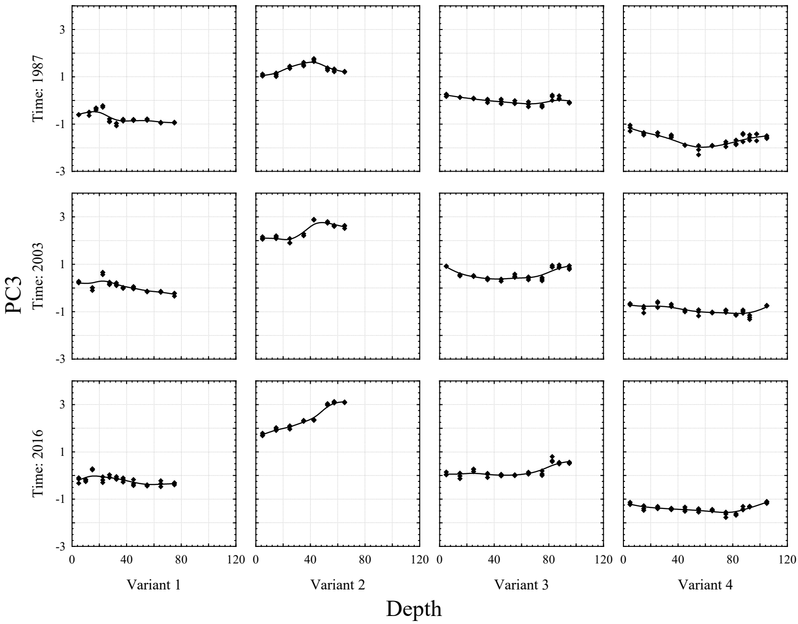


Fig. 3.2.6. Profile distribution of PC3 values depending on the type of technogenic edaphotop in different periods of the study

It should be noted that the alkaline barrier is the main factor in both pH changes and surface salinization of reclaimed lands. The absence of a protective layer of loess-like loam leads to rapid acidification of the soil solution due to the processes of chemical weathering of mining rocks in the contact layers with the mine dump.

Modelling is a suitable alternative technique that saves time and cost for the environment monitoring. Field experiments established 30-40 years ago in reclamation stations in areas affected by mining require additional research to justify the choice of a mitigation technology or rock deposits replacement in a way that would guarantee the least negative consequences for the environment. Thus, it is quite obvious that it is necessary to introduce a procedure of environmental impact assessment (EIA) for the recommended technologies of reclamation of disturbed lands. It is known, the EIA methodology involves the identification of impacts, the choice of mitigation technology, followed by modeling and forecasting its positive effect.

The applied model of the moisture-salt transfer process is based on the theory of physicochemical hydrodynamics of porous soils. Mass transfer processes are described by differential equations of motion and conservation of matter mass of the second order in partial derivatives of elliptic and parabolic types according to this theory.

One-dimensional versions of these equations are used for solving practical problems. This process is described by the equation of movement and of mass of matter mass keeping:

$$D\frac{\partial^2 C}{\partial x^2} - V\frac{\partial C}{\partial x} = m_0 \frac{\partial C}{\partial t} ,$$

where C – soil salinity, %;

D – hydrodispersion coefficient;

x – spatial coordinate;

t – time;

V – infiltration rate, м/добу;

m_0 – topsoil moisture, %. This is due to the fact that salt transfer in the aeration zone takes place mainly in the vertical direction.

The choice of measure to neutralize potentially toxic rocks is related to the ratio of precipitation and evaporation at each site. Evaporation is a negative component of the water balance. Evaporation involves a complex water vapor between the ground surface and the atmosphere. Its value depends on the depth of groundwater, lithological composition of the rocks, vegetation cover and complex climatic factors. The maximum evaporation for the Dnipropetrovsk province is 800–820 mm. The ratio between precipitation and evaporation is 0.5. The rate of vertical moisture-salt transfer was preliminarily estimated by the balance method according to the formula:

$$V = \frac{P-(E-W)}{1000T},$$

where P – precipitation, mm;
E – evaporation rate, mm;
W – water accumulation (moisture removal with plant biomass);
T – grass vegetation period, days.

The coefficient of water consumption (W) varied depending on the type of plant – from 450 to 550 m^3/t. In subsequent calculations, the formula was used to calculate the hydrodispersion coefficient:

$$D = V \cdot \frac{x}{2 \cdot \ln\left(\frac{C_2}{C_1}\right)},$$

where V – velocity of vertical moisture transfer, m/day;
C_2 – salinity at a point with the coordinate of the mine dump (x, m);
C_1 – mineralization depending on the surface of the dump.

The mathematical model was refined in the second stage by solving multivariate epignose problems to the best coincidence of the calculated values with the experimental data. The use of such an approach in the mathematical model of vertical salt transfer along profile of the dump of mine rocks allowed taking into account the surface runoff (Yevgrashkina et al., 2021).

The vertical transfer rate was calculated as the speed difference V_2–V_1 taking in account that this boundary pre-condition is used. The salinity forecast scenarios was made for the two- and three layers reclamation profiles during a period of three decades (Fig. 3.2.7 and 3.2.8).

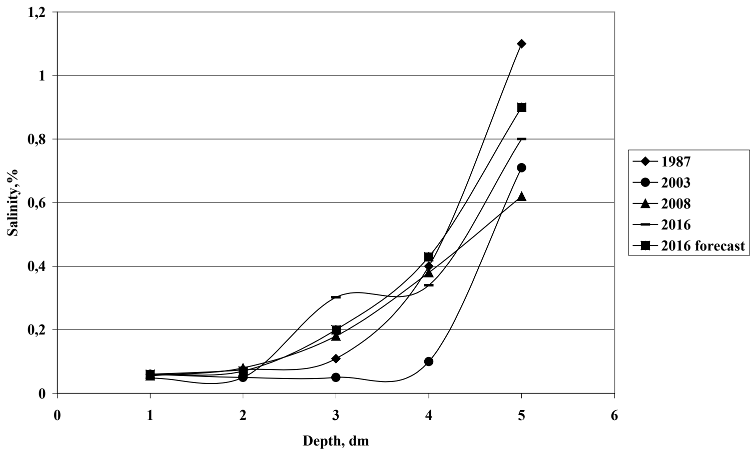


Fig. 3.2.7. Estimation and forecast of salinization of the two-layers profiles

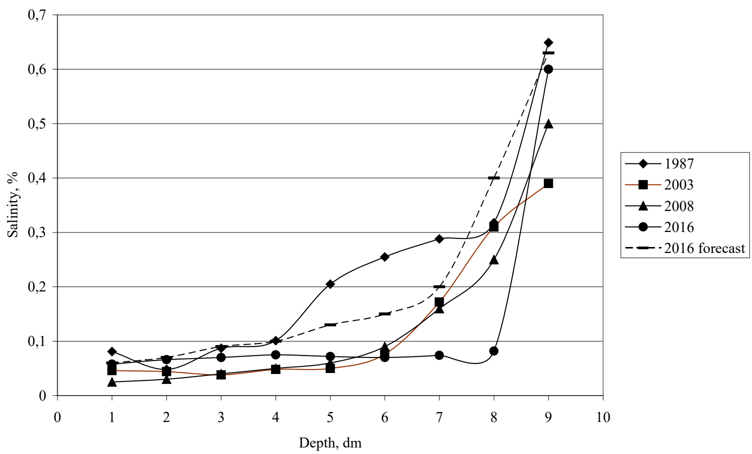


Fig. 3.2.8. Estimation and forecast of salinization of the three-layers profiles

The results of the forecasts for one of the two recommended reclamation profiles are in good agreement with the data of experimental observations for 1987, 2003, 2008 and 2016. The analysis of changes in the content of water-soluble salts at the contact of the lower layer of the soil with the mine rock in the trial MR + 50 cm Black Soil indicates a slow decrease in the soil mineralization. The tendency of slow increase in salinization of the upper soil layers of the artificial reclaimed profile is recorded. At the same time, the comparison of soil salinization data in the options MR + 50 cm Back soil and MR + 50 cm Loess Like Loam + 50 cm Black Soil testifies in favor of the three-layer reclamation profile. The same conclusion was made after trend analyse analysis of water-soluble salts vertical migration in technogenic edaphotops of reclaimed mine dumps.

It is obviously also that there is a certain pattern of growth of the content of soluble salts in the layers in the chernozem, which was dumped on the mine rock, approaching the mine rock. The topsoil looks like a volumetric filter of soluble salts migrating from the lower layer of mine rock. Thus, the salt concentration on the surface will be lower the larger the soil layer. This observation led to the theoretical assumption that the mine rock is a source of salt, and chernozem as volumetric filter for salts migration and absorbtion by the soil. Therefore, the obtained experimental data allowed building a mathematical model of the generalized dependence of the content of soluble salts in the layer of chernozem of different heights, poured on top of the mine rock. The database was grouped by the distance of a certain layer, starting from the mine rock, and the corresponding values are plotted on a scatter plot (Fig. 3.2.9). The trend in the form of an exponent is represented by a solid line. The possible real dependence is represented by a dotted line. The smoothing of the discrete series of values was performed by the exponent on the basis of the above-mentioned assumption. Quantitatively, the molecular diffusion of substances is described by Fick's first and second laws.

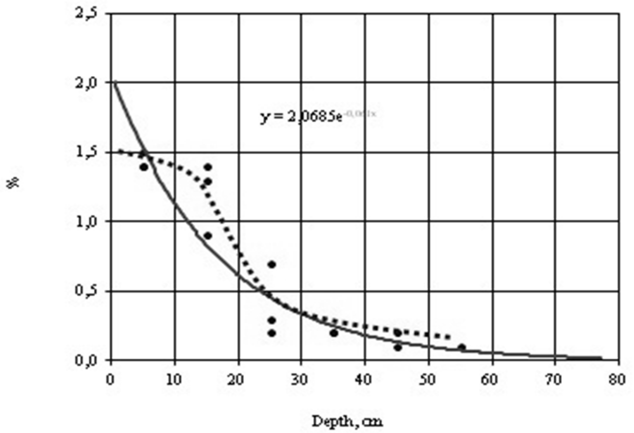


Fig. 3.2.9. Dependence of the content of soluble salts on the thickness of the soil layer

Under the above conditions, the differential equation of mass transfer of pollutants looks like the equation of diffusion of matter everywhere per unit area (Fick's first law):

$$j = -D\frac{dC}{dx} ,$$

where C is the mass concentration of the flow of the transferred substance through the selected plane, mg/m^3;
x is the current coordinate in the direction of flow, m;
D is the diffusion coefficient, m^2/s.

Therefore, according to the law of diffusion, the salts drift into the region with a lower concentration. For a steady state in the soil, this process can be written in the form of an equation in which there is no time factor, namely:

$$\frac{dC}{dl} = -k \cdot C ,$$

where C is the concentration of the migrating substance, mg/m^3 or %;

l is the thickness of the layer of loose soil, m (cm);

k is the filtration coefficient of dissolved salts in the soil, m^{-1}.

Analytical solution of equation with initial conditions, for (salt concentration at the boundary of the soil with the mine rock) has a general form:

$$C = C_0 \exp\left(-k \cdot l\right).$$

Since the nature of salt migration can be influenced by various factors, the real dependence of the salt content will primarily be described by a second-order differential filtration equation. For practical conditions, in our opinion, it is sufficient to apply a simplified version of the exponential dependence, which can be represented in an approximate normalized form:

$$C = C_0 \exp\left(-0,05 \cdot l\right),$$

where C – the salt content in the topsoil adjacent to the surface of the mine dump or at a depth selected for the initial level of reference in the soil, %.

According to the properties of the exponent, a decrease in the salinity of black soil in *e* times, i. e. 2.7 times, will be observed at a layer thickness of 20 cm. Almost zero concentration will decrease at a layer thickness of black soil at (3–4) 1/k , i.e. 3-4 times larger, namely – 60–80 cm.

Verification of this model and its subsequent identification for chernozem was performed three times on the basis of experimental data obtained in the Pavlograd reclamation hospital every eight years. The results of the distribution of salt content in soil samples taken in the reclaimed profiles of the two-layer variant are presented in Figure 3.2.10.

As we can see, the content of soluble salts in black soil depends not only on the soil layer, but also on the period from the beginning of reclamation. In this case, over time, there is an increase in the maximum concentration of salts (curve 2), coming from the lower layers of the rock to the black soil, and then, over the years – a gradual decrease (curve 3). The calculations showed that in real conditions, when the mode and duration of salinization are unknown, it is possible to use a model that takes into account all available experimental data.

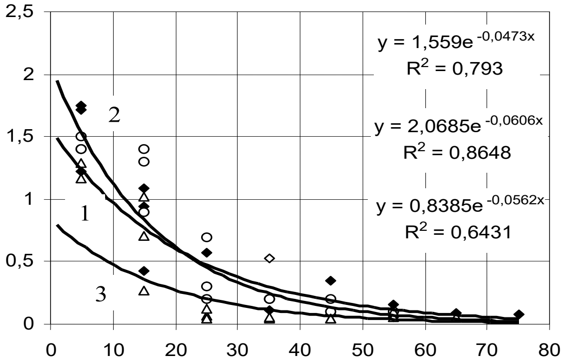


Fig. 3.2.10. Profile distribution of salt content (y, %) depending on the thickness of the layer (x, cm) of black soil

The introduction of a 50 cm layer of loess-like loam in the option 50BS + 50LLL + MR led to a significant decreasing of the chemical weathering process of underlying mining rocks (Fig. 3.2.11).

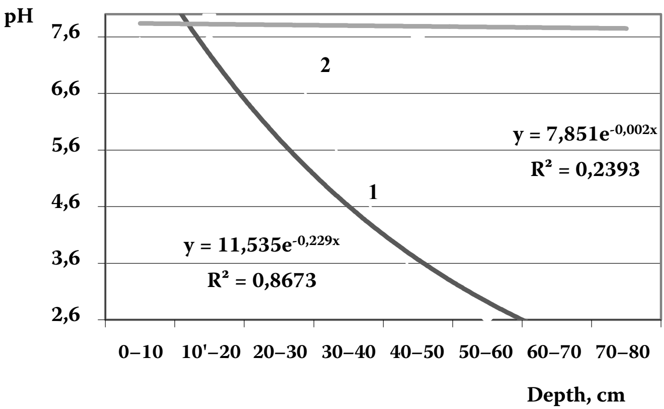


Fig. 3.2.11. Modeling of pH distribution along two land reclamation profiles: 1 – 50BS + MR; 2 – 50BS + 50LLL + MR

Therefore, pH stabilization in the trial 50BS + 50LLL + MR is possible in the range of 7.6–7.7. So, slow salinization of the topsoil was recorded for the three-layer reclamation profile. The introduction of a carbonate-containing layer of loess like loam is a reliable geochemical barrier to counteract the process of vertical migration of water-soluble salts from the surface of the mine dump. Creating a leaching regime with a downward flow of moisture is a guarantee to prevent the development of the process of soil salinization. In this case, irrigation can be carried out with minimum standards. Irrigation with ponds-accumulators water diluted by water of the Samara River can be tolerable to the grass and induces a low topsoil salinization risk in the artificial land reclamation profile.

3.3. Features of the water regime of the soil and the development of the root system of plants depending on the methods of reclamation

Moisture is an important factor that determines the life conditions of plants on reclaimed land. That is why much attention is paid to studying the conditions of moisture saturation and the dynamics of its change on man-made structures. The root systems of plants are essential for the stabilization of loose soil. Covering the particles of the soil, they fix them, preventing them from being eroded, wetting, and reduce its fluidity.

Analysis of moisture availability was carried out in a field experiment separately for each year. The soil mass laid on top was not fed by groundwater due to the relatively small thickness of the profile – from 30 to 120 cm and depended exclusively on atmospheric precipitation. The regime of these precipitations was completely different every year. Therefore, even if the determination of soil moisture fell on the same calendar days every year, averaging these data would not help to establish specific patterns or would lead to incorrect interpretation of the obtained experimental data. During the humidity recording, the main task was to establish the dynamics of moistening according to different edaphotopes and its penetration through bulk layers of soil, loess-like loam, and mine rock. Observations showed that the moisture content of the upper layers of bulk soil is very dynamic. The soil is quickly saturated with moisture during summer precipitation and loses it almost as quickly, as soon as the rain stops and warm weather sets in. The study of the dynamics of the moisture content of the bulk layer of chernozem made it possible to establish general regularities in years with different levels of moisture content. The dynamics of bulk soil moisture depending on the structure of the edaphotope in a dry year is shown in Table 3.3.1.

Table 3.3.1

Dynamics of soil moisture depending on the structure of the edaphotope, (%)

Day	The depth of the black soil layer, cm					
	30		50		70	
	1	2	1	2	1	2
1	2	3	4	5	6	7
0–30 cm						
5.05	23.5	–	23.5	27.3	26.1	23.7
20.05	25.1	–	23.9	23.8	28.1	20.3
5.06	23.5	25.0	24.8	18.4	20.1	19.4
25.06	29.5	22.5	30.3	23.4	31.8	24.5
5.07	12.4	15.2	12.8	15.3	21.3	16.3
21.07	9.7	16.7	9.6	10.3	8.4	9.4
6.08	23.0	23.9	26.3	20.3	27.7	18.2
Average	21.0	20.1	21.6	19.8	23.4	18.8
0–50 cm						
5.05	–	–	24.0	27.0	26.8	23.2
20.05	–	–	24.8	24.0	27.1	20.3
5.06	–	–	24.0	18.7	20.3	19.6
25.06	–	–	31.1	22.7	34.2	24.6
5.07	–	–	14.3	15.6	21.7	16.0
21.07	–	–	10.1	13.2	10.3	9.4
6.08	–	–	25.6	20.7	27.6	17.6
Average	–	–	22.0	18.4	24.0	18.7
0–70 cm						
5.05	–	–	–	–	27.8	23.0
20.05	–	–	–	–	27.7	20.9

Continuation of the table 3.3.1

1	2	3	4	5	6	7
5.06	–	–	–	–	20.6	19.8
25.06	–	–	–	–	33.3	25.0
5.07	–	–	–	–	21.1	15.2
21.07	–	–	–	–	12.7	9.7
6.08	–	–	–	–	27.3	17.7
Average	–	–	–	–	24.4	18.8

Note: 1 – without a layer of loess-like soil; 2 – with a layer of loess soil

On average, during the growing season, in the presence of a layer of loess-like soil, the moisture content in the upper 30-cm layer of reclaimed land is lower than in those cases when the fertile soil layer (regardless of its thickness) is applied directly to the mine rock. The average humidity of the 0-30 cm layer during the growing season in the version with a 30-centimeter fertile layer of bulk soil on loess loam and without interlayering was 20.1 and 21.0 % (difference 0.9 %). This difference consistently increased with the increase in the thickness of the fertile soil layer. So, the humidity was 21.6 % without a layer and 19.8 % – on loess-like loam, with a thickness of the fertile soil layer of 50 cm and 23.4 and 18.8 % with a thickness of 70 cm. The differences were 1.8 and 6.0 respectively. This regularity becomes even more noticeable if we compare the humidity in the upper 50 cm layer. On the dates of sampling, and on average during the growing season, the moisture content of the fertile soil layer in the variants without loess loam was much higher than the moisture content of it and the underlying loess loam (respectively, 22.0 % and 18.4 % in the bulk fertile soil layer with a thickness of 50 cm and 24.0 and 18.7 % in the 70 cm layer). The same regularity is preserved for the 0–70 cm layer.

On average, the moisture content of the bulk fertile layer (without interlayer and on loess loam) was 24.4 and 18.8 %, respectively. This regularity was observed both in wet and dry years, regardless of the actual amount of precipitation that fell and its distribution in time. Thus, the moisture-reducing effect of the loess-like loam screen on the higher fertile soil layer has been established. Exceptions to this rule were extremely rare, and if they were, they mainly concerned only the 0–30 cm layer and in variants with the same thickness of the fertile soil layer. The average values of soil moisture content by layers and by sampling dates are given in Table 3.3.2. Thus, despite significant differences between both options in soil moisture by dates and by layers, the moisture averaged over all soil layers and dates (vertically and horizontally) in both cases turned out to be the same – 26.8 %.

Table 3.3.2

Change in soil moisture (%) in layers of black soil with a thickness of 70 cm

Depth, cm	Day							
	27.06	18.07	7.08	Average	27.06	18.07	7.08	Average
	Without LLL layer				With LLL layer			
0–20	24.6	26.3	26.4	25,8	16.5	20.6	24.6	20.6
20–40	23.6	26.4	27.5	25,8	16.8	19.8	25.7	21.1
40–60	24.8	25.8	27.9	26,2	16.8	21.2	28.4	22.1
60–70	23.4	24.5	25.4	24,4	18.1	19.0	28.3	21.8
Average	24.1	25.8	26.8	25.6	17.3	20.2	26.8	21.4

It was established that there are no obvious destructive processes on reclaimed lands due to oversaturation with moisture, which is inevitable in the presence of a water barrier located close to the surface of the soil. This is possible only due to a certain water permeability of the mine rock, when meltwater and rainwater on the surface of the rock do not have time to accumulate in critically dangerous volumes. It has been observed that water stagnates above the mine rock only after spring snowmelt or intense rains, when it quickly seeps through the bulk soil mass than through the mine rock. In such cases, both the lower layers of the soil (chernozem or loess loam) and the rock itself are saturated with moisture.

Thus, mine rock is permeable to water. The moisture content of mine rock and soil, taken from the same depth, often did not differ, as evidenced by the data on the average soil moisture content shown in Table 3.3.3. Although during the warm season, changes in the percentage of substrate moisture occurred. It can be clearly seen that in the spring and for another month, the moisture content of the upper layer of the mine rock was higher compared to the bulk fertile layer of the soil, taken from the same depth. But in the future, the differences in humidity between the fertile layer of the soil and the mine rock in all layers and dates of determination were significantly smoothed out.

Table 3.3.3

Dynamics of humidity (%) of layers of mine rock and black soil (with and without loamy loam)

Day	Mining Rock	Depth			
		30 cm		70 cm	
		1	2	1	2
0–30 см					
11.04	33.0	24.8	26.0	25.8	26.4
11.05	33.5	26.1	28.0	27.9	21.8
11.06	19.3	24.1	25.1	24.7	24.7
11.07	23.4	16.9	21.5	22.8	20.0
11.08	19.7	18.3	22.4	21.0	21.4
11.09	24.7	32.1	29.6	31.6	26.7
Average	25.6	25.4	23.7	25.6	23.5
0–50 см					
11.04	32.1	–	–	25.1	25.9
11.05	30,1	–	–	29.1	21.9
11.06	19.3	–	–	23.9	25.0
11.07	22.3	–	–	24.7	20.7
11.08	19.7	–	–	22.8	22.6
11.09	24.1	–	–	31.0	25.3
Average	24.6	–	–	26.1	23.6
0–70 см					
11.04	29,9	–	–	24.4	25.3
11.05	29,2	–	–	29.0	22.7
11.06	19,7	–	–	24.7	23.8
11.07	21,2	–	–	25.1	20.4
11.08	20,5	–	–	23.9	24.3
11.09	24,1	–	–	31.3	24.5
Average	24,1	–	–	26.4	23.5

No significant differences were found when assessing the moisture content of the "connecting" layers of mine rock and bulk fertile soil layers, as well as all middle layers in either case (Table 3.3.4). As can be seen from the given data, the average seasonal moisture content in both the mine rock and the bulk soil consistently decreased from the upper to the lower layers. In particular, in the mine rock – from 26.4 to 20.5 %, in the variant with a layer of chernozem (70 cm) on the loess – from 24.0 to 20.7 %. At the same time, a trend was clearly observed, according to which the layer-by-layer soil moisture in the loess was always inferior to the similar variant of the experiment without loess-like loam.

Table 3.3.4

Moisture content (%) in the middle and adjacent layers of mine rock and bulk fertile soil layer

Depth, cm	Mining rock	Depth			
		30 cm		70 cm	
		1	2	1	2
20–30	26.4	24.4	24.0	25.8	24.0
30–50	23.1	21.9*	23.1	26.8	23.6
60–70	22.0	–	20.6	22.8	21.5
70–80	21.4	–	21.6	23.2*	21.8
70–90	20.8	–	–	21.3*	22.0
80–90	20.5	–	–	–	21.5
120–140	–	–	–	–	20.7*

*Humidity of adjacent layers of mine rock

The moisture content of the mine rock layers directly supporting the bulk soil layers practically did not exceed the moisture content of the soil layers in contact with the mine rock. All moisture indicators of the same soil layers differ slightly. Therefore, water on the surface of the mine rock does not accumulate and does not stand on the surface for a long time, but penetrates into the rock, gradually moistening it to the same extent as the bulk layers of the soil mass.

Therefore, the obtained experimental material shows that the mine rock is not waterproof. As the spring snow melts and during subsequent precipitation, water slowly but steadily seeps down along the mine rock profile. It is also possible that some of this retained water nourishes the layers of soil superimposed on the mine rock through the capillary system (upward current), if in the hot summer time the moisture from the entire thin bulk layer evaporates quickly.

Both of these factors (seepage of retained water deep into the mine rock and its upward capillary rise) can act both separately and simultaneously. In any case, water on top of mine rock does not stagnate for a long time and does not accumulate in critical volumes. This protects the fragile bulk soil layer on reclaimed land from inevitable wetting and rapid degradation.

The study of the impact of various methods of reclamation of lands disturbed by mining operations on the growth and accumulation of root mass requires additional attention. It is important to establish the reaction of the main field crops to the different structure of edaphotopes, the accumulation of organic matter in them, which contributes to the retention of bulk soil layers.

Layer-by-layer excavations and washing of roots from the soil, carried out in two trials of reclaimed lands after harvesting, showed that the roots penetrate the entire thickness of the loose fertile layers of the soil, but the mass of dry matter of the roots of the 4 crops was different (Table 3.3.5). It was the largest in alfalfa. In the 3rd year of life, the mass of its roots in trials without loess amounted to 99.8–99.9 centner/ha, and did not depend on the strength of the bulk soil layer.

Таблиця 3.3.5

Dry mass of the roots of agricultural crops depending on the profile (centner/ha)

Crop	Depth			
	30 см		70 см	
	Without LLL layer	With LLL layer	Without LLL layer	With LLL layer
Winter wheat	39.5	34.3	37.3	41.3
Barley	23.2	16.1	23.3	15.5
Alfalfa	99.9	94.2	99.8	88.6
Sainfoin	65.0	113.8	78.3	94.7

According to this indicator, sainfoin was significantly inferior to alfalfa in the trials without a layer (65.0 and 78.3 centner /ha of roots in the 30BS and 70BS), but it was significantly superior to it in the presence of half a meter of loess-like loam (113.8 and 94.7 centner /ha).

Agricultural crops formed a smaller mass of roots, which is due to their biological features. Increasing the thickness of the soil layer from 30 to 70 cm practically did not contribute to the increase in the mass of the roots of winter wheat, barley and alfalfa in the area without a layer of loess loam. If there was a protective screen made of carbonate loam between the rock and the black soil mass, then the root mass increased only in winter wheat, and in barley, alfalfa and sainfoin, it decreased by 3.7–16.8 %. It should be noted that the formation of a powerful root system of plants on reclaimed lands is not only a guarantee of obtaining a harvest, but also a natural enrichment of technosol with organic matter, a more effective cultivation of the substrates that make up reclaimed lands. If these crops are evaluated from this point of view, preference should be given to perennial leguminous grasses, which enrich the soil with nitrogen. It should be noted that in the options where the fertile soil layer is covered with loess-like loam, in comparison with the options without it, the mass of roots increased only in sainfoin and winter wheat (for a capacity of the fertile soil layer of 70 cm). In all other cases, including alfalfa, this indicator decreased compared to variants without a layer of loess loam. The increase in the thickness of the bulk soil layer did not contribute, with the exception of winter wheat, to an increase in the mass of roots per unit of soil volume due to an increase in the volume of fertile soil.

In our opinion, it is also important to characterize the distribution of the mass of the roots by the profile of technosol. The data of layer-by-layer excavations and washing of roots from the soil made it possible to calculate the mass of dry matter of roots in a layer of 0–30 cm per 1 ha. It was established that the largest share (65.8–99.4 %) of the entire mass of roots in the studied crops was concentrated in the upper 30-cm soil layer. The rest of the roots are located below and in the mine rock. Moreover, in the trials without loess and with a thickness of black sol mass of 30 cm, there were more roots than in the presence of loess-like loam and a soil thickness of 70 cm (Table 3.3.6). In alfalfa and sainfoin, this indicator exceeded 99 %

of the total mass. This means that perennial leguminous grasses are better able than cereal crops to create dense sod covers on reclaimed land, make the soil more structural and protect it from deflation and water erosion. This is a positive factor for the initial stage of biological reclamation of lands, when their structure is disturbed by movement and they have not yet formed as a complete bioedaphotope.

Table 3.3.6

The influence of the depth of the bulk layer on the mass of dry matter of the roots of cereal crops and perennial leguminous grasses, (centner/ha)

Crops	**Depth**			
	30 см		**70 см**	
	centner/ha	**%**	**centner/ha**	**%**
Without LLL layer				
Winter wheat	36.0	91.1	29.9	80.1
Barley	20.4	87.8	17.5	75.2
Alfalfa	99.1	99.3	68.4	68.5
Sainfoin	64.6	99.4	65.6	83.8
With LLL layer				
Winter wheat	26.0	75.7	31.9	77.3
Barley	13.0	81.1	10.2	65.8
Alfalfa	79.3	84.2	64.5	72.8
Sainfoin	93.0	81.7	72.3	76.3

Cereal crops (wheat and barley) play a positive role in the “cultivation” of the arable layer. The sod they form decomposes after harvesting and is created every year, while the roots of legumes are strong and “hold” the surrounding soil well for several years in a row, and every year more reliably. Under the capacity of a 30 cm bulk black soil layer on a substrate with a layer of loess loam, the absolute mass of dry matter of the roots in the 0–40 cm layer significantly decreased in all cultures, except for safflower (but in relative terms it also decreased in it – from 99.4 to 81, 7 %), totaling 75.7–84.2 % in comparison with 87.8–99.4 % in trials without a layer of loess loam. The greatest decrease in the mass of roots in the 30-cm layer occurred in variants with a thickness of 70 cm of chernozem layer, and quite independently of the screening coating of loess-like loam. The only exception when covering black soil with a layer of loess loam was wheat, in which the relative number of roots slightly increased – from 75.7 %, with a thickness of 30 cm of the soil layer, to 77.3 % with a thickness of 70 cm. For cultivation on a layer of black soil with a thickness of 70 cm, the relative mass of the roots of perennial leguminous grasses in the arable layer decreased approximately to the level of this indicator for cereals, but in terms of the absolute mass of roots, legumes still had an advantage – in a 30-cm layer there were 2.5–7 times more of them.

The decrease in the mass of the roots in the entire soil layer with an increase in its volume occurred precisely at the expense of the 0-30 cm layer. The dense mastering of the upper 10 cm soil layer by the roots in all trias attracts attention. This layer accounted for 50.9 to 63.5 % of the total root mass. With depth, the mass of roots, as well as their relative content, decreased. In the variant with the least powerful layer of chernozem mass – 30 cm without a loess substrate, 31.6 % of roots were contained in a layer of 10–30 cm. At a capacity of 70 cm without loess loam – 15.8 %, in the version 30BS + 50LLL – 17.6 %, in the version 70BS + 50LLL – 13.7 %. Roots in the middle part of bulk layers of black soil and loess were more evenly distributed. In the soil layer adjacent to the mine rock, the mass of the roots increased somewhat, amounting to 3–5.6 %. In the upper zone of the mine rock, in the presence of a layer of loess-like loam, the roots penetrated weakly, and all the more weakly, because a more powerful layer of black earth was poured on top of the screen.

The roots did not have enough living space in the variants without a layer of loess loam, where the total volume of the soil was relatively small. They penetrated into the upper zone of the mine rock in much larger quantities (in the 0–10 cm mine rock layer, they were 12.2 % in the 30 cm black soil layer and 11.6 % in the 70 cm layer). The limited spread of roots deep into the mine rock is due to the toxicity of the latter for living plant organisms. Some penetration of roots into mine rocks should be evaluated positively from the point of view of ensuring the vitality of plants even. Although there are practically no nutrients available to plants in coal, there is quite a lot of moisture there. This is a sufficient reserve of water supply for plants.

And this is important under the conditions of a limited volume of the substrate, especially since this moisture is covered by the soil and is not susceptible to rapid physical evaporation. Such moisture is even more fully and effectively used by plants through the felt of the roots.

Thus, during the sowing of agricultural crops, a rather powerful root system is formed in the bulk soil and in the upper layer of mine rock, which contributes not only to the consolidation of the fertile bulk upper layers, but also to the good growth and development of plants. Sainfoin and alfalfa form the largest root mass.

3.4. Growth and formation of productivity of agricultural crops depending on methods of land reclamation and fertilizers

The most complete assessment of the effectiveness of reclamation methods can be made by creating different capacities of reclaimed profiles in terms of impact on agricultural crops. Therefore, great attention is paid to the study of growth, development and yield of the main field crops. Research was conducted on fertilized and unfertilized backgrounds.

3.4.1. Productivity of winter wheat according to different predecessors

The obtained data on the biometric indicators of winter wheat Bezosta I and Odeska napyvkarlycova, shown in Tables 3.4.1 and 3.4.2, show that the structures of technozems and fertilizers have a great influence on the growth, development and productivity of plants. This is a consequence of the difference in fertility and strength of bulk layers of loess like loam and black soil. The height of plants of the Odeska Napyvkarlykova variety increased from 48.4 to 69.2 cm with an increase in the thickness of the bulk black soil layer and the application of fertilizers, from the option least supplied with nutrients (a layer of soil mass of 30 cm without an interlayer of loess loam and without the application of fertilizers) to the most supplied (layer 70 cm of black soil mass on a layer of loess loam with fertilizers). In the medium-growing variety Bezosta I, the plant height increased by 42.2 cm (from 62.3 to 104.5 cm), or by more than 67 %. The length of the ear on the poorest man-made edaphotope in Odeska Napyvkarlykova was 4.7 cm, and in Bezostoya I – 5.7 cm. With the increase in the fertility and strength

Table 3.4.1

Biometric indicators of winter wheat of variety Bezosta I

Trial		Height, cm	Bushiness		Ear length, см	Grain mass 1000, г
Depth, cm	Fertilizer		total	productive		
Without LLL layer						
30	0	62.3	2.5	2.4	5.7	31.5
	NPK	66.9	3.4	2.6	5.9	32.6
50	0	80.4	2.9	2.6	6.2	35.4
	NPK	82.8	3.4	2.9	6.4	37.2
70	0	82.2	2.9	2.8	6.3	36.9
	NPK	88.1	3.8	3.0	6.9	37.8
Without LLL layer						
30	0	89.6	3.5	3.0	6.9	37.4
	NPK	94.0	3.9	3.2	7.4	38.5
50	0	93.1	3.7	3.2	7.3	38.2
	NPK	95.5	4.8	4.0	7.7	38.9
70	0	96.1	4.6	4.0	7.5	39.3
	NPK	104.5	5.3	4.5	7.9	39.8

Table 3.4.2

Biometric indicators of winter wheat of variety Odeska Napyvkarlycova

Trial		Height, cm	Bushiness		Ear length, см	Grain mass 1000, г
Depth, cm	Fertilizers		total	productive		
Without LLL layer						
30	0	48.4	3.5	2.8	4.7	27.3
	NPK	52.7	3.7	3.1	5.0	27.8
50	0	54.9	3.7	3.4	5.5	32.4
	NPK	55.7	4.0	3.4	5.7	33.6
70	0	56.9	4.2	3.5	5.8	33.5
	NPK	58.8	4.0	3.5	6.0	33.9
With LLL layer						
30	0	62.0	4.2	3.6	6.0	34.6
	NPK	62.9	5.9	4.7	6.3	35.3
50	0	63.7	4.9	4.8	6.5	35.8
	NPK	65.4	5.8	5.7	6.7	36.6
70	0	67.3	6.1	5.5	7.0	37.1
	NPK	69.2	7.5	6.7	7.4	37.4

of black soil, it increased to 7.4 and 6.9 cm, respectively. Indicators of plant bushiness and weight of 1000 grains increased every year of research. This definitely had a positive effect on the yield. It is also important to note the significant positive effect of fertilizers on the main elements of productivity. Moreover, they were higher by 8–11 % in the trials where the soil layer was 30 cm, than when the layer thickness was 50–70 cm.

Undoubtedly, the completeness and fertility of various man-made edaphotopes can be most fully assessed by the yield of crops grown on them. Therefore, for a more complete assessment, we took into account the yield of winter wheat, corn, barley, alfalfa and sainfoin. Data on collection of biomass of winter wheat straw Bezosta I by year are shown in Table 3.4.3.

Table 3.4.3

The influence of methods of land reclamation on collection winter wheat straw Bezosta I, centner/ha

Trial		Year			Average	Increasing, %
Depth, cm	Fertilizer	1st	2nd	3rd		
Without LLL layer						
30	0	17.55	29.6	4.8	17.3	–
	NPK	19.2	32.8	7.7	19.9	15.0
50	0	24.8	32.9	21.2	26.3	51.9
	NPK	27.0	38.5	23.7	29.8	72.2
70	0	31.6	35.1	25.5	30.7	77.4
	NPK	33.4	42.1	29.8	35.1	103.0
With LLL layer						
30	0	34.3	37.8	35.1	35.8	–
	NPK	35.2	48.8	38.1	40.7	13.8
50	0	40.3	41.7	51.4	40.0	12.0
	NPK	43.0	53.2	41.0	45.8	28.0
70	0	41.0	45.1	42.4	42.8	19.6
	NPK	46.5	55.5	45.2	49.1	37.4

The relative effect of these factors decreases depending on the thickness of the layer of black soil mass increases, the yield increase decreased from 135.3 %, in the trial with a bulk layer of black soil mass of 30 cm, to 60.1 %

with a layer of 70 cm (Table 3.4.4). The straw yield was the highest in the version with a layer thickness of 70 cm of black soil mass, a layer of loess-like loam and fertilizers – 49.1 centner/ha.

Regrouping the data made it possible to separate the effectiveness of fertilizers and the layer of loess loam (Table 3.4.5). As can be seen, the presence of a loess-like loam screen by itself led to the same relative increase in the biomass of wheat straw (60.0 %) on average as with the application of fertilizers (60.4 %). It is characteristic that for the same layers of black soil mass on both fertilized and unfertilized backgrounds, almost the same relative increases in straw biomass were also obtained.

Table 3.4.4

Change in the yield of winter wheat straw Bezosta I under the influence of a layer of loess loam and fertilizers (average over 3 years)

Depth, cm	Without LLL layer and NPK	With LLL layer and NPK	Increasing	
			centner/ha	%
30	17.3	40.7	23.4	135.3
50	26.3	45.8	19.5	74.2
70	30.7	49.1	18.4	60.1

Table 3.4.5

The amount of winter wheat straw biomass Bezosta I depending on the thickness of the chernozem mass and the presence of a layer of loess loam (average over 3 years), centner/ha

Depth, cm	Without LLL layer	With LLL layer	Increasing	
			centner/ha	%
Without LLL layer and NPK				
30	17.3	35.8	18.5	106.8
50	26.3	40.0	13.7	52.4
70	30.7	42.8	12.0	39.4
With LLL layer and NPK				
30	19.9	31.3	11.4	104.6
50	29.8	35.2	5.4	53.7
70	27.0	35.1	8.1	40.0

A comparison of the relative yield increases obtained from the action of mineral fertilizers in their pure form allows us to state (Table 3.4.6) that their effectiveness largely depended on the presence of a loess-like loam screen and the thickness of the layer of black soil mass. So, without a screen, the increase in biomass of straw increased with the increase of the black soil layer from 2.6 to 4.4 t/ha, and with it from 20.8 to 22.1 t/ha. This indicates that it is very important to lay a layer of loess-like loam between the soil layer and the rock, and to bring the thickness of the thick soil up to 70 cm, because with its increase, the absolute productivity indicators also increase. We evaluated the productivity of the created recultivated profiles using the intensive variety of Odeska Napyvkarlykova winter wheat, which differs from Bezosta I in terms of morphological and biological features, plant height, bushiness, and response to edaphotope fertility.

Table 3.4.6

Biomass yield of Bezosta I winter wheat straw depending on fertilizers on different recultivated profiles (average over 3 years), center/ha

Depth, cm	Without fertilizers	NPK	Increasing	
			centner/ha	%
Without LLL layer				
30	17.3	19.9	2.6	15.0
50	26.3	29.8	3.5	13.4
70	30.7	35.1	4.4	14.4
With LLL layer				
30	19.9	40.7	20.8	13.8
50	29.8	45.8	16.0	14.3
70	27.0	49.1	22.1	14.9

Therefore, the addition of 0.5 m of loess like loam turned out to be practically equivalent to the application of mineral fertilizers on reclaimed lands without a layer of loess loam. The presence of a layer of loess-like loam led to an increase in the biomass of Odeska Napyvkarlykova winter wheat straw by an average of 10.1–11.1 centner/ha, while in its absence but with fertilizer application, the amount of biomass increased by only 4.7–8.3 centner/ha (Table 3.4.7).

Table 3.4.7

Increases in biomass of Odeska napyvkarlykova winter wheat straw biomass under different land reclamation options (on average over 2 years), center/ha

Depth, cm	With LLL layer		With fertilizers	
	centner/ha	%	centner/ha	%
	Without fertilizers		Without LLL layer	
30	20.3	49.4	4.7	18.4
50	12.0	36.5	8.1	67.4
70	10.9	27.6	8.3	21.1
	With fertilizers		With LLL layer	
30	26.6	104.6	11.1	26.9
50	14.3	35.0	10.4	23.2
70	12.7	26.6	10.1	20.1

Application of fertilizers on reclaimed lands with a layer of loess loam allowed to increase the average relative increase in biomass by 55.4 % compared to 37.8 % in options with a screen of loess loam without fertilizer application. However, the difference in absolute yield values was small. At the same time, the relative efficiency of fertilizer application on man-made edaphotops from loess loam significantly decreased (23.4 % increase in yield) compared to their application on two-tier reclaimed land (35.6 %). But in terms of absolute allowances, the results were the opposite.

Thus, for two varieties of winter wheat (Odeska Napyvkarlykova and Bezosta I), similar patterns were obtained, on the basis of which the following conclusion can be drawn. An important factor in the reclamation of mine dumps is the creation of a loess-like loam screen between the mine rock and the black soil mass. The second important factor is the thickness of the bulk soil mass. The largest yield of winter wheat straw can be obtained with the structure of the edaphotope, which includes a layer of loess-like loam above the mine rock, then a 70 cm layer of chernozem soil and the application of mineral fertilizers.

3.4.2. Yield of barley straw

The biomass yield of spring barley straw on reclaimed lands was less than that of winter wheat by approximately 2 times (Table 3.4.8).

Table 3.4.8

Yield of straw biomass of spring barley Donetsk 8 on soil reclaimed, center/ha

Trials		Year			
Depth, cm	**Fertilizers**	**1st**	**2nd**	**3rd**	**%**
Without LLL layer					
30	0	1.98	9.7	4.4	–
	NPK	2.25	13.3	6.2	33.3
50	0	9.3	12.3	17.1	138.3
	NPK	14.1	17.6	17.55	205.0
70	0	21.15	13.5	17.7	223.3
	NPK	21.9	19.6	19.0	273.3
With LLL layer					
30	0	23.7	13.0	24.2	–
	NPK	26.8	20.2	25.6	19.6
50	0	25.9	15.3	26.2	10.7
	NPK	27.0	20.9	25.4	24.9
70	0	30.4	16.3	26.6	25.8
	NPK	30.6	23.0	30.7	38.7

The effect of fertilizers was stronger in wet years, and weaker in dry years. The effect decreased with increasing capacity of the bulk layer, where there are more nutrients. Similar results were obtained for options with a bulk black soil layer thickness of 30 and 50 cm. Therefore, the application of mineral fertilizers on reclaimed land is an important factor in increasing the collection of barley straw biomass. Application of fertilizers when layers of soil were placed on mine rock provided higher and growing increases in straw collection (33.3, 205, and 273.3 %, respectively, for black soil layers of 30, 50, and 70 cm), than in the presence of a layer of loess loam, where the increases were only 10.7, 24.9 and 38.7 %. At the same time, on both backgrounds, the relative increases in the biomass of barley straw of the Donetsk 8 variety from the application of fertilizers were significantly higher than from the successive (from 30 to 70 cm) increase in the thickness of the layer of black soil mass (Table 3.4.9).

Table 3.4.9

Barley straw biomass increases in different land reclamation options (3-year average), centner/ha

Depth, cm	**With LLL layer**		**With fertilizers**	
	centner/ha	**%**	**centner/ha**	**%**
	Without fertilizers		Without LLL layer	
30	14.9	275.0	1.8	33.3
50	9.5	74.1	3.6	28.0
70	8.0	45.9	2.7	15.5
	With fertilizers		With LLL layer	
30	15.3	236.2	4.0	19.6
50	8.8	53.6	2.9	12.8
70	7.9	39.3	2.6	10.2

The creation of a layer of loess-like loam between the mine rock and bulk layers of black soil is the most powerful factor ensuring the high yield of barley straw on reclaimed lands.

The presence of a layer of loess loam under layers of chernozem mass 30, 50, and 70 cm thick on the background without fertilizers helped to increase the yield of barley straw by 275, 74.1, and 45.9 %, compared to trials without a screen of loess loam comparative to trial with fertilizer application – 236.2, 53.6 and 39.3 %, respectively. The value of the layer of loess loam for the formation of the biomass yield of barley straw consistently decreased as the thickness of the layer of black soil mass increased against the background of fertilizer application. This is confirmed by the conclusion made in a similar version of the experiment with winter wheat. The evaluation of the efficiency of applying fertilizers on reclaimed lands with different thicknesses of the black soil layer showed that in the presence of a loess-like loam screen, the absolute increases in straw collection with an increase in the thickness of the black soil layer from 30 to 70 cm consistently and quite noticeably decreased, regardless of whether fertilizers were applied or not. Yield increases from fertilization decreased regardless of the presence of a layer of loess loam. The efficiency of fertilization on reclaimed land without a layer of loess loam was much higher (25.6 % increase in straw yield) than with a layer of loess loam (14.2 %). Therefore, each of the studied factors – the thickness of the layer of black soil mass, the application of mineral fertilizers and the creation of a loess-like loam screen – participate in the formation of above-ground vegetative biomass of agricultural crops on reclaimed lands. The positive effect of the reclamation of disturbed lands reaches a maximum, if in the options with a layer of loess loam, the other two factors are fully realized, the increase of the soil layer to 70 cm and the introduction of full mineral fertilizer.

3.4.3. Yield of corn straw depending on different predecessors

The study of the potential productivity of corn on reclaimed lands was evaluated for three predecessors: black fallow, winter wheat and corn for grain. The same odd precursors are widely used in agricultural production in the steppe zone of Ukraine. The results of crop accounting are presented in Tables 3.4.10–3.4.12.

The productivity of grain crops according to the amount of straw in all predecessors increased with the increase of the soil layer from 30 cm (without loess loam screen and without fertilizer) to 70 cm, placed on loess loam with the introduction of full mineral fertilizer. The amount of corn straw increased from 29.5 to 66 centner/ha, for winter wheat from 17.9 to 56.5, and for grain corn from 22.5 to 48.1 centner /ha. The average increase in the yield of this crop due to the combined effect of the researched reclamation factors was 225.8, 315.6 and 213.8 % in the order of the named predecessors. It should be noted that the general range of variation in the yield of corn straw under winter wheat turned out to be much wider than for black steam and grain corn. It is possible to compare the yield of corn straw for different predecessors in the first and second years. In these years, it was sown on them at the same time. The first year was favorable for the growth and biomass formation of corn straw. It was in this year that the highest

Table 3.4.10

The influence of different sizes of the soil layer and fertilizers during land reclamation on the yield of corn straw after black fallow

Trials		Yield, centner/ha			
Depth, cm	Fertilizers	1st	2nd	3rd	%
Without LLL layer					
30	0	31.4	55.4	54.9	–
	NPK	44.6	60.5	60.2	16.6
50	0	54.9	61.8	62.9	26.8
	NPK	90.4	71.5	101.4	59.0
70	0	64.6	75.4	73.9	51.2
	NPK	85.3	78.7	79.8	72.2
With LLL layer					
30	0	68.2	81.4	74.4	–
	NPK	96.0	85.6	75.5	14.8
50	0	74.6	85.4	81.3	7.7
	NPK	96.2	93.0	84.6	22.1
70	0	82.1	94.9	91.5	19.7
	NPK	108.3	110.2	101.3	42.6

Table 3.4.11

Yield of corn straw grown on reclaimed lands after winter wheat

Trials		Yield, centner/ha				%
Depth, cm	Fertilizers	1st	2nd	3rd	4th	
1	2	3	4	5	6	7
Without LLL layer						
30	0	16.8	38.2	37.4	21.9	–
	NPK	17.4	42.7	42.7	22.1	8.9
50	0	39.5	39.4	41.4	59.4	57.0
	NPK	45.0	46.2	49.1	73.6	86.6
70	0	54.6	45.9	51.7	68.6	92.7
	NPK	61.0	59.0	59.5	81.0	127.4

Continuation of the table 3.4.11

1	2	3	4	5	6	7
With LLL layer						
30	0	82.2	48.3	56.3	84.3	–
	NPK	82.4	66.2	60.2	92.0	10.8
50	0	86.9	56.3	60.2	94.4	9.7
	NPK	90.6	69.0	69.1	99.4	20.8
70	0	92.5	59.4	72.0	101.9	20.0
	NPK	97.4	72.3	82.1	109.8	33.2

Table 3.4.12

Biomass yield of corn straw on reclaimed land after corn per grain

Trials		**Yield, centner/ha**			**%**
Depth, cm	**Fertilizers**	**1st**	**2nd**	**3rd**	
Without LLL layer					
30	0	33.0	31.5	43.7	–
	NPK	39.5	35.5	51.4	16.9
50	0	36.5	38.2	57.1	22.2
	NPK	44.0	42.6	74.9	49.3
70	0	38.6	41.9	83.0	51.6
	NPK	49.0	47.5	90.2	72.9
With LLL layer					
30	0	45.6	45.8	90.6	–
	NPK	51.2	48.3	98.2	8.7
50	0	48.2	50.6	94.2	6.1
	NPK	58.2	51.8	103.5	17.4
70	0	52.2	54.7	100.0	13.7
	NPK	62.7	59.4	108.6	26.9

absolute harvest of straw in our experiment was achieved for black steam – 110.2 centner/ha. Therefore, the average yield increases from increasing the strength of the black soil layer, applying mineral fertilizers and creating a screen of loess loam on corn confirm the trends and regularities established on winter wheat and spring barley. However, a detailed analysis revealed a number of provisions that turned out to be specific only for corn (Table 3.4.13–3.4.15).

Table 3.4.13

The influence of precursors on the biomass of corn straw depending on the structure of the edaphotope (average over 2 years), centner/ha

Trials		**Predecessor**		
Depth, cm	**Fertilizer**	**Black fallow**	**Winter wheat**	**Corn**
		Yield, centner/ha		
Without LLL layer				
30	0	55.0	37.8	32.3
	NPK	60.3	42.7	37.4
50	0	62.2	40.3	37.4
	NPK	67.5	47.7	35.2
70	0	74.6	48.8	40.3
	NPK	79.4	59.4	48.3
With LLL layer				
30	0	77.9	52.3	45.8
	NPK	80.6	63.2	49.8
50	0	83.4	58.2	49.3
	NPK	88.8	69.1	55.0
70	0	93.1	65.8	53.4
	NPK	105.8	77.1	61,1

Table 3.4.14

Additions of corn straw with different predecessors on reclaimed land (2-year average), centner/ha

Depth, cm	**Black fallow**		**Winter wheat**		**Corn**	
	centner/ha	**%**	**centner/ha**	**%**	**centner/ha**	**%**
Without LLL layer						
30	22.9	41.6	14.6	38.6	13.4	41.6
50	21.1	33.9	17.9	44.4	11.8	31.6
70	18.6	24.9	17.0	34.8	13.3	32.5
With LLL layer						
30	20.3	33.7	9.6	22.5	12.3	32.9
50	21.3	31.5	21.4	45.0	11.7	26.9
70	26.4	33.3	17.8	29.9	12.8	26.5

Table 3.4.15

The effect of fertilizers on the increase in the biomass of corn straw when it is grown according to different predecessors on reclaimed soil profiles (2-year average), centner/ha

Depth, cm	Black fallow		Winter wheat		Corn	
	centner/ha	%	centner/ha	%	centner/ha	%
Without LLL layer						
30	5.3	9.6	5.0	13.3	5.1	15.8
50	5.3	8.5	7.4	18.2	5,9	15.8
70	4.8	6.4	10.6	21.6	8.0	19.8
With LLL layer						
30	2.7	3.5	10.9	20.7	4.0	8.7
50	5.4	6.5	10.9	18.7	5.8	11.7
70	12.6	13.6	11.4	17.3	7.7	14.4

The stabilizing role of the loess loam screen was quite clearly manifested. The expediency of placing grain corn on the best predecessors in order to obtain the maximum return from the annually reclaimed areas was revealed. There was a fairly clear tendency to a decrease in yield increases depending on the best precursor to the worst, on the one hand, and to an increase as the power of the black soil layer increased, on the other.

The difference in the amount of corn straw between the options, which is determined by the application of fertilizers, turned out to be reliable. This shows that corn responded to the change of the studied factors to the greatest extent, including the introduction of mineral fertilizers.

3.4.4. Changes in the yield of cereal crops straw under the influence of the technical soils fertility and fertilizers

The selection of the most productive crops, not only by species, but also by variety, is of great importance for accelerating the payback of costs for reclamation of disturbed lands. Varieties of winter wheat reacted differently to reclamation options. The Bezosta I variety provided the highest amount of straw (Table 3.4.16).

Table 3.4.16

Biomass of straw of different varieties of winter wheat, centner/ha

Trial		Bezosta I	Istok	Odeska Napyv-karlikova	(±) to Bezosta 1 variety	
Depth, cm	Fertilizer				Odeska Napyv-karlikova	Istok
Without LLL layer						
30	0	4.8	7.8	4.8	0	+ 0.9
		7.7	9.2	6.4	–1.0	+ 1.2
50	0	27.6	25.4	16,4	–3.7	–1.3
		23.7	23.9	21.0	–2.0	+ 0.2
70	0	25.5	26.7	21.6	–3.0	+ 0.9
		29.8	21.7	23.0	–5.2	–1.6
With LLL layer						
30	0	35.0	38.9	25.4	–7.5	–4.0
		38.0	33.0	27.8	–7.9	–3.9
50	0	39.5	31.3	29.0	–8.1	–6.3
		40.95	33.9	32.9	–6.2	–5.4
70	0	42.4	39.8	36.5	–4.5	–2.0
		45.2	40.6	39.1	–4.7	–3.6

In the control, without a layer of loess-like loam, the level of straw biomass of all varieties was extremely low (within 5.9–7.4 centner/ha), but it consistently increased as the agrobackground improved in each of the experimental blocks – without a layer and on the understory layers of loess loam. However, in each variety, the level of straw biomass increased at different rates. In the block of variants without a layer of loess loam, i.e. on a poorer general agrobackground, approximate parity in yield growth was maintained between the varieties Bezosta I and Istok. However, even with the presence of a layer of loess loam under the soil layers, the Istok variety significantly lagged behind the Bezosta I variety in terms of straw biomass. At the same time, in all variants, except for one case (70 cm layer of black soil mass without fertilizer application), this lag became reliable.

The yield of the Odeska Napyvkarlikova variety decreased most significantly. It could not withstand competition with the Bezosta I variety in the first block of options with loose layers of black soil (without loess-like loam).

A particularly noticeable lag in productivity occurred in the variant with a loess-like loam screen. Thus, the absolute indicators of the straw biomass of the Odeska Napyvkarlikova variety in the version with a thickness of a layer of black soil mass of 50 cm without applying fertilizers were 13.0 t/ha lower than those of the Bezosta I variety, which exceeded the level of mathematical reliability. A characteristic feature was that the amount of yield reduction did not depend on the application of mineral fertilizers to the soil. The selection of crops for reclaimed land is also very important (table 3.4.17).

Table 3.4.17

The influence of the structure of technosol and fertilizers on the yield of cereal crops, centner/ha

Trial		**Winter wheat bezosta**	**Barley donetsky 8**	**Corn (dnyprovsky 320)**		
Depth, cm	**Fertilizer**			**Black fallow**	**Winter wheat**	**Corn**
Without LLL layer						
30	0	17.3	5.4	47.2	27.7	36.0
	NPK	19.9	7.2	55.0	31.2	42.1
50	0	26.2	12.9	59.8	45.0	44.0
	NPK	29.8	16.5	75.0	53.4	53.8
70	0	30.7	17.5	71.4	55.2	54.6
	NPK	35.1	20.2	81.3	65.1	62.2
With LLL layer						
30	0	35.7	20.25	74.7	67.8	60.6
	NPK	40.7	24.2	69.7	75.2	65.9
50	0	40.0	22.4	65.4	74.4	64.3
	NPK	45.8	25.3	91.2	81.9	71.2
70	0	42.8	25.5	89.4	81.4	69.0
	NPK	49.1	28.1	106.6	90.4	77.0

In terms of straw biomass, corn in all cases significantly exceeds the best varieties of winter wheat, especially spring barley, in terms of productivity. The advantages of growing corn are quite obvious even when placing it behind the worst of its predecessors – grain corn. On average, over three years, corn exceeded winter wheat by 37.7 % and spring barley by 75.5 % in terms of straw biomass. Even more convincing data on the superiority of corn was obtained when it was placed on a black pair, where the yield was higher than that of winter wheat and spring barley by 80.4 and 129.8 %, respectively. The range of yield fluctuations of all studied crops in variants without a layer is much wider than in the presence of a screen of loess loam. Spring barley in variants with black soil on a screen of loess loam was characterized by the smallest common range of variation, and corn on black steam in variants without an interlayer was the largest.

The greatest positive impact on the bioproductivity of grain crops is made by the full application of all reclamation factors. The creation of a loess loam screen is the leading of these factors. The most productive crop was corn for grain after black steam.

In general, the distribution of crops according to the decrease in the amount of straw biomass looks like this: in the first place is corn, placed after black steam; to the second – corn after winter wheat, to the third – corn after corn for grain, to the fourth – winter wheat after black steam, to the fifth – spring barley after stubble.

3.4.5. Productivity of perennial legumes

Data on the yield of alfalfa and sainfoin hay on man-made edaphotops are shown in Tables 3.4.18 and 3.4.19. As can be seen from the obtained results, the dynamics of biomass yield growth of these leguminous grasses as the number of reclamation factors increased was subject to all the regularities discussed above for grain crops. Even on the poorest edaphotopes, crops of perennial legumes produced a good yield. Increasing the strength of the soil layer, applying mineral fertilizers, and bedding black soil with loess-like loam contributed to the consistent growth of the vegetative mass of both types of grasses and a fairly high harvest of above-ground biomass. On average, for three years, the largest hay yield was in alfalfa (66 tons/ha). It turned out to be 16.4 centner/ha lower in sainfoin.

The rates of yield growth of both crops with an increase in the thickness of the black soil mass were approximately the same (for alfalfa without an interlayer – 16.3–114.3, on a loess-like loam screen – 11.4–23.4 %, for sainfoin, respectively 15.4–113 and 5.8–15.1 %).

When harvesting hay, safflower was inferior to alfalfa. So, alfalfa and sainfoin can be successfully grown on reclaimed land in Western Donbas. However, sainfoin tolerates a high level of groundwater worse than alfalfa and tends to liquefy more strongly from wetting.

Table 3.4.18

Yield of alfalfa hay for two trials on reclaimed land, centner/ha

Trials		**Yield, centner/ha**			**%**
Depth, cm	**Fertilizers**	**1st**	**2nd**	**3rd**	
Without LLL layer					
30	0	38.9	26.3	10.2	–
	NPK	44.0	32.0	11.7	16.3
50	0	49.2	37.1	26.1	49.4
	NPK	57.9	44.5	27.3	72.1
70	0	60.9	46.6	31.7	88.8
	NPK	70.7	56.0	34.6	114.3
With LLL layer					
30	0	59.5	49.9	0	–
	NPK	73.2	58.9	0	20.5
50	0	67.3	58.2	34.9	–
	NPK	78.1	64.0	36.6	11.4
70	0	75.5	66.8	43.5	15.7
	NPK	82.7	71.3	44.1	23.4

Table 3.4.19

The influence of methods of land reclamation on productivity sainfoin hay for two trials, centner/ha

Trials		Yield, centner/ha			%
Depth, cm	Fertilizers	1st	2nd	3rd	
Without LLL layer					
30	0	22.0	26.3	10.3	–
	NPK	25.4	19.3	11.3	15.4
50	0	31.6	25.8	18.9	56.8
	NPK	34.6	28.4	20.2	71.0
70	0	36.4	30.7	24.5	88.3
	NPK	41.5	36.4	25.7	113.0
With LLL layer					
30	0	42.9	0	0	–
	NPK	46.5	0	0	8.4
50	0	53.2	47.0	29.1	–
	NPK	58.3	49.7	28.7	5.8
70	0	55.4	50.0	36.0	9.3
	NPK	59.4	52.2	37.1	15.1

3.4.6. Bioproductivity of agricultural crops on lands recultivated with meadow-black soil

An important factor in increasing the yield of agricultural crops on insufficiently fertile meadow-black soil low-saline soils, filled with a meter-long layer on top of mine rock, is the introduction of mineral fertilizers (Table 3.4.20).

Placing a layer of loam between the bedrock and black soil provided a higher level of above-ground biomass compared to the option of applying a meter-long layer of meadow black soil to the mine rock. However, it is necessary to understand that meadow black soil is the main type of floodplain soils, which are first removed from the earth's surface in order to cover the formed dumps of mine rocks. It is cheaper to use it locally.

Table 3.4.20

Biomass yield of agricultural crops on two trials of mine dumps, reclamation, centner/ha

Crops	Meadow black soil		50BS + 50LLL + MR	
	Without npk	Npk	Without npk	Npk
Winter wheat straw	29.9	36.1	40.0	45.8
Barley straw	14.9	20.6	22.4	25.3
Corn straw	42.1	52.3	74.4	81.9
Alfalfa hay	41.4	46.8	53.5	59.6

3.4.7. Determination of the energy intensity of agricultural crops plant product

The results of measuring the heat of combustion of biomass of barley, corn and alfalfa are given in Table 3.4.21.

Table 3.4.21

Energy content of biomass of barley, corn and alfalfa, J/g

Soil	Straw		Hay
	Barley	Corn	Alfalfa
Black soil	16343.8	20635.2	17848.6

Taking into account the received data, calculations were made of energy removal by biomass of straw and hay, depending on the options for reclamation of mine dumps (Fig. 3.4.1). The largest output of energy with straw biomass was recorded for corn. Corn straw and corn cobs are most popular bio-feedstock for biofuel production in Ukraine. Currently, corn is cheaper to process into ethanol compared to cellulosic ethanol. Meantime, corn cob can be used as feedstock for the production of bioethanol and(or) biochar via slow pyrolysis process. It is estimated that switching from gasoline to corn bioethanol for use in cars as biofuel will lead to a relative reduction in greenhouse gas emissions of 20 %. Biochar produced from slow pyrolysis process can be used as soil enhancer to improve soil fertility. The physical and chemical properties of corn cob will greatly influence the quality of pyrolysis products as well as the yield percentage of products such as char, oil and gas.

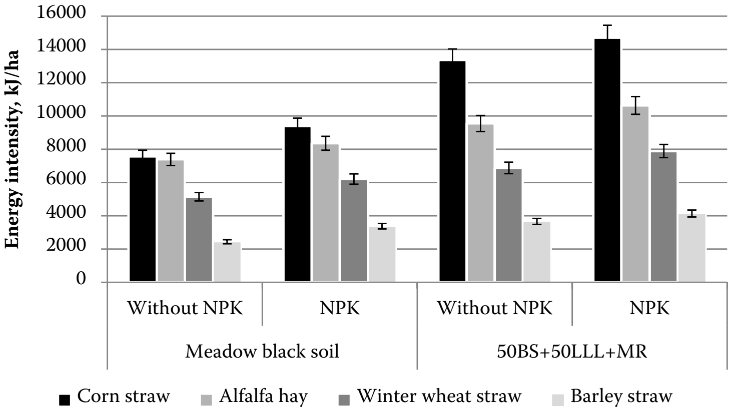


Fig 3.4.1. Energy intensity of biomass of agricultural crops in two variants of reclamation of post-mining lands (kJ/ha)

3.5. Seeds treatment with bioinoculants for winter wheat cultivation in the reclaimed lands

The improved growth, yield, and nutrient uptake in wheat plants demonstrated the potential of mycorrhizal inoculation to reduce the effects of drought stress on wheat grown under field conditions in semiarid areas (Al-Karaki et al., 2004). The arbuscular mycorrhiza symbiosis with crop roots increased with rising soil temperatures in the spring, in time to enhance late-season P accumulation and grain production (Mohammad et al, 1998). Field AMF inoculation increased aboveground biomass, grain yield, harvest index, aboveground biomass P concentration, and content, straw P content, aboveground biomass N concentration and content, grain N content, and grain Zn concentration (Pellegrino et al., 2015).

The main reclamation objective included the cultivation of field grain and energy crops. The scheme for reclamation of disturbed land was based on the study of the effectiveness of capping the mine dumps with different layers of black-soil mass both with and without a shielding layer of loess-like loam. The following artificial models (trials) of technogenic edaphotops were used to look into the peculiarity of upward migration of heavy metals from the coal mine dump: mine rock (MR) + 30cm of the bulk layer of black soil (30BS); M + 50BS; MR + 50BS; MR + 50cm of the loess-like loam (50LLL) + 30BS; MR + 50LLL + 50BS; MR + 50LLL + 0BS. The pH GIS maps were created in the ArcMap 9.3.1 application of ESRI's ArcGIS Desktop GIS software, using SAS Planet version 141212.8406. Interpolation methods were used to build GIS maps in the ArcMap software component and to assume intermediate values of raster points based on the available discrete set of known values. Two strains of Glomus fasciculatus were cultivated at the Institute of Agroecology and Nature Management UAAS. Winter wheat variety Albatros Odesky was taken as the object of field experiments.

GIS maps of layer-by-layer assessment of pH distribution over the area of six experimental plots in the Pavlograd land reclamation station are shown in fig. 3.5.1.

a *b* *c*

Fig. 3.5.1. Layer-by-layer distribution of pH in the black soil over the area of six reclamation profiles (*a* – 0–10 cm; *b* – 10–20 cm; *c* – 20–30 cm)

The 2D soil pH change is connected with the movement of water-soluble salts from the dumped mine rocks to the upper horizons of the artificial reclamation.

The field experiments at the Pavlograd land reclamation station of DSAEU established the effect of a higher level of winter wheat yield in the trials with a protective layer of loess-like loam (Fig. 3.5.2 and 3.5.3).

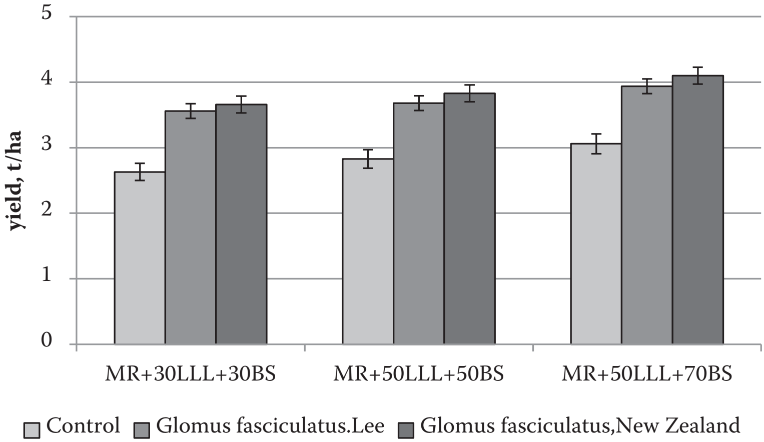


Fig. 3.5.2. The mycorrhiza seeds treatment effect on the yield of winter wheat in reclamation option without a layer of loess loam, t/ha

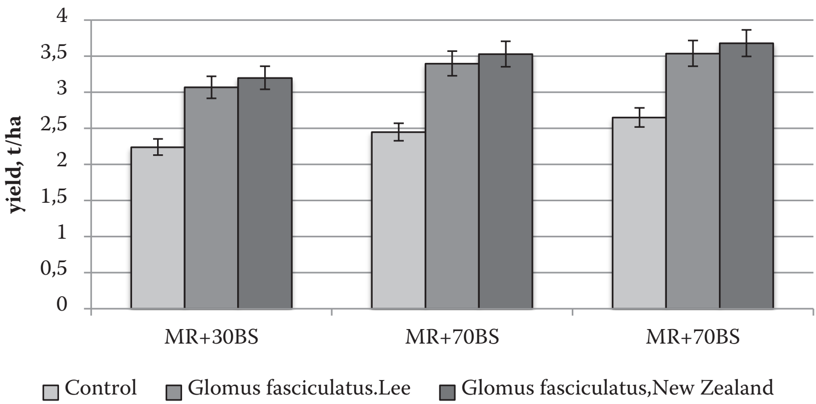


Fig. 3.5.3. The mycorrhiza seeds treatment effect on the yield of winter wheat in reclamation option with a layer of loess loam, t/ha

The obtained results show that a bigger winter wheat yield can be obtained after the seeds treatment with mycorrhiza *Glomus fasciculatus, New Zealand*. It is obvious that winter wheat seeds treatment with mycorrhiza leads to partial removal of the phytotoxic effect of underlying rocks on the development of the root mass in the arable soil layer.

3.6. Environmental feasibility of forest reclamation of post-mining lands in the Western Donbass

Experimental forest land reclamation station was established in spring 1976 in the minefield area of "Pavlogradskaya" mine. Rectangular shaped plot has total area of 3 hectares. The basis of the area was formed with thick layer (8–10 meters) of mine rock intercharged with various topsoil layers. Intensive deformations of the upper layers of the lithosphere and land subsidence with subsidy depth of 7–9 meters were registered.

Two variations of artificial soil profiles with different bulk thickness of mine rock and topsoil were created on the surface of mine dump site. The list of described hereabove artificialy created soil profiles (types) (stratigraphy downward) include:

– Type 1: mine rock;
– Type 2: 0.5 m – loess;

The trees were strip planted across 2 different artificial soil profiles with width between rows 2.5 meters and distance between plants in row from 0.75 to 1.5 meters.

The data of studies of three plants are presented: English oak (*Quercus robur* L.), Silver birch (*Betula pendula* Roth.) and European pear (*Pyrus communis* L.)., which were planted on Type 1 and Type 2 soils. The determination of metals concentration in the technosoil was conducted employing method of the plasma Optical Emission Spectrometry (ICP-OES) on the spectrometer Technologist 5100 (Agilent) with inductively connected plasma. Samples of the plants were crushed to the powder state and after the batch of the plant material (0,3 g), was put into chemical flask and 10 ml of concentrated HNO3 and 2 ml of 30 % H_2O_2 were added and mixture was resting for 1 hour. After that, acid solution was filtered and analyzed for the metals content. Analysis for the heavy metals was performed in the University of Girona, Spain.

Mine rock was defined as unfavorable in their texture properties: with excessively large plasticity, significant shrinkage ability, high stickiness, significant coherence and low wear rate. Considerable variation of characteristic which are typical for artificial soil of remediation layer indicates the heterogenity of these substrates, diversity of properties that can be attributed to the time and place of coal mining, waste rocks storage conditions, etc.

The data on mine rocks volumetric, specific mass density and porosity are shown in the Table 3.5.1.

Table 3.5.1

Mine rocks water-physical properties

№	Meaning	Volumetric density,g/cm^3	Specific density, g/cm^3	Porosity, %
1	Average	1,64	2,52	34,78
2	Min	1,55	2,43	33,20
3	Max	1,75	2,69	36,21
4	SD	0,1	0,15	1,23

It is obviously that mine rocks have high volumetric, specific mass density and porosity. Meantime, during intense oxidation and weathering of rocks, water-physical properties or those are improved. The surface of mine rock reclamation areas often forms water-retaining layer that optimize significantly conditions for plants development on artificial topsoils of different types.

Analysis of the sulfur content in rocks on reclamation areas indicated that amount of pyrite in studied samples was changing from 1.8 to 3.3 %. The upper horizons of mine rocks contacting with atmosphere contained less pyrite compared to backfill horizons. Small portion of monitoring data to reflect the mining rocks pH and salinization profile distribution are shown in the Table 3.5.2 and 3.5.3.

Table 3.5.2

The pH profile distribution

Depth, cm	Average	Min	Max	SD
Type 1				
0–25	4.61	4.44	4.94	0.28
25–50	3.14	2.87	3.28	0.23
50–75	2.61	2.59	2.63	0.02
75–100	5.46	5.21	5.83	0.33
Type 2				
0–25	8.16	7.93	8.53	0.33
25–50	8.14	7.98	8.23	0.14
50–75	6.92	6.77	7.02	0.13
75–100	7.59	7.24	7.83	0.31
100–125	6.64	6.38	6.84	0.24
125–150	6.42	6.03	7.09	0.59
150–175	6.17	5.91	6.42	0.26

Table 3.5.3

The salinization distribution in two artificial soil profiles

Depth, cm	Average	Min	Max	SD
Type 1				
0–25	1071.0	948.00	1309.00	206.2
25–50	1924.7	1803.00	2090.00	148.4
50–75	2583.3	2310.00	2790.00	246.8
75–100	2170.0	2110.00	2280.00	95.4
Type 2				
0–25	144.67	135.00	156.00	10.6
25–50	140.67	132.00	151.00	9.6
50–75	59.67	50.00	65.00	8.4
75–100	96.00	61.00	123.00	31.8
100–125	172.67	128.00	205.00	40.0
125–150	1828.67	1638.00	1956.00	168.2
150–175	1157.00	1021.00	1360.00	179.2

Acidity of mine rock (pH) in (plot Type 1) along one meter profile was ranging from 2.61 to 5.46. Low pH levels were observed in the intergarged layer of rock with depth 50–75 cm. Creation of artificial soil profile allows keeping pH close as neutral or slightly alkaline in the stratum 1 meter. It was possible to fix pH within 6,17–6,64 due to geochemical barrier consisting of carbonated loess loam (0.5 m) and sand (0.5 m).

In comparision to type 1(mine rock one meter profile) type 2 (artificial profile) was characterized far less amount of salinization. By the other words during more then three decades weathering process led to pH and EC stabilization in reclaimed minelands.

Features of trees and bushes development on the experimental forest restoration plots were defined according to vitality indicators, long-term dynamics of linear growth and above-ground phytomass. Significant difference in the rate of growth and vitality of plants on rock and topsoils was observed during the first years of the experiment. During the following years, the difference became even more noticable. The vitality of trees and bushes on the mine rock was insufficient. Plants were poorly branched and had poor leaf covering. The annual increase in height was 5–30 times less, and average crown width was 16–25 times shorter compared to plant on other types of topsoil. Quantitative analysis of aboveground biomass fractions of experimental trees allowed to compare the productivity of different types of forest cultures depending on the particularities of this artificial topsoils and identify the most promising construction of artificial topsoils and types of forest crops (Travleyev et al., 2005). It was established that indicators of aboveground biomass development for experimental plants on the plot were close to those indicators for reclamation plants developing on undisturbed lands. Higher overall productivity for undisturbed lands was achieved due to higher planting density.

Evaluation of non-branching part of the trunk and heights of the crown of three tree species are given in the Tables 3.5.4 and 3.5.5.

Table 3.5.4

Basal diameter of non-branching part of the stem of trees, cm

Type	English oak	Silver birch	European pear
1	11.62±0.83	8.44±3.90	8.73±3.70
2	12.44±1.39	12.10±6.61	14.69±9.31

Table 3.5.5

Height of the crown of three species of trees, cm

Type	English oak	Silver birch	European pear
1	527.20±29.21	630.31±17.30	412.00±15.14
2	813.13±67.89	827.24±27.11	788.96±41.23

In general studied trees species had bigger basal diameter of non-branching part of the trunk and crown height on the reclamation plot compared to plants growing on the mine dump on 40–50 %. English oak plants on the first type of topsoil (mine rock) had created a sustainable forestry plantation. Trees had closed in rows and between rows and trees give fruits, but linear growth rates are lower compared to other experimental groups.

Silver birch had spread around the site by itself, but mainly at the border between first and second topsoil type's areas. Trees have well-developed crowns and a good vitality. Linear growth rates for border between first and second type of substrate.

European pear survived mainly on the second type of substrate. Main indication indexes of above ground phytomass for experimental cultures on the recultivation plots were better than for those growing on the mine rock.

The determination of heavy metals concentration in the leaves is essential in environmental studies. The trees accumulate heavy metals from soils in all seasons and transfer these elements, together with other nutrients, to leaves in the vegetation period. The minerals accumulation is strongly affected by the chemical composition of the soil from which trees get their nutrients (Dulama et al, 2012). The results of evaluation of heavy metals content in the leaves for both experimental types are given in the Table 3.5.6.

It was established that concentration of manganese in leaves decreased in reclamation type 2 compare to trees that grew on the mine dump.

The results of evaluation of heavy metals content in the bark tissue for both experimental types are given in the Table 3.5.7. The level of chromium, manganese and nickel in bark tissue had the same tendency to decrease in type 2 compare to type 1.

The results of evaluation of heavy metals content in the bark tissue for both experimental types are given in the Table 3.5.8.

Table 3.5.6

Heavy metals content in the leaves, ppm

Type	Cr	Cu	Mn	Ni	Sb	Sn	Zn
Betula pendula							
1	1.11±0.10	7.49±0.71	1077.93±51.6	5.09±0.28	3.52±0.25	3,38±0.18	75.44±3.4
2	2.51±0.18	5.70±0.27	588.43±15.0	9.76±0.01	0.8±0.02	3.42±0.21	279.78±2.59
Quercus robur							
1	2.53±0.16	5.96±0.08	1542.96±36.29	9.05±0.13	0.8±0.04	2,86±0.12	34.2±1.28
2	1.94±0.08	6.55±0.46	378.97±9.39	3.64±0.26	0.8±0.02	2.1±0.15	25.91±0.71
Pyrus communis							
1	1.7±0.07	5.17±0.22	194.49±9.74	10.01±0.48	1.33±0.10	1.7±0.03	44.17± 1.11
2	1.7±0.06	4.39±0.19	187.12±11.92	5.94±0.30	2.31±0.12	1.7±0.01	43.85±2.61

Table 3.5.7

Heavy metals content in the bark, ppm

Type	Cr	Cu	Mn	Ni	Sb	Sn	Zn
Betula pendula							
1	2.30±0.15	4.60±0.16	301.75±4.7	1.77±0.13	0.8±0.02	3.03±0.11	107.00±1.76
2	1.39±0.10	5.42±0.12	292.10±3.8	1.30±0.01	0.8±0.03	2.08±0.07	104.46±1.9
Quercus robur							
1	2.49±0.14	5.97±0.32	200.0±3.2	1.49±0.01	1.49±0.01	3.11±0.10	28.02±2.15
2	1.86±0.05	6.33±0.12	170.7±2.75	1.34±0.03	1.34±0.03	2.12±0.12	35.44±0.69
Pyrus communis							
1	1.37±0.03	6.72±0.61	169.43±4.13	1.82±0.18	1.31±0.12	1.7±0.04	52.49±2.5
2	1.25±0.01	6.25±0.02	61.93±0.99	0.86±1.22	0.8±0.02	1.7±0.09	41.09±1.4

Table 3.5.8

Heavy metals content in the wood, ppm

Type	Cr	Cu	Mn	Ni	Sb	Sn	Zn
1	2	3	4	5	6	7	8
Betula pendula							
1	2.72 ± 0.10	2.95± 0.09	86.87±5.50	1.10±0.04	3.52±0.25	2.46± 0.10	42.37± 1.25
2	4.19±0.12	3.67±0.05	160.66±5.7	0.8±0.01	0.8± 0.02	2.93± 0.05	53.89 ±4.00

Continuation of the table 3.5.8

1	2	3	4	5	6	7	8
Quercus robur							
1	1.62± 0.14	4.78±0.04	10.03±0.04	1.10 ± 0.03	1.49±0.10	1.98±0.04	28.37±2.54
2	1.73±0.91	4.06±0.33	39.76±1.78	0.8±0.02	1.37±0.10	2.19±0.1	19.49±0.69
Pyrus communis							
1	9.74±0.13	3.51±0.10	156.33±2.2	0.8±0.01	0.8±0.02	6.48±0.55	32.07±2.13
2	1.27± 0.05	4.02±0.11	11.83±0.05	0.8±0.03	0.8±0.01	1.7±0.08	16.66±0.78

Analysis of the data indicates the opposite trends of distribution of heavy metals in the wood of two trials.

It was established, that main indicators of aboveground phytomass for experimental cultures on the reclaimed plots were better than for those growing on the mine dump. Studied trees species had bigger basal diameter of non-branching part of the trunk and crown height on the reclamation plot compared to plants growing on the mine dump on 40–50 %. English oak plants on the first type of topsoil (mine rock) had created a sustainable forestry plantation. Silver birch had spread around the site by itself, but mainly at the border between first and second topsoil type areas. Main indication indexes of above ground phytomass for experimental cultures on the recultivation plots were better than for those growing on the mine rock.

In the same environmental conditions, heavy metals accumulation of heavy metals by functional plants' parts is heavily depend on soil or substrate contamination rate. Concentration of manganese in leaves decreased in reclamation type compare to trees that grew on the mine dump. The level of chromium, manganese and nickel variation in bark tissue had the same tendency. The opposite trend of distribution of heavy metals in the wood of two trials was fixed.

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4. THE PROSPECTS OF GROWING SWITCHGRASS AND MISCANTUS ON MARGINAL LANDS FOR THE PRODUCTION OF BIOFUEL

The use of perennial grass biomass to obtain solid fuel briquettes and ethanol production is one of the promising areas of bioenergy. However, growing energy crops on high-quality arable soils can pose a threat to food security. Therefore, the involvement of marginal disturbed lands in Ukraine in the process of production of biofuel raw materials is considered expedient. Two types of energy crops – switchgrass (*Panicum virgatum* L.) and miscanthus (*Miscanthus* Anders.) have gained popularity in recent decades. They are characterized by high photosynthesis efficiency, carbon sequestration in the soil, undemanding moisture supply and availability of nutrients in the substrate (Dohleman et al., 2009; Ziolkowska, 2014; Nakajama et al. 2018). These characteristics create good prerequisites for cultivation these crops on low-productivity, technologically disturbed and reclaimed lands (Skousen et al., 2012; Skousen and Brown, 2014; Ussiri, 2019). Biomass yield and adaptive plasticity of switchgrass and miscanthus depend on such factors as climate, physical and chemical characteristics of the soil, cultivation technologies, etc. (Boehmel et al., 2008; Jakovljeviž et al., 2015). Thus, the careful selection of the assortment of plants and the development of advanced technologies for their cultivation for a certain type of territory is an important condition for the economic feasibility of biofuel production on marginal lands. An analysis of existing research on switchgrass and miscanthus has shown that, under conditions of sufficient moisture, the biomass productivity of miscanthus is significantly higher than that of switchgrass (Heaton et al., 2008; Anderson et al., 2012; Mitchell et al., 2012; Scagline et al., 2015). Thus, the yield of above-ground dry biomass of miscanthus can reach 40–60 t/ha, while the switchgrass yield varies within 10–16 t/ha. Both crops have almost the same efficiency of absorbing sunlight. Meanwhile, miscanthus showed higher rates of photosynthesis, efficiency of water and nitrogen use. However, the yield of miscanthus can decrease to 13–20 t/ha in conditions of severe lack of moisture. Propagation of miscanthus is possible only vegetative, the cost of planting areas of this culture with segments of rhizomes is quite high. The profitability of such plantations on unproductive lands may be low. At the same time, the cost of planting switchgrass plantations with seeds is much lower. This is an advantage of switchgrass under conditions of water and nutrient scarcity (Khanna et al., 2008; Sadeghpour et al., 2014).

It is known that many marginal lands are formed in industrially developed areas. Most of such land is unsuitable for agricultural production. Production of biofuel raw materials using perennial plants with low growth requirements may be an alternative under such conditions. The ability of miscanthus and switchgrass to accumulate heavy metals mainly in the roots is another advantage of growing these plants on disturbed land. The simultaneous use of perennial cereals for the extraction or binding of heavy metals by the root system provides an opportunity to link the production of biomass for bioenergy with soil decontamination and restoration (McIntyre, 2003; Yang et al., 2005; Van Ginneken et al., 2007; Balsamo et al. al., 2015). This is a prerequisite for the creation of new workplaces for the production and sale of bio-raw materials in such territories (Dauber et al., 2012; Barbosa et al., 2015).

Various soil amendments (sewage sludge, ash, biochar, etc.) can be applied to improve the condition of disturbed soils and increase the yield of energy crops. However, there is still a significant lack of information on the long-term consequences of the use of soil additives related to the growth and absorptive capacity of plants, the quality of biomass and its thermal characteristics.

4.1. Biological characteristics and technologies of growing switchgrass and miscanthus

Switchgrass (*Panicum virgatum* L.) is a perennial grass common in natural ecosystem of the central and southern parts of the United States. This plant is one of the main components of tall grass prairies. The plant has reddish upright stems that reach 0.5-3 m in height. Inflorescence is an open panicle 15–40 cm long. A characteristic feature is white fluff at the point where the leaf emerges from the stem. Its durability and ability to form new above-ground shoots is a distinctive feature of switchgrass. Vertical shoots develop from their nodes, forming stems and leaves. Thus, a whole colony of vegetative shoots arises around the mother plant (Christian and Elbersen, 1998; Zegada-Lizarazu, 2012). There are many varieties within the species of switchgrass. Some of them were selected in nature, some obtained as a result of selection. Varieties and hybrids of switchgrass are divided into upland and lowland depending on the nature of leaf distribution and plant height (Casler and Vogel, 2014). Generative and elongated vegetative shoots with the main mass of leaves in the upper part prevail in climbing cultivars. On the contrary, lowland varieties have few generative stems and many vegetative, mostly shortened ones.

The root system of switchgrass is dense, can reach 3 m. Its main mass (70–80 %) is concentrated in the arable layer. In the first year of vegetation, the roots in the tillering phase develop weakly, sink into the soil slowly (to a depth of 15 cm). Then there is a more rapid development of the roots and by autumn they reach a considerable depth. The root mass is almost 1.5 times greater than the aerial part of the plant and its increase often occurs until late autumn (Wullschleger et al., 2010; Vogel et al., 2011). Switchgrass has relatively small seeds with a high level of dormancy. The most effective time for sowing seeds is early spring (second decade of April). The optimal seed wrapping depth during the early spring sowing period is 0.5–1 cm, and during the late spring period (the second decade of May) it should not exceed 1.5 cm (Humentyk et al., 2018). Switchgrass seeds begin to germinate at a temperature not lower than +6+8 °C. Seedlings withstand minor frosts down to −2 °C, and at temperatures of −3–5 °C, they mostly die or are severely damaged. The intensity of switchgrass seed germination and the completeness of seedlings are determined by such indicators as temperature and soil moisture. The germination period of plants increases at low temperature and soil moisture. The prolonged shortage leads to the death of plants. However, the decisive factor is the soil moisture, because it decreases with time and the temperature increases. The reserves of soil moisture formed from melting snow do not always provide the necessary conditions for the growth and development of plants. Soil moisture during the sowing period and the amount of moisture in the arable layer constantly changes and depends on weather conditions (Kurylo et al., 2012; Mandrovska, 2013).

Strong weediness of plants during the crop seedling period in the first year of vegetation is the weakest link in the technology of switchgrass growing. General action herbicides are usually used a few weeks before sowing. Their use before sowing is carried out according to lower standards (Kulik, 2013).

The width of the rows is an important factor that determines the productivity of switchgrass. Narrow row spacing accelerates the closing of the soil in the spring and increases the amount of light absorbed by the plant during the growing season. This in a certain way affects the yield of the crop and reduces the need for weed control, because the plants will grow faster in the spacing with a smaller feeding area. However, the problem of self-thinning arises at the same time. As a result, the total volume of biomass from the area decreases. The possibility of disease and grass growth increases. Studies on the width of row spacing in switchgrass crops showed that under drought conditions, crops with wide row spacing (50 cm) had higher yields compared to crops with narrow row spacing: 15 and 30 cm (Ocumpaugh et al., 1997; Bransby et al., 1997; Planting and Managing..., 2009). The increase in yield was especially noticeable after several years.

It was established that the accumulation of water from atmospheric precipitation in the spring and summer periods improves with a narrow width between rows (15cm). The weediness in the first years of life decreases, and biomass yield increases. Shading of plants increases with their growth. Intraspecific antagonism increases and productivity begins to be inferior to crops with wider (30–45 cm) rows (Roik, 2011; Moroz et al., 2011; Kulyk, 2012). Thus, optimal conditions for switchgrass can be created by certain agro-technical measures and means, selecting varieties taking into account the agrobiological features of the region.

Miscanthus (*Miscanthus* Anders.) is a perennial grass. This plant natural range is located almost throughout Southeast Asia. Only three species are used among the 16 existing species in the regions with a temperate climate as decorative, anti-erosion and bioenergy crops. These are *Miscanthus sacchariflorus* (Maxim.) Hack., *Miscanthus sinensis* Anders., and *Miscanthus× giganteus* J. M. Greef et Deuter ex Hodk. et Renvoize. Giant miscanthus is used more often for bioenergy. It is a spontaneous sterile triploid hybrid between a diploid form of Miscanthus sinensis and a tetraploid form of *Miscanthus sacchariflorus*. It is characterized by more vigorous growth and biomass than the parental species (Clifton-Brown et al., 2004; Price et al., 2004). This hybrid can reach a height of more than 3–4 m and form strong stems with a diameter of 10–12 mm under favorable conditions. In October, an inflorescence is formed on the last internode of the stem – a panicle 25–30 cm long. The root system of miscanthus is spindly, spreads from underground rhizomes, can reach a depth of 3 m, but most of the roots are located in a layer up to 100 cm.

Miscanthus reproduces only vegetatively, by rhizomes; vegetation begins at the end of April and ends in October. Shoot formation occurs throughout the growing season. Miscanthus yield largely depends on water supply. Miscanthus needs a significant amount of water (approximately 700 mm of precipitation) to form a large volume of biomass.

Under dry conditions, growth slows down, vegetation ends earlier, It leads to a significant decrease in yield (Dohleman and Long, 2009; Emerson et al., 2014; Kiesel et al., 2017).

Miscanthus rhizomes are planted in previously prepared soil in early April, when the upper layers of the soil still contain enough moisture. The length of rhizomes should be within 5–15 cm and have at least 4–5 buds (Humentyk et al., 2013; Kurylo et al., 2015). Planting is carried out at a depth of 8–10 cm with a density of 14,000–15,000 pieces/ha with a row width of 70 cm. The system of soil tillage measures after planting rhizomes and harvesting biomass requires regulation of the water-air regime and the destruction of weeds.

4.2. Assessment of miscanthus and switchgrass productivity on different types of post-mining substrates

Model experiment with giant miscanthus and switchgrass were established at the Pokrov educational and research station of land reclamation. The model experiment (Fig. 4.2.1) provided for the cultivation of the studied crops in lysimeters with different technosol models (Fig. 4.2.2):

Fig. 4.2.1. Pot experiments with miscanthus and switchgrass

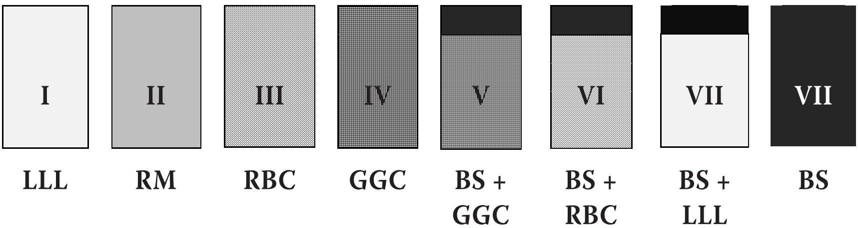


Fig. 4.2.2. Soil profiles in the pot experiment

I – loess like loam (LLL), taken from the side of the open pit quarry (0–150 cm); II – technical mixture of rocks (TM), which consists of loess-like loam and red-brown clay, taken from the side of the quarry (0–150 cm); III – red-brown clay (RBC), taken from the side of the quarry (0–150 cm); IV – grey-green clay (GGC), taken from the side of the quarry (0–150 cm); V – black soil (BS) 0–50 cm + grey-green clay (50–150 cm); VI – black soil (0–50 cm) + red-brown clay (50–150 cm); VII – black soil (0–50 cm) + loess-like loam (50–100 cm); VIII – black soil (0–150 cm); IX – geochemically active dark grey schist clay (DGSC), selected in a layer of 0–20 cm (60 cm) + sand (90 cm); X – dark grey schist clay, selected in a layer of 20–40 cm (60 cm) + sand (90 cm); XI – dark grey schist clay, selected in a layer of 40–60 cm (60 cm) + sand (90 cm).

The soil texture and particles size were determined with "Mastersizer" 3000E particle size analyzer (Fig. 4.2.3) in the geomorphology and soil laboratory at the University of Malaga (Spain). The Mastersizer 3000 uses the technique of laser diffraction to measure particle size distributions from 10nm up to 3.5mm. The patented folded optical design in the Mastersizer 3000 provides an impressive particle size range from 10nm up to 3.5mm using a single optical measurement path. The data obtained allowed to see some differences in the particle sizes of analyzed technosols to understand texture impact on productive indexes of energy crops (Table 4.2.1).

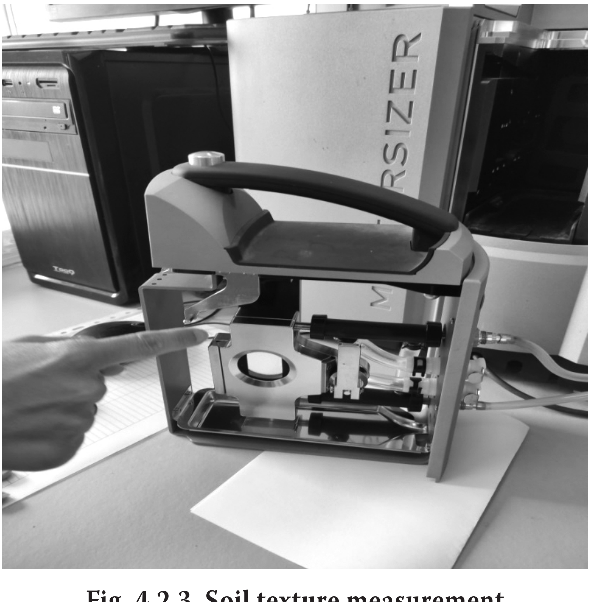


Fig. 4.2.3. Soil texture measurement

Table 4.2.1

Technosols soil texture, μm

Rock	Medium sand (200–630 um)	Fine sand (125–200 um)	Very fine sand (63–125 um)	Sand (63–2000 um)	Coarse silt (20–63 um)	Fine silt (2–20 um)	Silt (2–63 um)	Clay (< 2 um)
LLL	0	0	0	1.45	33.24	60.2	93.45	5.1
RBC	0	0.1	1.53	1.64	7.22	70.72	77.94	20.42
GGC	2.52	2.96	5.29	10.77	24.83	56.77	81.6	7.63
DGC (0–20 cm)	0.55	4.94	14.14	19.63	34.31	42.78	77.09	3.28
DGC (20–40 cm)	0	0.18	5.7	5.88	28.29	57.16	85.45	8.67
DGC (40–60 cm)	0	0	0	0	8.49	74.11	82.6	17.4

Biometric parameters and biomass productivity were determined at the end of the vegetation season (second half of September). Plant height was measured using a measuring ruler. Stem diameter was determined with a caliper at a height of 15 cm above the soil surface. The number of stems was counted per 1 m2. Above-ground biomass was cut at a height of 10 cm from the ground surface and weighed in a wet state. Wet biomass was dried to constant weight to estimate aboveground dry matter yield.

The pot experiment with miscanthus showed that during the first year after planting, the plants form 7–13 orthotropic shoots with a height of 130–160 cm. Plants grown on red-brown clay, loess-like loam and technical mixture were the most developed. Plants growing on grey-green clay had the smallest growth. In the first year of life on mining substrates, miscanthus plants are able to form an average yield of dry above-ground biomass in the range of 4–5 t/ha. The highest productivity (6.4–6.8 t/ha) was recorded on loess like loam and its mixture with red-brown clay. The lowest yield was recorded on grey-green clay (Fig. 4.2.4).

The height of miscanthus plants increased by 10-30 % in the second year of life, and starting from the 3rd–4th year was from 171.5 cm to 200 cm (Fig. 4.2.5). The number of shoots in 2-year-old plants increased by 2–2.5 times. In the future, the intensity of the formation of orthotropic shoots decreases and averages 26–50 % per year. Thus, three-year-old plants have from 23–24 shoots on black soil with the addition of red-brown and grey-green clays to 40 shoots on a mixture of clays (Fig. 4.2.6).

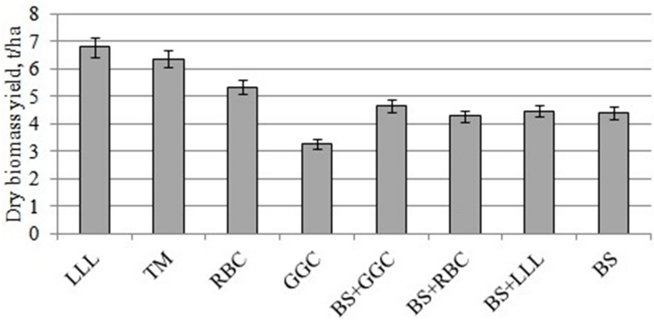


Fig. 4.2.4. Dry biomass yield of 1-year-old miscanthus plants grown on rock substrata

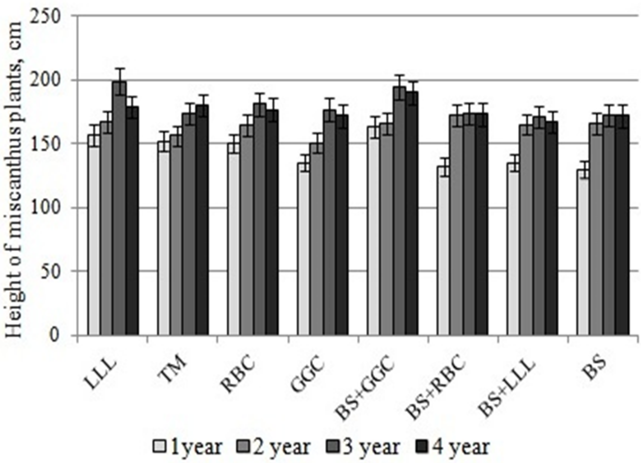


Fig. 4.2.5. Height of miscanthus plants grown on post-mining substrata

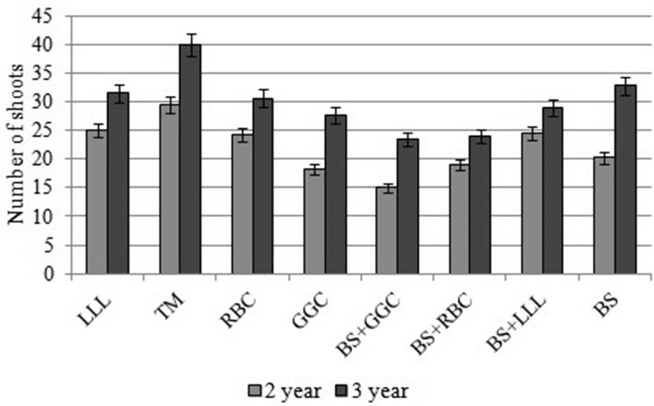


Fig. 4.2.6.The number of shoots on one miscanthus plant grown on post-mining substrata

The thickness of the shoots is a value that changes slightly with age and depends more on growth conditions. This parameter ranges from 7.1 mm (GGC) to 8.8–9.5 mm (LLL and TM, respectively).

The yield of above-ground dry biomass increases over time and reaches its maximum in lysimeters in the third or fourth year. Depending on weather conditions, and especially the level of water supply, miscanthus is able to produce 10-13 tons of dry biomass from 1 ha annually on red-brown clay, mixed clay and loess loam. On other studied substrates, the yield is slightly lower and amounts to 7.8–9.5 t/ha (Fig. 4.2.7).

The growth and development of miscanthus on biogeochemically active dark grey schist clay is much slower than on other mining substrates. The height of plants in the first year of life does not exceed 130 cm. At the end of the year, the average number of shoots is from 3.3 pcs. (on a layer of 0–20 cm) to 8.7 (on a layer of 20–40 cm). Biomass yield is also low and amounts to 2.1–3.2 t/ha.

The intensity of vertical and horizontal growth of miscanthus increases with age. In the second year, the height of plants increases by 6–25 %, the formation of side shoots – 3–3.5 times, biomass productivity – 1.6–2 times.

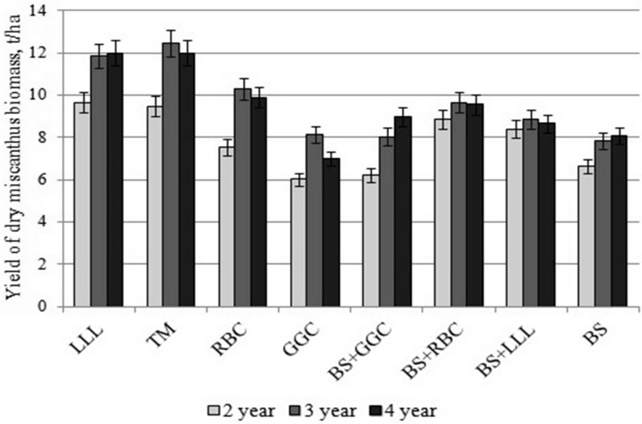


Fig. 4.2.7. Yield of dry above-ground miscanthus biomass on post-mining substrata

The growth of biomass in subsequent years is slowing down. As a result, the average height of the miscanthus cover on dark grey shale clay is 140–150 cm, the number of side shoots per bush is 25–31, the yield of dry biomass is 4.3–6.2 t/ha. Plants grown on a layer of 20–60 cm give the highest productivity.

The average height of one-year-old plants in the model experiment with switchgrass was 54.1 cm. The tallest were plants grown on red-brown loam (RBL) and grey-green clay (64.1 and 62.9 cm, respectively), the lowest – on black soil (41.1 cm) and on black soil with the addition of loess like loam (47.1 cm). During the second year of cultivation, the plant increased in growth from 30 to 65 %. The ratio of plant height for different substrates remained the same as in the previous year. The height of switchgrass ranged from 83 to 116 cm at the end of the third year of cultivation. Plants growing on red-brown loam and grey-green clay turned out to be the tallest, and plants on black soil were the shortest (Fig. 4.2.8). The total height of switchgrass with an inflorescence was from 117.4 cm (BS + LLL) to 145.3 cm (RBL).

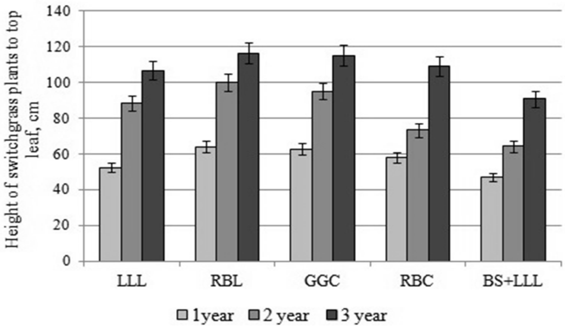


Fig. 4.2.8. Height of switchgrass plants grown on post-mining substrata

The yield of above-ground biomass of switchgrass plants in the first year of cultivation was low and did not exceed 1.5–2 t/ha. Plant productivity more than doubled during the second year. Plants grown on red-brown loam, were the most productive, almost 6 t/ha, the least productive was on black soil and black soil with the addition of loess like loam, only 2.1 t/ha and 2.3 t/ha, respectively. The yield of three-year-old plants ranged from 6.05 t/ha to 11.8 t/ha (Fig. 4.2.9). In this way, the yield increase was from 100 to 150 %.

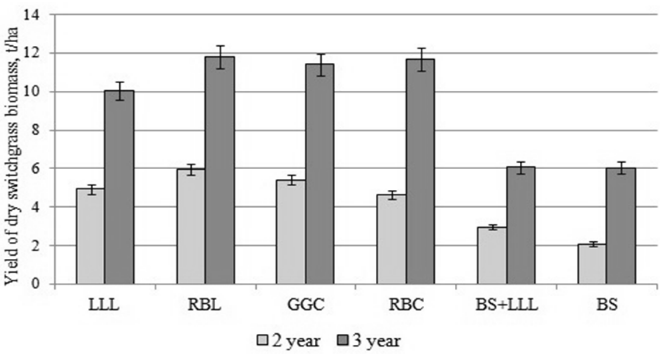


Fig. 4.2.9. Yield of dry above-ground switchgrass biomass on post-mining substrata

The height of switchgrass in the first year of growing on dark grey schist clay ranged from 53.5 cm (layer 0–20 cm) to 60.3 cm (layer 40–60 cm). The number of shoots on one plant was 12–21 pcs. The plants were most developed at a layer of 20–40 cm. The yield of dry above-ground biomass in this variant was also the highest and amounted to 6.02 t/ha against 4.48 and 5.53 t/ha obtained in other layers.

Switchgrass plants continued to build biomass over the following years. As a result, the height of the plants to the flag leaf ranged from 95.1 (at the 40–60 cm layer) to 125.2 cm (at the 0–20 cm layer) in the third year of the experiment. Despite the fact that the plants were the lowest in the 40–60 cm layer, they formed the largest number of lateral orthotropic shoots – 108 pcs. At the same time, the plants growing on a layer of 0–20 cm were the highest. In fact, the number of shoots on them was the smallest – only 70.7 pcs. Two-year and three-year plants did not differ much in terms of aboveground dry biomass yield. As a result, productivity was 4.6–7.1 t/ha.

Switchgrass appeared to be more adapted to growing on dark grey schist clay compared to miscanthus. Its productivity is 10–30 % higher than that of miscanthus (Fig. 4.2.10). A layer of 20–40 cm was the most suitable for growing both crops. Plant development in this variant was the best compared to other layers.

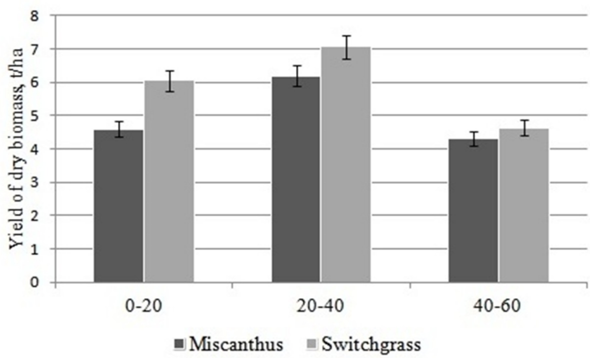


Fig. 4.2.10. Productivity of three-year plants of miscanthus and switchgrass on dark grey schist clay

Based on the research results obtained during three and four years, the following can be stated: a) loess like loam, red-brown clay and their mixture are the most favorable for growing miscanthus. Dark grey schist clay is not suitable for growing miscanthus as an energy crop due to low productivity. Red-brown clay, loess and red-brown loam, as well as grey-green clay are the best substrates for switchgrass. Options with black soil and dark grey shale clay turned out to be the worst in yield. However, the productivity of switchgrass on dark grey schist clay is higher than that of sedge. Therefore, the use of this substrate for obtaining switchgrass raw materials is quite reasonable.

4.3. Soil amendments effect on growth, heavy metals uptake and thermal features of miscanthus and switchgrass

The field experiment with miscanthus and switchgrass was conducted over four years. Seedlings were planted in the experimental plots into a technical mixture of loess-like loam and red-brown clay passed through a long-term phytomelioration stage. The humus content in the substrate was not exceeded 1.5 %. The ratio of humic and fulvic acids was in the range 0.2–0.5, which indicates a low level of humus accumulation and active destruction of the soil mineral part.

The following five amendments were used to determine the effect of various additional fertilizers: ash of sunflower husk in amount 10 t ha^{-1}, municipal sewage sludge (10 t ha^{-1}), mixture of ash and sewage sludge (10 t ha^{-1}), a double dose of sludge (20 t ha^{-1}) and mineral fertilizer with a balance of nutrients N_{60}:P_{60}:K_{60} kg ha^{-1}. All amendments were put into the soil in dry form annually once in spring.

The biometric parameters and biomass productivity were defined at the end of vegetation season (second part of September). Plant height was measured with a measuring ruler. The stem diameter was determined by caliper at 15 cm height above the ground surface by clamping the caliper on to a random plant tiller. The number of stems per m^2 was counted as well. Than the above-ground biomass was cut to a height 10 cm from the land surface and weighed in a wet state. The wet biomass was dried until a constant weight in order to estimate the above-ground dry matter yield.

The content of mineral elements in biomass was determined. For analysis, biomass samples weighing 2 g each were combusted in a muffle furnace at 450 °C by means of drying method and then dissolved in 5 ml of 6N spectral purity hydrochloric acid. The content of mineral elements in obtained mineralizates was measured by AAS using Varian Cary-50 spectrophotometer at the soil unit of Girona University (Spain). The received data represented the arithmetic means of three replicates of each sample, their ranges and standard deviations values.

The thermal characterisctics of plant biomass was measured using thermogravimetric analysis. It was performed at derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. The weight of sample used for analysis was 100 mg. The differential mass loss and heating effects were recorded, and the results of the measurements were processed using software package supplied with the device. The samples of biomass were analyzed dynamically at a heating rate of 10 °C/min in an air atmosphere. The reference substance was aluminum oxide. As a criterion for assessing the thermal stability of biomass, the activation energy of thermal oxidative destruction was determined using the double logarithm method of Broido (1969).

4.3.1. Soil amendments effect on the growth of miscanthus and switchgrass

In the first year after planting, active growth of above-ground and underground biomass was observed. At the end of the growing season, the height of miscanthus plants was from 85 to 100 cm, switchgrass from 105 to 120 cm. At the end of the first growing season, miscanthus plants formed 18–25 orthotropic shoots per 1 m^2 with a diameter of 6.1–7.0 mm. The number of lateral shoots of switchgrass ranged from 72 to 100 pieces/m^2. Their average diameter was 2.3–2.7 mm. Due to rapid growth, the yield of above-ground dry biomass of 1-year switchgrass plantations was higher than that of miscanthus. But the reaction of the latter to the introduction of sewage sludge and mineral fertilizer was stronger, which led to an increase in productivity by 2–2.3 times. As a result, yields in these areas of switchgrass and miscanthus were almost identical (Fig. 4.3.1).

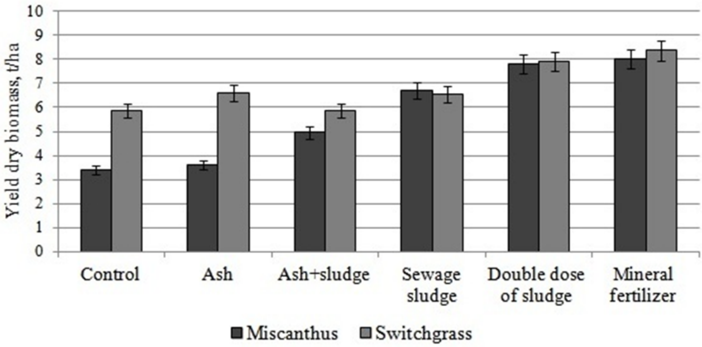


Fig. 4.3.1. Biomass yield of 1-year-old miscanthus and switchgrass plants in plots with added soil amendments

During the second year of cultivation, the productivity of miscanthus already slightly exceeded the productivity of switchgrass. In the control plots, the yield of its above-ground biomass was 5.04 t/ha compared to 4.3 t/ha of switchgrass. The response to fertilizers was also more pronounced. Thus, in the variant with a combination of ash and sewage sludge, the yield increased by 45.2 %, in the area with sewage sludge by 96.8 %. The addition of mineral fertilizer and a double dose of sewage sludge led to an increase in yield by 136.1 % and 130.1 %, respectively. At the same time, the increase in productivity of switchgrass on plots with mineral fertilizer, sewage sludge and a combination of ash and sewage sludge was only 33–36 %. Only in the version with a double dose of sewage sludge, the yield increased twice. The addition of ash had the weakest effect (6–8 %) for both species. Thus, the maximum yield of plants in the second year of growing was for miscanthus 11.6–11.9 t/ha (Double SS and mineral fertilizer), for switchgrass 8.4 t/ha (Double SS).

It is known that both Miscanthus and Switchgrass generally reach full productivity by the end of the third year of cultivation (Burli et al., 2000; Clifton-Brown et al., 2017). Depending on the conditions, the average biomass yield in this period is 8–14 t DM/ha for Switchgrass and 10–30 t DM/ha for Miscanthus (Fike et al, .2006; Wullschleger et al., 2010; Anderson et al., 2011; Kalinina et al., 2017). Usually, on the reclaimed lands productivity is lower and, as a rule, does not exceed 5–6.5 t DM/ha for Switchgrass and 7–11 t DM/ha for Giant Miscanthus (Marra et al., 2013; Scagline et al., 2015; Cherney et al., 2018).

As a rule, Miscanthus has more growth power than Switchgrass. However, under conditions of poor fertility and insufficient water supply, it could not provide decent competition. As a result, the canopy height of both plant species in the control plots was almost the same, 131.1–131.5 cm. The application of amendments led to an increase in the parameters of vertical and horizontal growth from 2 % to 40 %. The use of ash had the least effect, and the influence of double dose of sewage sludge was the strongest. The thickness of the shoots has also increased. In switchgrass, the stem diameter under the influence of ash and a mixture of ash and sludge changed slightly, up to 5 %. The application of sewage sludge and mineral fertilizer increased this indicator by 11–18 %. In Miscanthus, only a double dose of sludge had an improving effect (13.9 %), other amendments did not have a significant impact (1–1.6 %). In this way, the response of Switchgrass plants to amendment application was better than Miscanthus, which contributed to an increase in biomass yield from 7 t DM ha^{-1} (control) to 15–17 t DM/ha (sewage sludge). In miscanthus, the maximum yield (12.4–13.3 t DM/ha) was achieved using mineral fertilizer and double dose of sludge.

By the fourth year of the study, the yield of the switchgrass control plants was almost unchanged, while the favorable water regime led to an almost two-fold increase in the yield of the miscanthus control plants. Thus, the minimum productivity of four-year plants of switchgrass and miscanthus on the technical mixture without amendments was 7.2 t/ha and 13.6 t/ha, respectively.

The introduction of soil additives helped to increase the yield. Just as in previous years, the addition of ash had the least effect, the yield of plants in these plots did not differ significantly from the control. The best effect was obtained from the addition of sewage sludge at a dose of 20 t/ha. In this variant, yield increased by 2.3 tymes for miscanthus and by 3.2 times for switchgrass. Thus, the maximum productivity of switchgrass was 23.3 t/ha, miscanthus – 31.8 t/ha (Fig. 4.3.2).

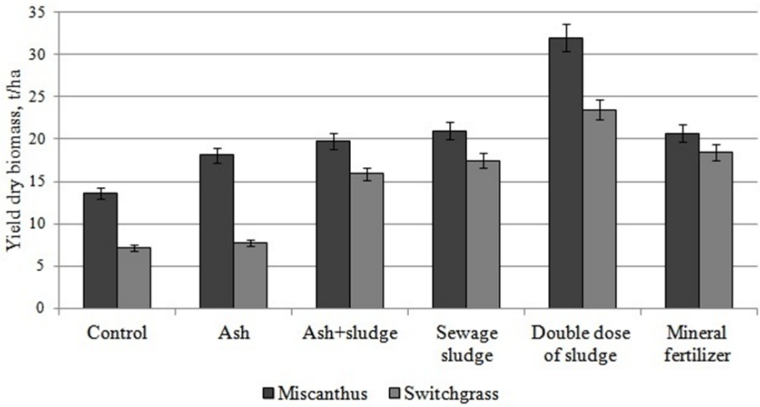


Fig. 4.3.2. Biomass yield of 4-year-old miscanthus and switchgrass plants in plots with added soil amendments

Based on the obtained results, it can be stated that on unproductive lands, depending on the type of substrates, switchgrass is capable of producing from 5 to 7.5 t/ha of dry biomass, miscanthus – from 8 to 14 t/ha. However, switchgrass is more stable than miscanthus, the yield of which is highly dependent on the conditions of the water regime. Prolonged drought can lead to significant crop losses of this crop. The introduction of soil amendments helps to increase the productivity of switchgrass and miscanthus by one and a half, two, and even three times. The most effective additive is sewage sludge, under the influence of which the yield of switchgrass can reach 17.5–23.5 t/ha, miscanthus – 21.0–32.0 t/ha.

4.3.2. Soil amendments effect on heavy metals uptake by miscanthus and switchgrass biomass

A large number of marginal lands are formed in industrialized areas. Such sites are usually contaminated with heavy metals, which can also spread throughout the neighborhood. Therefore, most of these lands are unsuitable for agricultural production. Biomass production using perennials with low growing requirements may be an alternative here. The application of this approach provides double benefits, both in degraded land management and in phytoremediation, due to stabilization or extraction of toxic elements by plants (Van Ginneken et al., 2007; Balsamo et al., 2015). Perennial grasses show suitable characteristics for the phytoremediation process once plants display rapid growth, high biomass yields, deep and extensive root systems, simple agronomic techniques, and tolerance to contamination Moreover, the use of perennial energy and fiber crops with genetic potential to tolerate, extract or stabilize heavy metals give the possibility to associate soil decontamination and restoration with the production of biomass for bioenergy, fiber, and other economically valuable products (McIntyre, 2003; Yang et al., 2005). Additionally, together with the reduction and mitigation of the risk posed by heavy metals for humans and ecosystems, new jobs in the restored land as well as markets for their products might be created in the region (Dauber et al., 2012; Barbosa et al., 2015). Plants differ in their ability to absorb heavy metals from the soil. Besides, application of various soil amendments (sewage sludge, ash, biochar etc.) can affect the bioavailability of metals and the biomass quality (Brian & Jackson, 1991; Bolan & Duraisamy, 2003; Singh, 2008). There is still a significant lack of information on the long-term consequences of using soil amendments related to the growth and absorption capacity of plants, the quality of biomass and its thermal characteristics.

Switchgrass and miscanthus are promising potential agents for long-term remediation of soils contaminated with heavy metals (Zhang et al., 2015; Korzeniowska & Stanislawska-Glubiak, 2015). In turn, various amendments can affect the absorption capacity of plants, increasing or decreasing the heavy metals uptake (Castaldi et al., 2004; Singh & Agrawal, 2010; Pavel et al., 2014; Zhou et al., 2014; Antonkiewicz et al., 2018).

In our experiment, the content of Mn and Fe was the highest in plant biomass (Table 4.3.1). In the control plot, the content of heavy metals in the biomass of miscanthus was higher than in switchgrass by 20–30 %. On the plots with amendments, the content of Mn and Zn was also higher in miscanthus. At the same time, Cu and Pb accumulated more intensively in switchgrass biomass. It was detected that the amendment application modified the physicochemical properties of soil, thereby enhancing the availability of heavy metals in the soil and increasing their accumulation in biomass (Fig. 4.3.3). The mineral fertilizer use had the least effect (from 0.1 % to 90 % for miscanthus and from 32 % to 48 % for switchgrass). The addition of double dose of sewage sludge had the most significant effect and caused an increase in content of heavy metals by 90–165 % for miscanthus and by 124–333 % for switchgrass compared to the control. When analyzing heavy metals content in the miscanthus biomass, it was detected that amendments affect Mn accumulation most intensively. In the switchgrass biomass, greatest effect was noted for Cu.

Table 4.3.1

Heavy metals content in the biomass of Miscanthus and Switchgrass, mg kg^{-1}

	Control	Ash	Ash + sludge	Sewage sludge	Double dose of sludge	Mineral fertilizer
Miscanthus						
Fe	159.9±1.22	246.7±0.92	250.7±1.04	242.5±0.87	262.7±1.19	179.6±0.85
Mn	62.0±0.36	142.5±0.91	151.3±1.12	138.6±1.53	163.5±1.71	118,1±0.98
Zn	14.6±0.26	26.0±0.25	27.4±0.23	24.0±0.26	29.3±0.22	18.0±0.26
Cu	5.4±0.11	7.8±0.15	8.8±0.17	8.6±0.21	14.3±0.23	6.3±0.11
Pb	6.4±0.18	8.4±0.12	9.2±0.15	10.4±0.26	12.1±0.11	6.4±0.11
Switchgrass						
Fe	129.5±0.74	181.0±0.93	211.0±1.20	205.1±1.25	250.0±1.51	195.0±0.64
Mn	49.5±0.56	78.3±0.59	83.5±0.71	84.8±0.91	112.0±1.28	67.6±0.78
Zn	11.0±0.17	16.0±0.26	17.3±0.20	19.0±0.26	24.6±0.32	14.5±0.21
Cu	4.2±0.11	8.4±0.23	9.1±0.15	7.8±0.15	18.2±0.15	6.2±0.06
Pb	4.5±0.11	8.6±0.17	8.3±0.11	11.0±0.17	14.2±0.21	6.4±0.10

The application of the amendments led to an increase in heavy metal uptake by the miscanthus and switchgrass biomass (Fig. 5, 6). In control, the level of heavy metals uptake was higher in miscanthus compared to switchgrass. The introduction of amendments has changed this ratio. The introduction of mineral fertilizers, ash and mixture of ash and sewage

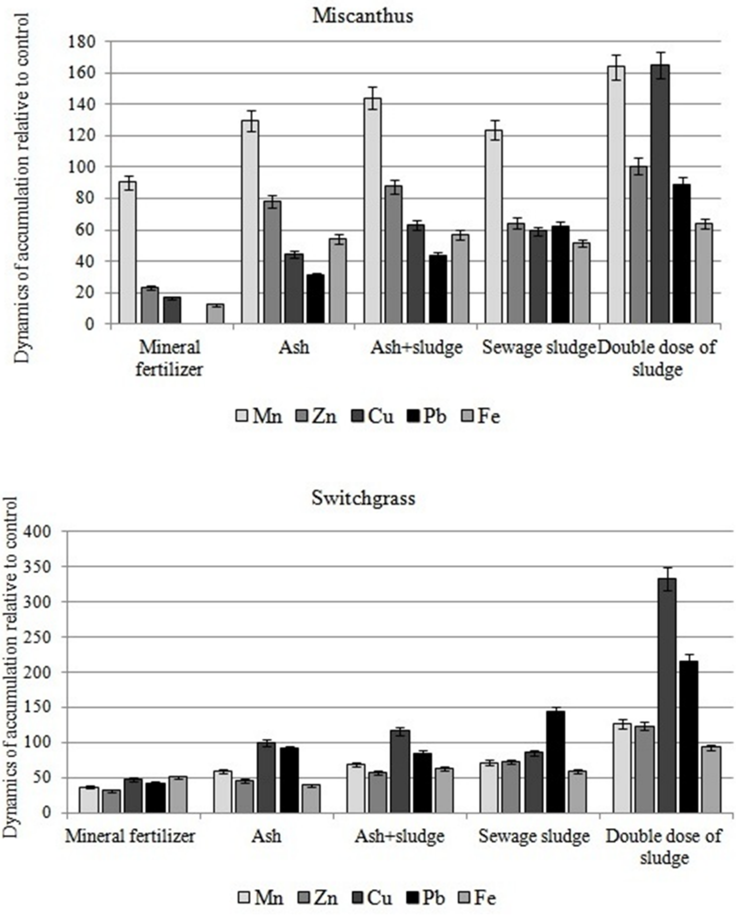


Fig. 4.3.3.The effect of the amendments applying on the content of heavy metals in plant biomass, %

sludge contributed to an increase in the uptake of Zn, Cu and Pb by the biomass of both plant species on average 1.5–2.6 times (Fig. 4.3.4). The application of single dose of sewage sludge enhanced the uptake of these

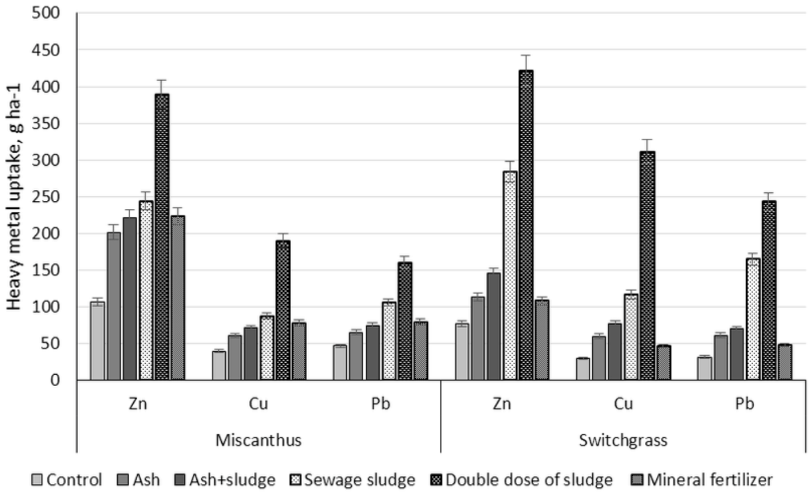


Fig. 4.3.4. Heavy metal uptake (Cu, Zn and Pb) by the 3-year-old plants of miscanthus and switchgrass

metals by the miscanthus 2.2–2.7 times, whereas for switchgrass the uptake level increased 3.7–5.2 times. The applying of double dose of sewage sludge had the greatest effect. However, while in miscanthus the uptake capacity was increased by 3.4–4.8 times, in switchgrass it was augment by 5.5 (Zn), 7.7 (Pb) and 10.6 (Cu) times. It was also found that sewage sludge significantly influences the Fe accumulation in switchgrass biomass. As a result, Fe uptake by the 3-year-old Switchgrass plants amounted to 3068.8–4280.0 g ha^{-1}, which is 23–24 % more compared to miscanthus (Fig. 4.3.5).

Thus, based on the results, heavy metals by the intensity of their absorption by studied plants can be arranged in increasing order: Cu > Pb > Zn > Mn > Fe. The content of heavy metals in the biomass of miscanthus was higher than in switchgrass by 20–30 %. The amendment application modified the physicochemical properties of soil, thereby enhancing the availability of heavy metals in the soil and increasing their

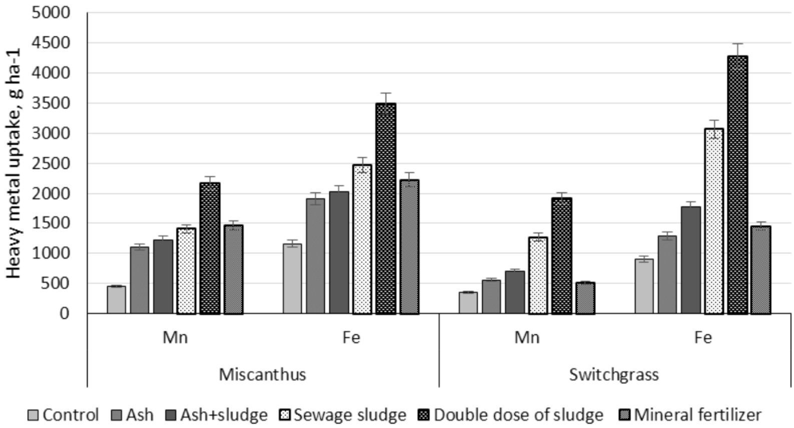


Fig. 4.3.5. Heavy metal uptake (Mn and Fe) by the 3-year-old plants of miscanthus and switchgrass

accumulation in biomass. The addition of double dose of sewage sludge had the most significant effect and caused an increase in content of heavy metals by 90–165 % for miscanthus and by 124–333 % for switchgrass.

The application of the amendments led to an increase in heavy metal uptake by the miscanthus and switchgrass biomass. The introduction of mineral fertilizers, ash and mixture of ash and sewage sludge contributed to an increase in the uptake of heavy metals by the biomass of both plant species on average 1.5–2.6 times. The application of a single dose of sewage sludge enhanced the uptake of metals by 2.2–5.2 times. The applying of a double dose of sewage sludge led to an increase in the uptake capacity by 3.4–4.8 times for miscanthus, and by 5.5–10.6 times for switchgrass.

4.3.3. Soil amendments effect on thermal features of miscanthus and switchgrass

The chemical composition and thermal characteristics of miscanthus and switchgrass dry biomass are similar. The main components are cellulose (42–50 %) and hemicellulose (22–30 %). Lignin provides the rigidity of the cell structure. Lignin content is 20–25 % (Yan et al., 2010; Brosse et al., 2012; Friasa and Hao Feng, 2013; Aboytes-Ojeda et al., 2016).

Thermogravimetric analysis showed that the decomposition of the biomass of both studied species occurs in two periods (Table 4.3.2).

Table 4.3.2

Thermal decomposition of Miscanthus and Switchgrass biomass

Stage	Miscanthus				Switchgrass			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
Leaves								
I	50–160	90	8.8	7.03	30–170	80	8.6	9.2
II	160–280	260	24.6	22.72	170–290	270	30.2	28.8
III	280–380	300	32.4	33.36	290–370	300	31.6	25.8
IV	380–540	420	10.6	27.34	370–550	420	9.4	28.6
Stems								
I	60–150	100	8.0	5.66	50–170	100	7.4	6.08
II	150–280	270	26.8	26.66	170–290	270	31.0	33.92
III	280–400	300	29.0	37.57	290–350	300	25.6	22.0
IV	400–580	430	9.2	24.44	350–570	420	7.0	33.2

The first period consists of one stage of decomposition of volatile components and evaporation of water. The second period consists of three stages: the disruption of hemicellulose, the destruction of cellulose and lignin, and the completion of the lignin decomposition and carbonate residue burning. It was noted that the first stage of the switchgrass biomass destruction was longer and the percent of weight loss was greater (by 7.4 % in stems and by 30.9 % in leaf biomass). A lower content of volatile components and water was characteristic of stem biomass of both species. The stage of hemicellulose decomposition in the switchgrass biomass was more active. The reaction rates in the leaves and stems were higher by 22.8 % and 15.7 %, respectively. At the same time, the destruction of cellulose and lignin was more intense in the miscanthus biomass. More complete biomass combustion was observed in switchgrass. The share of residual mass in switchgrass was 7.6 % (leaves) and 4.8 % (stems), and in miscanthus 9.55 % (leaves) and 5.67 % (stems).

The application of soil amendments has led to changes in the thermal characteristics of plant biomass. So, in the leaf miscanthus biomass, the amount of volatile components decreased from 14.6 % (variant with a double dose of sludge) to 22.8 % (variant with ash). In addition, the first stage of thermolysis took place at higher temperatures. The hemicellulose degradation interval has also shifted to higher temperatures region. As a result, the peak of this component decomposition was almost veiled by the peak of destruction of cellulose, which can be clearly seen on the DTG curves (Fig. 4.3.6).

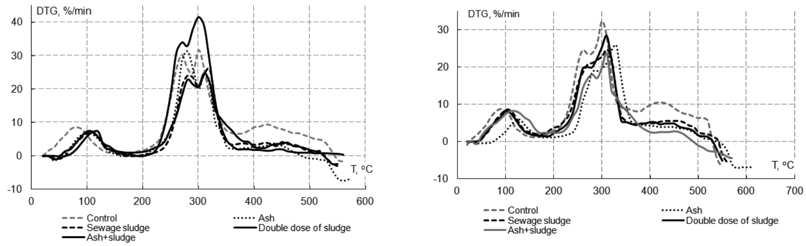
The rate of passage of the fourth stage was 2–4 times lower compared to the control, and the share of unburned residue increased by 21–65 %. Moreover in variants with amendments, the magnitude of the thermal effect was lower at almost all stages of decomposition (Fig. 4.3.7).

In the case of stem miscanthus biomass, the addition of soil amendments had a minor effect. Only in the ash + sludge variant, the destruction of hemicellulose and cellulose passed more active by 8–13 %. As in the case of leaf biomass, a tendency to increase the amount of unburned residue also took place. However, the increase in ash content was small, in the range of 2.3–14.1 %. Only the application of sunflower husk ash increased the value of this parameter by 32.9 %.

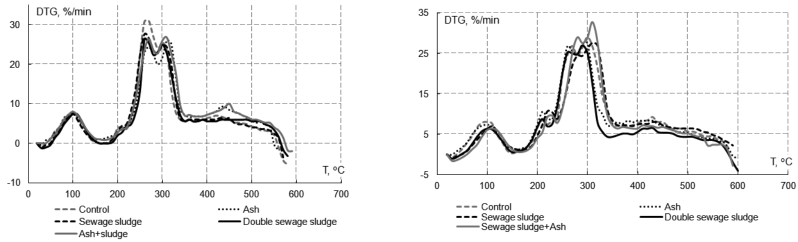
In the leaf biomass of switchgrass, under the influence of soil amendments, the content of water and volatile components decreased by 17.4–37.0 %, and the process rates of the first stage were lower. In variants with sewage sludge, the decomposition of hemicellulose proceeded slower by

22.5–24.5 %, while in the variants "ash" and "ash + sludge", on the contrary, it was faster by 4.0–12.6 %. By the simultaneous addition of ash and sewage sludge, the destruction of cellulose also occurred much faster (by 31.6–70.5 %) than in the control and other variants of the experiment (Fig. 4.3.6).

Switchgrass Miscanthus



Leaves



Stems

Fig. 4.3.6. DTG curves of the thermal decomposition of Switchgrass and Miscanthus biomass

In all experimental variants, the lignin decomposition process was 2.2–4.7 times slower than in the control, and share of residual mass increased by 50.0–73.7 %. Similarly to miscanthus, the magnitude of the thermal effect of the control samples was higher (Fig. 4.3.7). In stem switchgrass biomass, the first stage of thermolysis took place in a similar way in all experiment variants, and the content of volatile components decreased by 7.2–20.0 %.

The destruction of hemicellulose slowed down in biomass grown on plots with amendments. Among the experimental and control options, there were no particular differences in the stages of cellulose and lignin decomposition. The amount of unburned residue considerably increased (by 50–60 %) only in the variants of “ash” and “ash + sludge”.

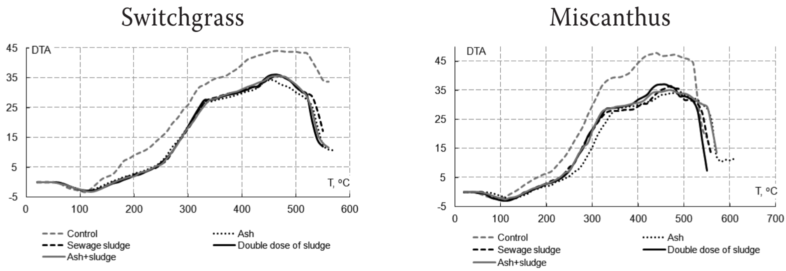


Fig. 4.3.7. DTA curves of the thermal decomposition of Switchgrass and Miscanthus leaf biomass

According to the activation energy data, the biomass of switchgrass grown without amendments (control) has greater thermal stability than miscanthus biomass (Table 4.3.3). The addition of ash led to an increase in the thermal stability of the miscanthus leaf biomass at the initial stage of destruction by 39.5 % and at the stage of main components decomposition by 18.7 %. The effect of other amendments was insignificant.

In stem biomass, thermal stability at the initial stage increased by 25 % with a single dose of sewage sludge and decreased by 20 % with ash. In other variants, the changes were within 14 %. The influence of amendments on the thermal stability of stem biomass during the decomposition of the main components was not detected.

The adding of a single, double dose of sewage sludge and a combination of sludge and ash increased the thermal stability of switchgrass leaf biomass at the initial stage of thermolysis by 28.4 %, 40.2 % and 31.9 %, respectively. The values of activation energy at the stage of decomposition of the main components have not changed significantly. The use of amendments (except for a double dose of sludge) led to a significant decrease in the thermal stability of stem biomass at the initial stage of decomposition. The difference was 33.4–41.0 %. Changes in this parameter during the destruction of the main components did not exceed 8 %.

Table 4.3.3

Activation energy of Miscanthus and Switchgrass biomass thermal decomposition

Experiment variant	Leaves		Stems	
	Activation energy, kJ/mol		Activation energy, kJ/mol	
	Initial	Main components	Initial	Main components
Miscanthus:				
Control	49.56	48.43	54.03	46.81
Ash	69.13	57.49	43.34	42.78
Sewage sludge	43.78	49.40	67.46	46.74
Double dose of sludge	47.29	50.77	46.73	46.74
Ash + sludge	51.93	53.01	61.87	52.50
Switchgrass:				
Control	55.28	51.23	78.39	52.90
Ash	56.92	54.94	49.82	54.95
Sewage sludge	71.00	58.04	46.23	48.45
Double dose of sludge	77.52	45.50	64.41	59.31
Ash + sludge	72.94	55.40	52.23	49.89

Thus, it can be stated that, by changing soil characteristics, amendments indirectly affect the thermal behavior of miscanthus and switschgrass biomass. The greatest modifications are characteristic for leaf biomass and are associated mainly with the decomposition of volatile components and hemicellulose, as well as with the formation of an unburned residue. Amendments significantly affect the thermal stability of biomass at the initial stage of thermolysis. As regards the destruction of the main components (hemicellulose, cellulose and lignin), the effect of soil amendments is minimal.

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5. PRODUCTIVE AND ENERGETIC POTENTIAL OF THE WOODY PLANTS GROWN ON MARGINAL LANDS

5.1. Thermal characteristics of the biomass of herbaceous and woody plants

Wood biomass is an important renewable energy resource with a short carbon cycle (Poletto et al., 2012). This circumstance has led to an increased interest in the wood thermal characteristics including the kinetic laws its thermal degradation (Adeleke et al., 2019). The chemical composition of hardwood varies widely. This is due to a number of factors. The most important of them are the species accessory, soil and climate conditions. The chemical composition plays a decisive role in determining the quality of wood as an energy source. The quantity and ratio of the wood components determine its thermal features and the specificity of decomposition in the combustion process (Martinez et al., 2018). Thermal degradation of wood can be represented by the sum of reactions of thermal destruction of the main components as hemicellulose, cellulose and lignin. Thermal decomposition of hemicellulose, cellulose and lignin occurs in the intervals of 225–325 °C, 305–375 °C and 250–500 °C, respectively (Shen et al., 2009). Cellulose is characterized by greater thermal stability than hemicellulose and lignin (Vichnevsky et al., 2003). Extractive substances of wood contribute to main components thermal destruction. Despite the small amount, they can significantly affect both the physical and thermal characteristics of wood. Extractive substances, in turn, are most susceptible to environmental factors (Sebio-Puñal et al., 2012; Rodrigues et al., 2017). The component composition of hemicelluloses of herbaceous (miscanthus and switchgrass) and woody plants differs. Compared to woody trees (especially conifers), the hemicellulose of miscanthus and switchgrass consists mainly of xylans, while the hemicellulose of wood raw materials contains a significant proportion of other polysaccharides (Table 5.1.1). A disadvantage of miscanthus and switchgrass biomass can be considered higher ash content than that of wood (Tumuluru et al., 2012; Geng, 2018; Krutul et al., 2019). The energy value of biomass is equal to wood and is 17.0–19.0 MJ/kg.

Thermal destruction of biomass is carried out in three stages: in the first stage, volatile substances evaporate, in the second stage, the main components (hemicellulose, cellulose, lignin) are decomposed and charcoal is formed, and in the third stage, the decomposition of lignin is completed and the charcoal formed in the previous stage is oxidized. In general, the thermal degradation of biomass is represented by the sum of the thermal reactions of decomposition of individual components.

Table 5.1.1

Chemical composition of miscanthus and switchgrass biomass and woody species

Components	Chemical content of biomass, %			
	Miscanthus	Switchgrass	Poplar	Pine
Extractive substances	7.7–8.0	5.2–6.3	5.5–12.6	3.4–4.5
Glucans	42.8–44.0	37.9–39.1	40.7–45.3	43.1–47.0
Xylans	22.0–23.4	25.0–28.8	14.2–15.5	7.5–10.4
Arabinans and manans	6.5–7.8	5.7–6.2	4.8–5.9	13.3–14.0
Lignin	23.9–24.5	20.1–22.7	20.8–24.9	27.5–29.9
Ash	2.7–4.6	1.7–2.1	0.1–0.3	0.2–0.3

As a result, the intervals of component destruction partially overlap (Prins et al., 2006; Shen et al., 2009). Growth conditions can affect the thermal characteristics of biomass. Changes in the thermal processes of thermolysis are caused mainly by extractive substances (Boateng et al., 2006).

5.2. Productive potential of poplar on technosol

The Poplar genus is a promising energy crop for cultivation on low-productivity lands. It is attractive not only in light of the processing infrastructure for converting wood into pulp and paper products, but also as a productive bioenergy plant for obtaining solid biofuels (Christersson, 2008; Manzone et al., 2009). Poplar has a number of advantages and is characterized by great genetic and phenotypic diversity within the genus. This is a manifestation of the outcrossing nature and high genetic load inherent in many forest tree species. The ability of poplar to cross between species allows obtaining species hybrids with combinations of features absent from trees found in nature. The ease of clonal reproduction contributes to the establishment of useful genetic traits for further commercial cultivation of biofuel raw materials (Labrecque and Teodorescu, 2005, Panacci et al., 2009, Kutsokon et al., 2014).

The most widespread classification of poplars (Stettler et al., 1996; Dillen et al., 2011) divides them into five groups:

Aigeiros. This group is represented by poplar deltoid (*Populus deltoides*) and black poplar (*P. nigra*). Both species are used in interspecific hybridization with each other and with compatible species from the *Tacamahaca* group.

Leucoides. Large-leaved poplars are included in this group. For example, *P. heterophylla* grows in the central and eastern parts of North America.

Populus. This group is represented mainly by aspens (*P. tremula*, *P. grandidentata*, *P. tremuloides*, as well as an important Eurasian species of white poplar (*P. alba*).

Tacamahaca. This group contains balsam poplars, including reference species for genome sequencing: *P. trichocarpa*, *P. suaveolens*, *P. maximowiczii*, *P. angustifolia*. Many species of this group are compatible with species from the Aigeiros group. As a rule, the obtained hybrids differ in powerful growth and development.

Turanga. The most important species of this group is *P. euphratica*, which is characterized by high resistance to extreme heat and adverse soil conditions.

9 poplar hybrids obtained from the crossing of species of the Aigeiros group were tested in the conditions of the Pokrov experimental station of land reclamation of DSAEU (Table 5.2.1).

In the first year, the survival degree of the saplings and their development intensity were studied. At the end of the year, the clones that showed the best results were selected for further reproduction and cultivation.

Table 5.2.1

Energy poplar cultivars and their parentage

Clonal names	Parentage	Sex
Blanc du Poitou	Populus × euroamericana (Dode) Guinier	M
Dorskamp	Populus × euroamericana	M
Ghoy	Populus deltoides Bartr. Ex Marsh × Populus nigra L.	M
Marilandica	Populus × euroamericana	F
Robusta	Populus nigra var. plantierensis × Populus deltoides ssp. angulata Henry	M
Heidemij	Populus × euroamericana	M
Ijzer-5	Populus × euroamericana	M
Tardif de Champagne	Populus × euroamericana	M
Vereecken	Populus nigra	M

Researches of the second year were devoted to the effect of biological agents on the survival and growth of the clones, which was picked out last year. The four trials of the field experiment with two bets polplar clones were laid: treatment with vermicomposting extract (VCE), trichodermin, mycorrhiza and mixture of these three agents. The choice of these agents was justified by their role in improving the soil nutrition regime. Before planting in the substrate, the saplings were soaked, and after planting, they were irrigated with an aqueous solution of VCE in a ratio of 1 : 100. In the same way and in identical ratio the trichodermin preparation was used. In the tretment with mycorrhiza, the roots of the saplings before planting were dipped into a suspension. The dilution was 1 g for two saplings. Growth indicators were assessed by morphometric parameters. The plant height and length of the annual shoots were measured by a tape measure, the shoot diameter by a caliper. The leaf area was determined by scanned image using a computer program AreaS 2.1. The dry weight of the leaf and the leaf mass per area (LMA) were identified as well.

The received data were analyzed statistically using the software package StatGraphics Plus5 with all tests of significance being made at a type 1 error rate of 5 %.

The survival percentage of 9 poplar clone saplings planted in 2016 was very different between varieties (Fig. 5.2.1).

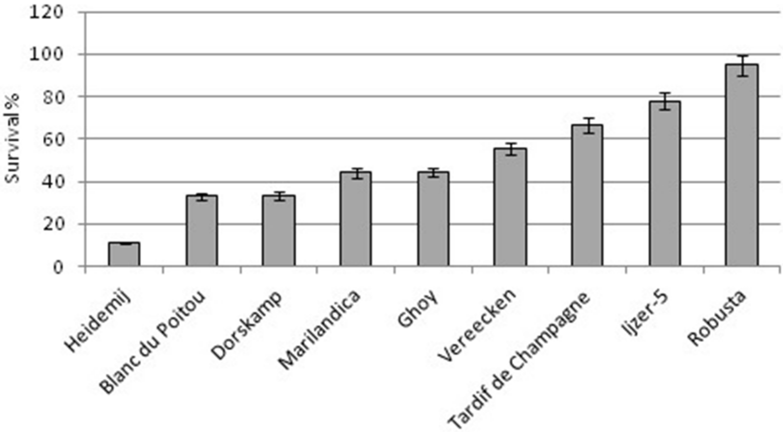


Fig. 5.2.1. Survival of poplar clones on marginal soils, %

The worst indicators were observed for the clone Heidemij – only 11 %. Clones Tardif de Champagne, Ijzer-5 and Robusta showed a high level of survival (70, 80 and 95 %, respectively). For the rest clones, this index varied in the range of 33–55 %. During the growing season processes of plant growth and development passed in the best way for the clones Ijzer-5 and Robusta (Fig. 5.2.2). By the end of the year the average height of these plants was 80–93 cm, and some specimens reached 170 cm. Clone Dorskamp also showed good growth rates, but bad survivability does not give grounds for the expediency of its further cultivation on marginal soils.

The clone Tardif de Champagne, despite the good sapling survival, showed a low growth rate and therefore also lacks a good potential. Thus, according to the results obtained in the first year of cultivation, two clones – Ijzer-5 and Robusta – were evaluated as the most promising and selected for further research. Researches of the second year were devoted to the effect of biological agents on the survival and growth of these two clones.

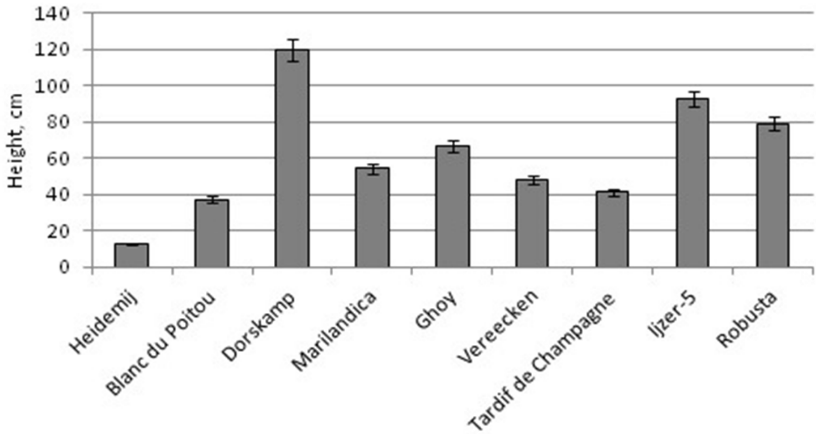


Fig. 5.2.2. The height of poplar clones at the end of the first year grown on reclaimed mineland

It was revealed that the sapling survival rate of both clones in the control, experiments with vermicomposting extract, mycorrhiza and a mixture of agents was practically the same and amounted to 87–93 %.

Treatment with trichodermin had a supressive action, as a result of which the survival of clones Ijzer-5 was 73 %, and of clones Robusta was even lower – 66.7 %. The year 2017 was more drought-ridden than the year 2016. The total amount of precipitation for March-October was only 260 mm against 383 mm in 2016. This affected the experimental plants. Indeed, growth rates were lower than in the previous season. For example, the length of an annual shoots did not overtopped 60 cm. Treatment of clones Ijzer-5 with biopreparations promoted growth acceleration of all experimental specimens by 10–19 %. The clone Robusta responded to the influence of biopreparations by growth intensification from 8.5 to 46 %. Only treatment with trichodermin had no effect on this parameter (Fig. 5.2.3).

Measurements of the annual shoot diameter showed that in the clone Ijzer-5 it is 22–30 % higher than in the clone Robusta in the control plot and experiments with vermicomposting extract, mycorrhiza and trichodermin,

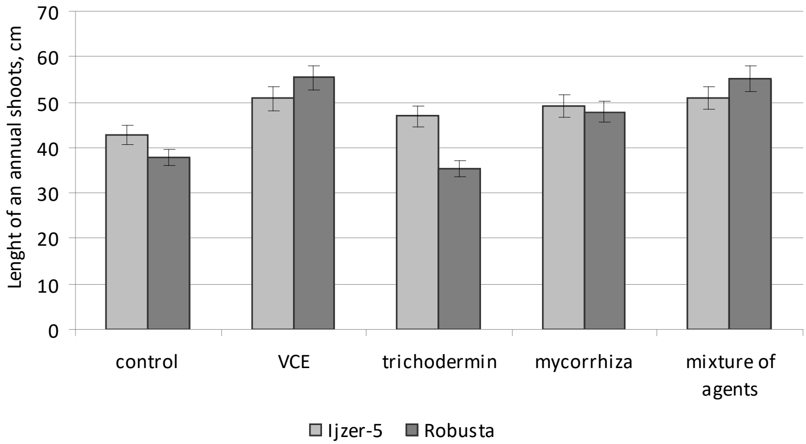


Fig. 5.2.3. The length of an annual shoots of poplar clones grown on reclaimed mineland in 2017

and 4.5 % less in the experiment with the mixture of agents. Treatment with biopreparations stimulated the activity of annual shoot lateral meristems in all experimental variants in both clones. The treatment with vermicomposting extract gave the best result for the clone Ijzer-5, and for clone Robusta in the experiment with a mixture of agents (Fig. 5.2.4).

For clone Ijzer-5 an increase of the leaf area in all experiment variants was observed from 19.5 to 38 %. The treatment with trichodermin had the greatest impact. In clone Robusta, quite the contrary, trichodermin caused a decrease in leaf area by 25 % compared to the control. In other variants, an increase of this parameter was noted, but less intense than for clone Ijzer-5, only by 13.5–20.5 % (Fig. 5.2.5). At the same time, clone Robusta showed a higher degree of increase of the total assimilation surface area (from 20 to 55 %) compared to clone Ijzer-5 (from 20 to 32 %). Treatment with trichodermin was an exception. This agent had a stimulating effect only on the clone Ijzer-5 plants, whereas in the clone Robusta the total assimilation surface area decreased by 52 % compared to the control. One of the attribute

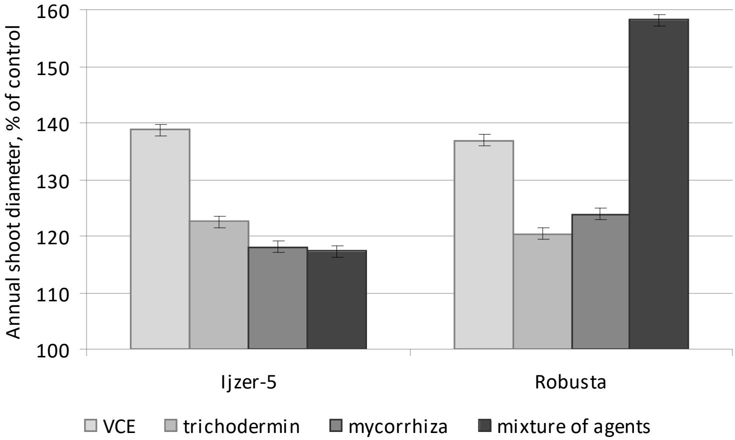


Fig. 5.2.4.Diameter of annual shoots of poplar clones grown on reclaimed mineland, % of control

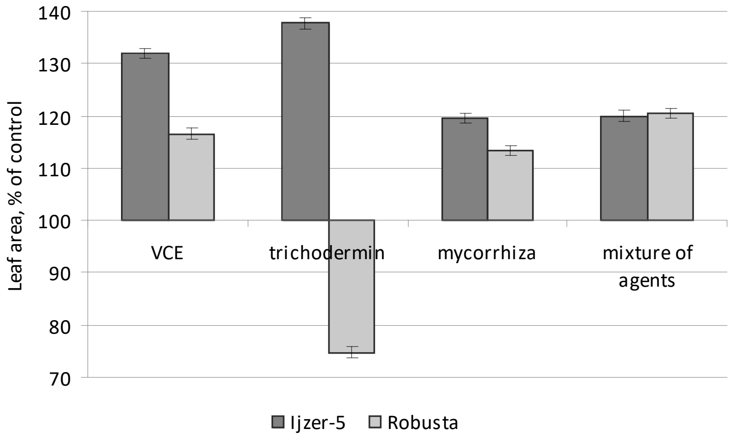


Fig. 5.2.5. Change in the leaf area of poplar clones under the influence of biopreparations, % of control

among the leaf structural organization is the leaf mass per area (LMA), which is the ratio between leaf dry mass and leaf area. LMA is closely correlated with the photosynthesis intensity, potential growth rates and ecological flexibility (Puglielli *et al.*, 2015; Poorter *et al.*, 2009; Wright *et al.*, 2002). Factors such as light, CO_2 concentration, water supply and mineral nutrition can significantly influence the LMA. However, since in this study these factors were the same in all variants of the experiment, it is possible to trace the impact of biopreparations on the LMA.

Comparison of control samples showed that LMA of the clone Ijzer-5 was 18.5 % more than those of clone Robusta. Treatment with biopreparations led to an increase in this parameter for both clones in all experiment variants. However, it was insignificant for clone Ijzer-5 (6–13 %), and stronger for clone Robusta (from 17 to 48 %). There is a positive linear correlation between the LMA value and the leaf dry mass (Fig. 5.2.6).

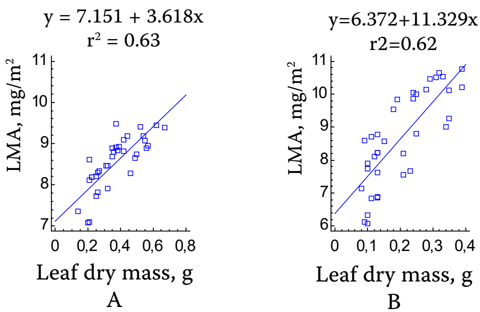


Fig. 5.2.6. Relationship between LMA and leaf dry mass. Lineare regression has been calculated for the clones Ijzer-5 (A) and Robusta (B), $p \leq 0.01$

Increase in leaf dry mass lead to increase in LMA. It can be assumed that the growth of LMA is due to the increase in mesophyll volume by formation of more quantity of structural and functional photosynthesis elements. Thus, in plants that have undergone treatment with biopreparations, photosynthetic processes are more intense. This is indirectly confirmed by their more vigorous growth and development.

5.3. Thermolysis processes of poplar clones wood

To obtain the wood thermal stability information a comparative thermogravimetric analysis of poplar wood samples grown on different soil types was carried out. The analysis was performed using the derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. Differential mass loss and heating effects were recorded. The results of the measurements were processed with the software package supplied with the device. Samples of annual wood were analyzed dynamically at a heating rate of 10 °C/min in an air atmosphere. The mass of samples is 100 mg. The reference substance was aluminum oxide.

The description of thermolysis processes of six poplar clones grown at the Boyarka experimental station is given in table 5.3.1.

Table 5.3.1

Thermal features of the poplar clones wood decomposition

Cultivar	Stage	Interval, °C	Extrempoint, °C	Max. rate, %/min	Weight loss, %	Share of residual mass, %
1	2	3	4	5	6	7
Dorskamp	I	50–210	110	7.0	5.86	
	II	210–420	320	40.0	64.44	
	III	420–580	430	2.8	25.33	4.37
Blanc du Poitou	I	40–200	100	7.6	5.63	
	II	200–430	320	38.4	69.14	
	III	430–550	450	3.0	19.30	5.93
Heidemij	I	30–150	110	7.8	5.43	
	II	150–380	290	31.0	58.09	
	III	380–550	450	8.8	28.14	4.73
San Giorgio	I	40–170	90	7.8	6.03	
	II	170–380	310	39.4	61.10	
	III	380–550	450	8.8	28.14	4.73

Continuation of the table 5.3.1

1	2	3	4	5	6	7
Robusta	I	40–190	80	7.6	7.27	
	II	190–380	300	49.6	60.20	
	III	380–570	450	7.2	29.49	3.04
Vereecken	I	30–180	90	8.0	6.80	
	II	180–370	290	36.4	56.40	
	III	370–570	440	8.0	30.60	6.20

Thermal decomposition of wood clones of poplar grown at the Boyarka experimental station begins at a temperature of 30–50 °C. The first stage of decomposition of volatile components and water evaporation was the longest in case of "Dorskamp" wood combustion. At the same time, the speed of the burning process in "Dorskamp" clone wood was the lowest. The "Heidemij" and "Vereecken" clones samples had the lowest moisture content in the wood and the highest speed of passing the initial stage. The initial stage of thermolysis takes place with heat absorption and the presence of endothermic effects on the curves (Fig. 5.3.1).

Destruction of the main components of wood (hemicellulose and cellulose) takes place in the temperature range 190–400 °C. A high content

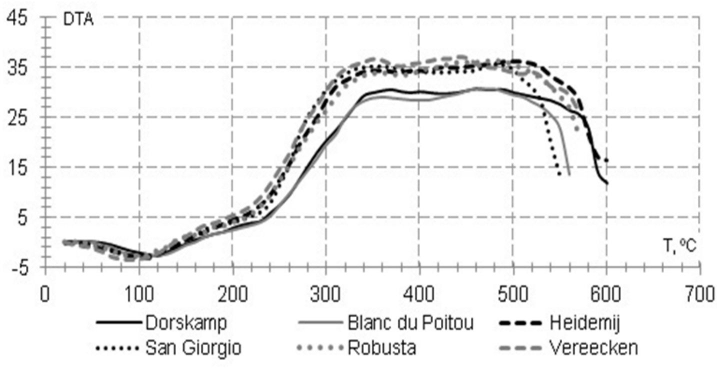


Fig. 5.3.1. DTA curves of poplar wood thermal decomposition

of hemicellulose in the wood lead to their decomposition a delay. The ranges of decomposition of hemicellulose and cellulose are superimposed on each other. As a result only one extreme point is observed on the DTG curves (Fig. 5.3.2). The decomposition of holocellulose in clones of “Dorskamp” and “Blanc du Poitou” takes place at higher temperatures. The mass loss of these two clones is greater than other cultivars.

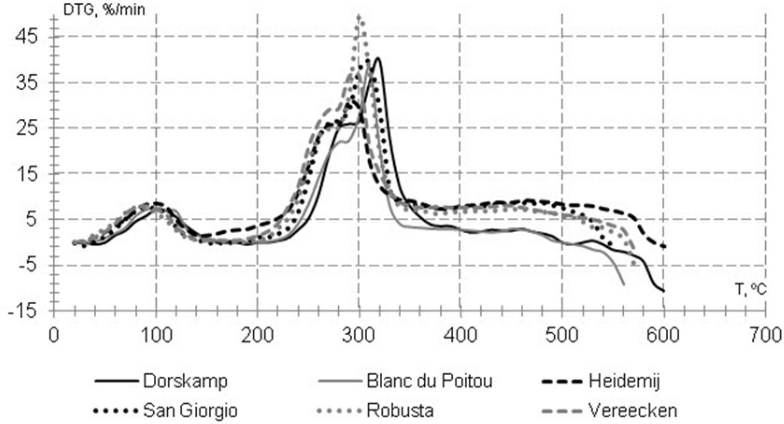


Fig. 5.3.2. DTG curves of poplar wood thermal decomposition

The highest speed of passing this stage was characteristic of the “Robusta” clone wood. The slowest process was in the wood of the ‘Heidemij” clone. The last stage of thermolysis takes place with the decomposition of lignin and the formation of a non – combustible residue. The process is slow, with a relatively constant speed, without pronounced peaks. More complete wood burning was observed for the “Robusta” clone (3.04 %), despite the fact that the share of residual mass of other cultivars was also small – in the range of 4.4–6.2 %.

The lowest speed and mass loss were observed in clones of “Dorskamp” and ‘Blanc du Poitou”, which indicates a low content of lignin in the wood of these cultivars. The largest mass loss and the proportion of non-combustible residue were characteristic of the “Vereecken” clone. More complete wood burning was observed for the “Robusta” clone (3.04 %).

The decomposition stages of holocellulose and lignin were accompanied by exothermic reactions with pronounced thermal effects in the temperature range of 310–520 °C. The activation energy indicator is a good indicator of the thermal stability of wood.

The activation energy was determined at the beginning of the process of wood destruction and subsequent decomposition of the main components. It was found that the smallest amount of energy is required to start the destruction process in the wood of the “Blanc du Poitou” and “Heidemij” clones, and the largest in the wood of the “Vereecken” clone (Table 5.3.2).

Thus, the lowest thermal stability at the time of destruction of the main components is characteristic of clones “Heidemij” and “Vereecken”, and the greatest for “Blanc du Poitou” and “San Giorgio’ clones.

Table 5.3.2

Activation energy of Poplar wood thermal decomposition

Cultivar	Activation energy, kJ/mol	
	Initial	Main components
Dorskamp	63.84	66.89
Blanc du Poitou	35.02	69.30
Heidemij	44.44	52.62
San Giorgio	49.19	70.59
Robusta	53.51	57.71
Vereecken	83.65	53.50

Comparative thermogravimetric analysis of “Tardif de Champagne” poplar clone grown in Boyarka and Pokrov stations is shown in Table 5.3.3 and 5.3.4.

The initial stage of thermal decomposition of clone wood takes place against the background of endothermic reactions with weakly expressed thermal effects in the temperature range of 90–120 °C.

The speed of the process is low. One peak at a temperature of 80–90 °C was observed in this range. The loss of biomass was 10 %. The beginning of destruction of hemicellulose at the stage of decomposition

Table 5.3.3

Thermal characteristics of Populus woods decomposition. Boyarka station

Stage	Boyarka			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	30–200	90	13.2	10.0
II, III	200–400	310	44.8	58.8
IV	400–540	470	10.2	23.0
Share of residual mass, %				8.2

Table 5.3.4

Thermal characteristics of Populus woods decomposition. Pokrov station

Stage	Pokrov			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	20–150	80	16.0	10.0
II, III	150–380	290	34.0	61.2
IV	380–540	430	10.4	23.2
Share of residual mass, %				5.6

of holocellulose in the clone "Tardif de Champagne" shifts to the range of higher temperatures. Therefore, the decay ranges of hemicellulose and cellulose overlap. Only one peak with an extreme point at 310 °C (Boyarka) and 290 °C (Pokrov) is observed on thermogravimetric curves (Fig. 5.3.3).

The main decomposition of lignin occurs in the temperature range of 300–500 °C. The most pronounced exothermic effects are observed in the temperature zone of 300–380 °C (cellulose degradation) and 460–500 °C (lignin decomposition). Some differences in the thermal characteristics of wood clone grown in different climatic and soil conditions were observed. The evaporation stage of water and volatile compounds in a clone of "Tardif de Champagne" clone grown at the Pokrov reclamation station was shorter. The reaction rate was higher, and the initial process took place at lower temperatures. The rate of decomposition of holocellulose was less.

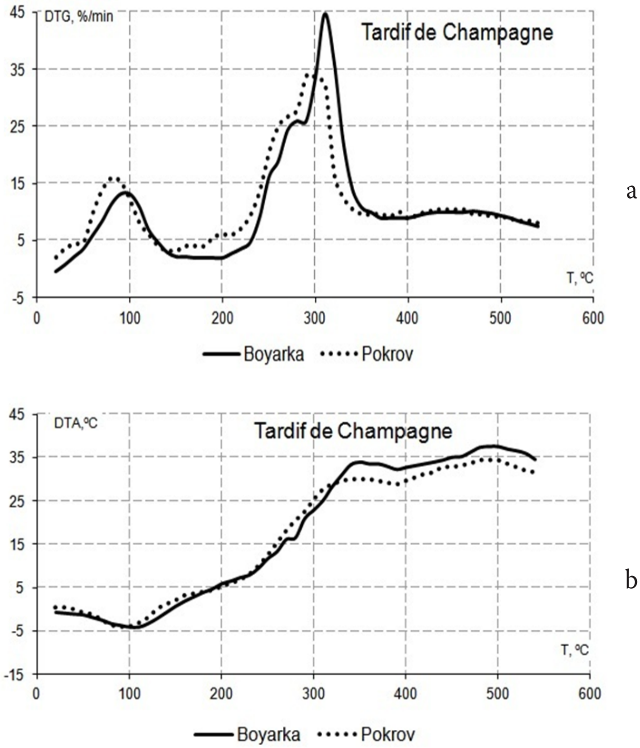


Fig. 5.3.3. DTG and DTA curves of "Tardif de Champagne" poplar clone wood thermal destruction in Boyarka and Pokrov stations

The extreme point was observed at a temperature of 290 °C. The rates of lignin decomposition were almost the same in both combustion variants. However, the extreme point in the wood of "Tardif de Champagne" clone grown in Pokrov land reclamation station has shifted to the range of lower temperatures. The content of coke residue was less, and the combustion of wood was more complete.

Comparative thermogravimetric analysis of "Ghoy" poplar clone grown in Boyarka and Pokrov stations is shown Table 5.3.5 and Fig 5.3.4.

The initial stage of thermal decomposition of clone wood takes place against the background of endothermic reactions with weakly expressed thermal effects in the temperature range of 90–120 °C.

Table 5.3.5

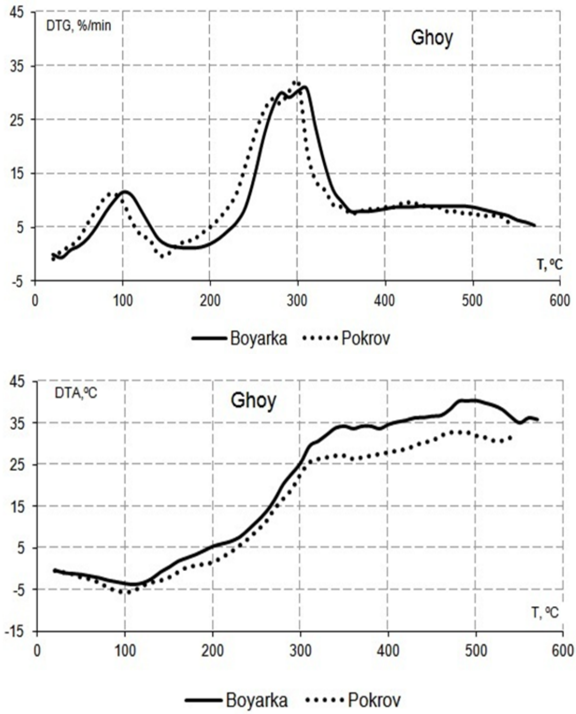
Thermal characteristics of Populus woods decomposition. Clone "Ghoy"

Stage	Boyarka				Pokrov			
	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %	Interval, °C	Extremum point, °C	Maximum rate, %/min	Weight loss, %
I	40–180	100	11.6	8.2	30–150	90	11.2	9.2
II	180–290	280	30.0	21.8	150–280	270	28.8	24.8
III	290–380	310	30.8	31.2	280–370	300	32.0	29.6
IV	380–570	440	9.0	31.6	370–540	420	9.6	26.2
	Share of residual mass, %			7.2	Share of residual mass, %			10.2

The speed of the process is low. One peak at a temperature of 80–90 °C was observed in this range. The loss of biomass was 10 %.

The beginning of destruction of hemicellulose at the stage of decomposition of holocellulose in the clone "Ghoy" shifts to the range of higher temperatures. Therefore, the decay ranges of hemicellulose and cellulose overlap. Only one peak with an extreme point at 310 °C (Boyarka) and 290 °C (Pokrov) is observed on thermogravimetric curves (Fig. 5.3.4a). The main decomposition of lignin occurs in the temperature range of 300–500 °C. The most pronounced exothermic effects are observed in the temperature zone of 300–380 °C (cellulose degradation) and 460–500 °C (lignin decomposition). Some differences in the thermal characteristics of wood clone grown in different climatic and soil conditions were observed.

The evaporation stage of water and volatile compounds in a clone of "Ghoy" grown at the Pokrov reclamation station was shorter. The reaction rate was higher, and the initial process took place at lower temperatures. The rate of decomposition of holocellulose was less.



a

b

Fig. 5.3.4. DTG and DTA curves of "Ghoy" poplar clone wood thermal destruction in Boyarka and Pokrov stations

The extreme point was observed at a temperature of 290 °C. The rates of lignin decomposition were almost the same in both combustion variants. However, the extreme point in the wood of "Ghoy" clone grown in Pokrov land reclamation station has shifted to the range of lower temperatures. Thermal effects in the Boyarka option were slightly higher than in the Pokrov option (Fig. 5.3.4b). The content of coke residue was less, and the combustion of wood was more complete.

5.4. The thermal characteristics of local and invasive trees wood

One of the tasks of renewable energy is to obtain high-quality products in short-rotation coppice with fast-growing woody species.

One solution to this problem is to expand the list of these species, including promising clones of willow, poplar and paulownia (Gronli et al., 2002; Ates et al. 2008; Rosúa and Pasadas, 2012; López et al., 2012; Kharytonov et al., 2017). Currently, improving the efficiency of the use of woody biomass focuses mainly on research and improvement of combustion technologies (Lyytimäki, 2019). There is an opinion that the energy properties of woody biomass depend on the soil, climate and type of wood. According to the influence of the type of wood, some studies have been conducted and published (Prins et al., 2006; Khalil et al., 2008; Liu et al., 2012), while the influence of the conditions for growing raw materials on the characteristics of wood has not been studied completely.

The main objective of this case study was to study the thermal characteristics of new for renewable energy wood fast-growing species (*Elaeagnus*, *Ailanthus*, *Paulownia*), and their comparison with traditional (*Salix and Populus*) grown in short-rotation coppice. Samples of spontaneous flora of new for renewable energy wood fast-growing species (*Salix*×*hybrida*, Popu*lus*×*hy*brida, *Elaeagnus angustifolia and Ailanthus altissima*) were taken from plants of 3 years age, grown on black soil (BS), gray-green clay (GGC) and a mixture of loess-like loam (LLL) and red-brown clay (RBC) also passed through a period of long-term phytomelioration. During last decade Paulownia tree is using in agroforestry because of its fast growth rate and the high amount of the wood quantity generated in a short time period. Each Paulownia tree aged 5–7 years old can generate 1 m^3 timber in a surface with density of 2000 plants/ha, offering a total production of 330 t/ha. In the areas planted with a smaller number of plants per surface unit can reach a production of 150 t/ha (Icka et al., 2016). Paulownia clone in vitro 112 saplings were obtained from "Paulownia Group Ukraine" and planted in May 2017 on black soil and loess-like loam (LLL) that has passed the period of long-term phytomelioration.

The thermal decomposition of studied wood plants takes place in two periods: the decomposition of volatile compounds and the destruction of the main components: hemicellulose, cellulose and lignin (Table 5.4.1). The first period occurs in temperature range 50–180 °C and characterized by low speeds and percentage of weight loss. The second period, in turn, is divided into two or three stages. Three stages are clearly traced on the DTG curves in the process of thermolysis of *Elaeagnus* wood: decomposition of hemicellulose with an extreme point of 270 °C, destruction of cellulose with a peak in the temperature range of 290–300 °C, and decomposition of lignin without pronounced peaks (Fig. 5.4.1). The greatest mass loss is observed during the second stage and was 53.4–54.4 %.

Table 5.4.1

Thermal decomposition of Elaeagnus wood

Elaeagnus								
Stage	**LLL + RBC**				**GGC**			
	Interval, °C	**Extremum point, °C**	**Maximum rate, %/min**	**Weight loss, %**	**Interval, °C**	**Extremum point, °C**	**Maximum rate, %/min**	**Weight loss, %**
I	50–170	90	11.2	8.0	30–180	90	17.8	15.0
II	170–280	270	32.8	24.6	180–280	270	27.6	21.6
III	280–360	290	32.8	28.8	280–360	300	37.4	32.8
IV	360–540	400	10.2	33.32	360–490	380	7.2	23.0
	Share of residual mass 5.28 %				Share of residual mass 7.6 %			

The type of the thermolysis of *Salix* and *Populus* is almost the same (Table 5.4.2). The wood of these species has a similar amount and composition of hemicelluloses. The temperature ranges of decomposition of hemicellulose and cellulose overlap in both species. It is manifested by the presence of only one peak on the DTG curves at a temperature of 300 °C (Fig. 5.4.2). The weight loss at this stage was 59.4–61.2 %.The decomposition of lignin and the formation of a non-combustible residue take place in the temperature range 390–550 °C with a weak peak at 440–450 °C.

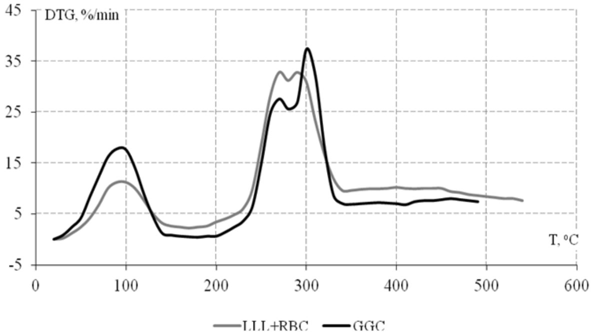


Fig. 5.4.1. DTG curves of thermal decomposition of Elaeagnus wood

Table 5.4.2

Thermal decomposition of Populus, Salix and Ailanthus wood

Populus								
Stage	**BS**				**GGC**			
	Interval, °C	**Extremum point, °C**	**Maximum rate, %/min**	**Weight loss, %**	**Interval, °C**	**Extremum point, °C**	**Maximum rate, %/min**	**Weight loss, %**
I	50–160	90	10.6	7.8	60–160	90	9.4	5.8
II, III	160–400	300	33.0	60.6	160–390	300	42.0	61.2
IV	400–550	440	8.4	8.2	390–550	440	11.4	7.2
	Share of residual mass 7.8 %				Share of residual mass 7.2 %			
	Salix				***Ailanthus***			
Stage	**LLL + RBC**				**LLL + RBC**			
	Interval, °C	**Extremum point, °C**	**Maximum rate, %/min**	**Weight loss, %**	**Interval, °C**	**Extremum point, °C**	**Maximum rate, %/min**	**Weight loss, %**
I	60–190	90	10.8	8.4	50–180	100	7.6	5.05
II, III	190–390	300	39.4	59.4	180–420	320	38.4	64.64
IV	390–540	450	10.8	23.2	400–590	460	9.2	24.6
	Share of residual mass 9.0 %				Share of residual mass 5.67 %			

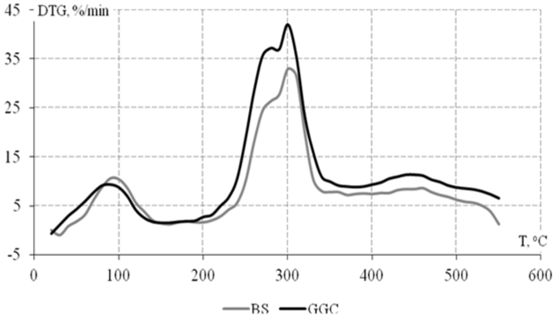


Fig. 5.4.2. DTG curves of thermal decomposition of Populus wood

For *Populus*, *Salix* and *Elaeagnus*, the decomposition stages of cellulose and lignin are accompanied by a pronounced exothermic thermal effect (Fig. 5.4.3).

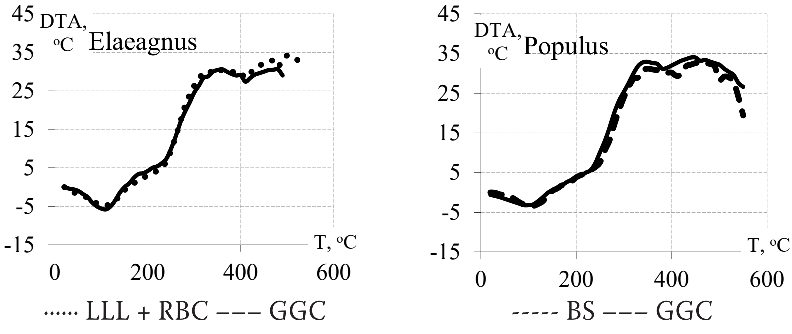


Fig. 5.4.3. Thermal effects of wood thermolysis of Elaeagnus and Populus

Differences in thermal characteristics of plants growing on different substrates are observed. Thus, the thermolysis in wood of *Elaeagnus* plants growing on gray-green clay begins and ends at lower temperatures than in wood on a technical mixture (LLL + RBC). The rate of destruction at the initial stage is 59.0 % more, weight loss is 87.5 %. At the stage of decomposition of the main components, hemicellulose and lignin decompose at a lower rate, and cellulose, on the contrary, with a higher. The share of residual mass is greater: 7.6 % versus 5.3 % on LLL + RBC.

Populus wood has noticeable differences in the rate of decomposition of holocellulose. It was 27.3 % more than that grown on black soil comparative with wood grown on gray-green clay. The combustion of raw materials was more complete on this substrate as well.

Thermolysis of *Ailanthus* wood begins at 50–60 °C and ends at 590–610 °C. In the first period, the process speed is low, and weight loss doesn't exceed 7 %. The extremum point was observed only at a temperature of 320 °C in the decomposition range of holocellulose (Fig. 5.4.4).

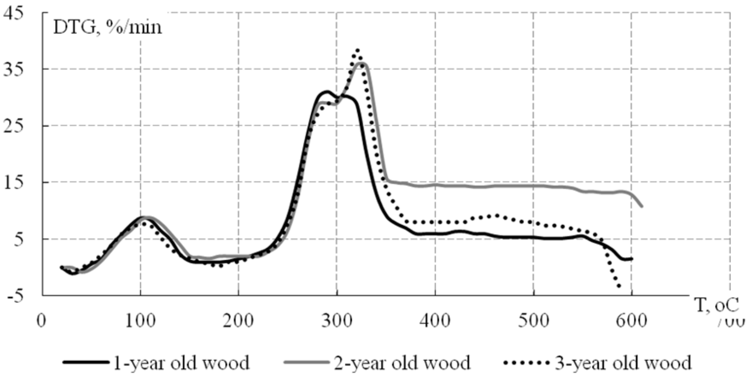


Fig. 5.4.4. DTG curves of thermal decomposition of Ailanthus altissima wood

Depending on the age of the wood, weight loss was 56.0–64.6 %. The holocellulose content and its decomposition rate are highest in three-year-old wood. Higher decomposition rates of lignin and its highest content are characteristic of two-year old wood. At the initial stage of thermolysis, the highest activation energy is characteristic for 1-year old wood

(63.32 kJ/mol), and at the stage of decomposition of the main components, for 3-year old wood (66.87 kJ/mol). The data of thermogravimetric analysis revealed some differences in the process of wood combustion of Paulownia clone 112 grown on different substrates (Table 5.4.3). The process of decomposition of wood components began at a temperature of 60–70 °C. The first stage of water evaporation and removal of volatile compounds in the sample grown on loess like loam was longer, the process speed was 32 % higher. However, the percentage of mass loss was almost the same in both versions of the experiment. This can be explained by the higher thermal stability of wood grown on loess like loam. The LLL wood mass sample initial activation energy was bigger on 34 kJ/mol comparative to 50.6 kJ/mol of BS sample or up to 67 %. The LLL woody sample initial stage was characterized also by endothermic reactions with the most pronounced thermal effect in the temperature range of 110–120 °C (Fig. 5.4.5).

Table 5.4.3

The wood thermal decomposition of Paulownia clone 112 grown in two substrata

Stage	LLL				BS			
	Range, °C	Extrem. point, °C	Max. rate, %/min	Weight loss, %	Range, °C	Extrem. point, °C	Max. rate, %/min	Weight loss, %
Water evaporation	60–190	110	7.4	5.4	70–160	110	5.6	4.82
Holocellulose degradation	190–400	270	46.2	67.6	160–350	270	41.8	58.09
Lignin destruction	400–500	410	6.6	14.4	350–500	360	6.4	24.52
Burnout of coke residue	500–560	–	4.2	7.0	500–560	–	2.2	6.64

The stage of decomposition of holocellulose is characterized by exothermic reactions and consists of two phases: destruction of hemicellulose and decomposition of cellulose. Due to the relatively large number of hemicelluloses and their specific composition, the beginning

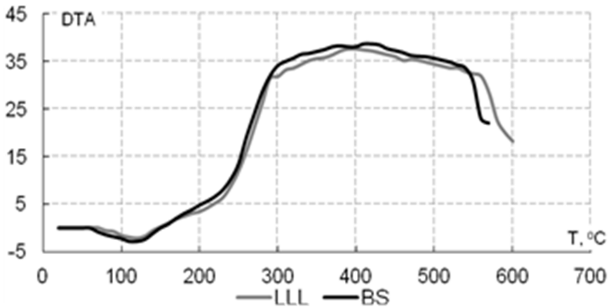


Fig. 5.4.5. DTA curves of Paulownia clone 112 wood thermolysis

of decomposition of hemicellulose is delayed, and the extreme point is shifted to the zone of higher temperatures. Therefore, the destruction ranges and extremum points of hemicellulose and cellulose partially overlap. This is shown by only one peak on the DTH curve in this region (Fig. 5.4.6)

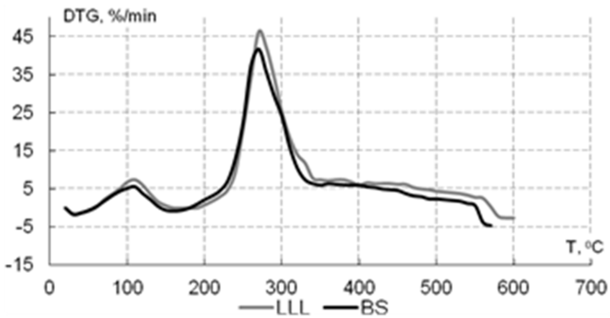


Fig. 5.4.6. DTG curves of Paulownia clone 112 wood thermolysis

The stage of holocellulose decomposition in a wood sample of *Paulownia* grown on loess-like loam ends later. The maximum decay rate and mass loss were 10 % higher. The activation energy values in both variants did not differ significantly from each other and were 65.1 kJ/mol (LLL) and 63.8 kJ/mol (BS). The most pronounced thermal effect was observed in the zone of cellulose destruction. The main decomposition of lignin, which began at the previous stage, occurs in the temperature range of 350–500 °C and is accompanied by the greatest thermal effects. The process is quite slow, with no pronounced peaks. However, one extreme point was observed at temperatures of 410 °C (LLL) and 360 °C (BS). Thus, the main decomposition of lignin in wood grown on black soil occurred at lower temperatures. The mass loss in this sample was also greater. The combustion of coal formed at the previous stages and the formation of a non-combustible residue occurred at the last stage at a temperature of 560 °C. This process was faster in the loess-like loam variant. The percentage of residual mass was 5.6 % (LLL) and 5.9 % (BS).

A preliminary analysis of the influence of species belonging, soil, climate conditions and wood age on the thermal characteristics of wood biomass was carried out. The decomposition ranges of hemicellulose and cellulose in the *Populus* and *Elaeagnus* wood are separated. This made it possible to observe two peaks in the DTG curves in the region of destruction of holocellulose. In the range of holocellulose destruction, *Salix*, *Populus*, *Ailanthus* and *Paulownia* clone 112 wood has only one peak, because of the large amount and specific composition of hemicellulose. The beginning of the decay is shifted to higher temperatures and the extreme point is overlapped by the peak of cellulose decomposition. Thermolysis of all studied species is accompanied by endothermic reactions in the first period of destruction (evaporation of volatile compounds) and exothermic in the second (degradation of the main components). Stages of cellulose and lignin decomposition are characterized by pronounced exothermic thermal effects. The thermal indexes of wood slightly change with age. So, in the 3-year old wood of *Ailanthus*, the content of holocellulose is greater, and the lignin is less than in the 1-year old and 2-year-old. The main differences in the wood thermal characteristics of *Paulownia* and *Populus* clones grown on different substrates are changes in the duration of thermolysis stages, shifts in temperature intervals and extreme points, changes in mass loss rates. This phenomenon is most likely due to the influence of substrates on the complex of extractive substances of wood, which largely determine its thermal behavior. To identify more accurate patterns it is necessary to conduct a more detailed systematic analysis of what is planned in the near future.

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6. AGRICULTURAL CROP RESIDUES GASIFICATION

Ukraine is in the number of countries which have stocks of all kinds of fuel and energy resources (oil, natural gas, coal, peat, uranium, etc.), but the coverage, production and the use are not equally distributed and they do not create the necessary energy safety level, especially in light of existing political situation. The agricultural complex is one of the most important sectors of Ukrainian economy (Velychko, 2015). Agricultural wastes and woody biomass are key components of renewable energy potential in Ukraine. Energy crops currently represent a "virtual" part of the potential, since, except for several experimental plantations (Bielski, 2015). There are two major sources of the feedstock in agricultural forestry sector, which are primary, and secondary agricultural residues. Primary agricultural residues are those materials which remain in fields as by-products after the primary product of crops has been harvested. These include different materials like cereal grain straws, of wheat, barley, rice, etc., corn stover (stalk and leaves), etc. Secondary agricultural residues are specific type of residues and include quite wide variety of biomass by-products of processing of agricultural products for food or feed production (Czernik and Bridgwater, 2004). Bagasse, sunflower husks, rice husks, nut shells, cocoa bean shells and other biomass of such kind is generated and collected at the enterprises which process agricultural crops for food/feed production.

6.1. Dependency of the process operational parameters on main feedstock characteristics

Food processing by-products represent a huge amount of waste resources that could be valorized for recovery of compounds for fuels and energy via thermos-chemical, biological and microbial methods. The biomass pyrolysis is attractive because solid biomass and wastes can be readily converted into liquid products. Although the primary agricultural residues represent the largest share of the technical potential (83 %), distribution of secondary agricultural residues are more equal and there are more options to process it using infrastructure of the facilities where agricultural feedstock is processed (Geletukha et al., 2010). Ukraine has quite a big potential of agricultural residues which mainly consists of straw from cereals and production residues from sunflower and maize from grain. At present, less than 1 % of the primary agricultural residues potential is used for energy purposes (combustion in boilers, production of pellets and briquettes), mainly because of undeveloped infrastructure and logistics system for the feedstock supply. The situation with secondary agricultural residues is much better though their technical potential is in comparably lower than for primary. Over 77 % of sunflower husks biomass, for example, is directly burned in boiler systems, another 20 % is used for pellets production. Almost all sunflower see processing facilities have biomass boilers for utilization of sunflower husks. Agricultural residues from the waste streams of commercial processes have typically been considered to have very little inherent value, mainly constituting a disposal problem in the past. Most of the waste generated by sunflower and crop processing for bioenergy facilities are also confronted with the costs associated with collection and transportation in addition to the supply uncertainties in particular case.

Although direct burning of secondary agricultural residue was widely introduced into de practice during last 10 years, when wood or other solid biomass is directly combusted and coupled to a steam turbine, it is not possible to achieve high rate of efficiency. Only combined energy cogeneration cycles allow versatile and high effective use of biomass residues but in this case using of biomass in combustion/boiler system requires primary production of power from biomass (Wang et al., 2014).

As far as solid biomass cannot be fed into a gas turbine or diesel engine – a liquid or gaseous fuel is required to operate an advanced cycle, which means direct liquefaction or gasification of biomass is required.

An economic analysis was conducted for biomass gasification and pyrolysis and electricity generated to meet local market demand, including the higher-value peaking power. Biomass-based gasification eliminates the need for waste disposal and reduces electricity consumption from the grid, making it a valid investment (Lau et al., 2002).

Although pyrolysis technologies are more developed and available at the present day, they are preferable to others. Pyrolysis is a type of advanced conversion that can be used to produce a combustible gas, oil or solid char (sometimes known as biocoal.

Pyrolysis is one of thermos-chemical processes, which convert the solid biomass in to liquid (bio-oil), gas, and char. Biomass pyrolysis converts essentially 80–95 % of the feed material into gases and bio-oil. The pyrolysis process is to be optimized to maximize the production of gaseous fraction (Williams & Besler, 2006).

Pyrolysis has been practiced for centuries for production of charcoal. This requires relatively slow reaction at very low temperatures to maximize solid yield. More recently, studies into the mechanisms of pyrolysis have suggested ways of substantially changing the proportions of the gas, liquid and solid products by changing the rate of heating, temperature and residence time (Tilmann, 2000; Wang et al, 2002).

There are few fundamental studies, experimental and theoretical, dealing with the biomass combustion and emission characteristics and physical and chemical properties of various biomass feed stocks. There are several studies made on development of reliable kinetic and thermos-transport models for investigation of biomass thermal conversion process. Although some certain adjustment to every type of feedstock and to every type of combined energy cycle is required.

In light of existing situation in the alternative energy sector of Ukraine, it is important to obtain a better understanding of this technology and their potential for implementation and existing markets.

The aim of the present study is to perform a technical and economic assessment of the pyrolysis operation as a secondary agricultural residues utilization process. The study included pilot test at the facility that might be suitable for implementation of biomass utilization combined cycle for evaluation of operating costs and revenue potential for a generic gasification process, and a cost sensitivity study. To perform general evaluation of the technological process of oxidative pyrolysis, laboratory pyrolysis unit was constructed. The general scheme of the pyrolysis unit is shown in Figure 6.1.1.

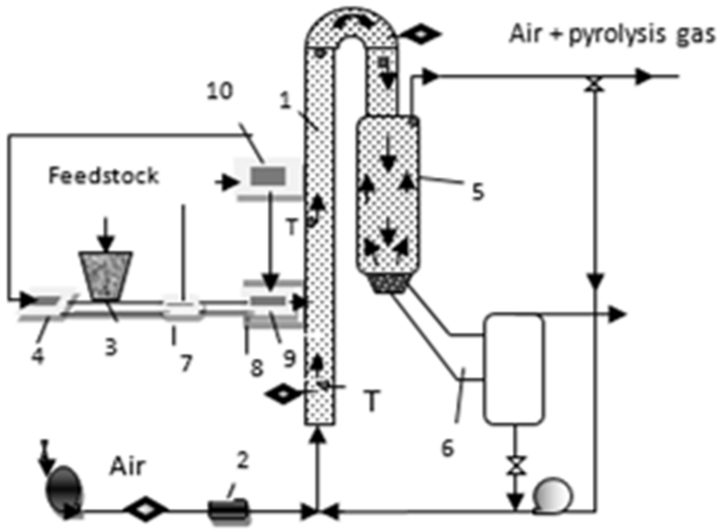

Fig. 6.1.1. The general scheme of the pyrolysis unit

The unit consists of elbow shaped chamber (2) with internal diameter of 100 mm with total length of 5700 mm, which allows conducting the pyrolysis on fluidized bed. In the lower part of the chamber, the air primary heated up in caloriefer is blown (1). Before entering the chamber, air goes through the numerous ceramic rings to average out air velocity profiles along the tube section. The feedstock is loaded into the camera by the screw dispenser. The design of the dispenser is allows to control feed volume and impermeable inlet joint. In the pyrolysis chamber inlet the automatic moister control sensor (7) was installed. Thus in the feedstock before entering the chamber and passing though the moister the moister is automatically measured. The data from sensor is automatically transformed to converter (10) which controls the feed (4).

In the pyrolysis camera satellite-lifting motion of particles is supported when satellite motion of particles velocity is 1.5–2 times lower that the air movement. As particles have almost similar size and mass, the layer of particles can be considered as uniform substance with average thermos-physical parameters. Drying, heating and party pyrolysis is occurs during the movement of the particles suspended in air. The cyclone is installed on the camera outlet where the separation the gaseous and solid phases is taking place. Solid particles fall into cyclone bunker where further devolatilisation is taking place up to full decomposition. The air mixture of gaseous products of pyrolysis is sucked out through the smokestack and 10 % of the mixture is returned back each time for the gas enrichment which increases it's calorific value. To avoid the condensation of resins, which gaseous products of pyrolysis contain, the cyclone, pyrolysis chamber, bunker and connecting pipes were insulated. The experimental on evaluation of the process of biomass thermal conversion was performed in the following stager. First stage is system heating up, the determination of initial moister content in the feedstock. Second stage is the setting of the process parameters (biomass and air feed rate), which define the overall process parameters. Third stage is achieving stability of the process (up to 15 minutes) and determination of its general efficiency indicators – the ration of certain pyrolysis products in the mixture, temperature along the pyrolysis camera. Fourth stage is process finishing and evaluation of the mass balance. Comprehensive experimental study was conducted to analyze new configuration for combined cycle heating system based on pyrolysis gas generation process for most common types of secondary agricultural residues.

At the beginning stage, biomass heating up process results with moister evacuation (strongly marked endothermic process), where moister content, accordingly, is one of the main process indicators. It was shown the condition of the plant material which is used as a feedstock for fuel production process. This process affects certain parameters, such as heating up time, particle satellite movement velocity, bulk yield of the gaseous products, gas permeability of the waste layer and its hydraulic resistance, biomass and air feed rate, initial temperature of air heating, actual biomass feed rate. Initial moister content of processed biomass is very variable (Table 6.1.1). Feedstock with higher moister content requires more energy per batch, which is supported by increasing of temperature during the process of organic matter conversion.

Table 6.1.1

Compartment of energy potential of most common types of secondary agricultural residues

Type of biomass	Moister content, %	Energy capacity MJ/kg	KW hours/kg
Sawdust	20	14.1	3.9
	6	18.2	
Buckwheat husks	12	13.8	3.8
	2	17.9	
Rice husks	12	14.3	3.9
	2	18.5	
Sunflower husks	17	14.2	3.9
	4	18.3	

In order to adjust moister control sensor, the moister content was measured for biomass samples (sawdust) with moister content 1–40 %. Results of the measurements and optimal diapasons of drying for each type of biomass are depicted on plots “a”, “b”, “c” and “d” in the Figure 6.1.2.

After few runs of the pyrolysis unit analysis of the obtained data showed that it was necessary to decrease of the feedstock moister content, because overall energy gain of the process depends on the energy capacity of the feedstock entering the pyrolysis chamber.

Whereas biomass-drying stage is included into pyrolysis unit scheme, the adjustment of the drying and pyrolysis regimes is required. Such adjustment, as experimental study demonstrated, could be performed by incorporation of online moister control automatic sensor.

To support required temperature in the camber, it is crucial to provide certain feedstock and air proportion which can be defined theoretically. Accordingly, there is certain dependency of decomposition process parameters for the feedstock with certain moister content on the temperature regime and amount of air in mixture. The regulation of gas air mixture proportions also can be achieved by regulation of pressure pulsing. To evaluate the rate of impact of thermal treatment regimes on the quality and content of obtained gas mixture, mathematical model was developed.

As main indicator of obtained gas quality the volumetric output of gaseous products from the feedstock was taken As those having impact on the indicators of Y group, such parameters as amount of air (X_1), air temperature (X_2), moister content in the feedstock (X_3) and air pressure drop (X_4).

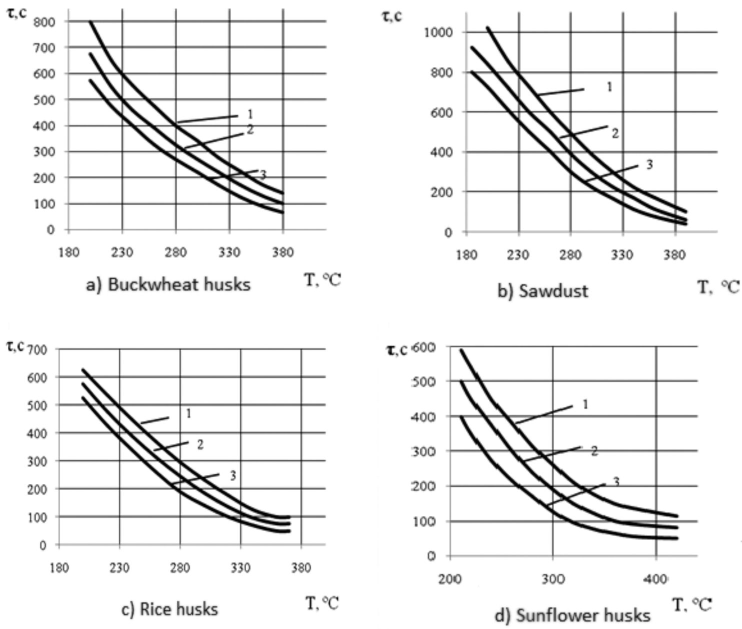

Fig. 6.1.2. Dependence between heating temperature and moister content for different types of processed biomass:
1 – particle with 40 % moister content; 2 – particle with 20 % moister content; 3 – particle with zero moister content

General data obtained during experimentation with pyrolysis unit regimes are given in the table 6.1.2.

For developing of the process model, orthogonal central composition plan of the second order was used. After elimination of the factors and its interactions, which had coefficients had lesser module meanings of set thresholds of significance for general level of significance $\alpha = 0.5$, following dependencies were obtained: *Hydrogen*: $\grave{Y}_1 = 4.124 - 0.3322X_1 + 0.1X_2 - 0.3157X_3 - 0.1415X_4 - 1.0483X_{12} - 0.7983X_{22} - 0.985X_{32} - 0.7983X_{42} - 0.5563X_1X_2 - 0.98125X_1X_3 - 0.09377X_1X_4 - 0.1071X_2X_3$; *Methane*: $\grave{Y}_2 = 3.4584 - 0.1319X_1 + 0.0634X_2 - 0.2561X_3 - 0.5382X_4 - 0.764X_{12} - 0.514X_{22} - 0.639X_{32} - 0.514X_{42} + 0.1251X_1X_2 - 0.606X_1X_3 - 0.0987X_2X_3$; *Carbon oxide*: $\grave{Y}_3 = 4.132 - 0.1574X_1 + 0.0713X_2 - 0.2484X_3 - 0.55969X_4 - 0.8307X_{12} - 0.581X_{22} - 0.556X_{32} - 0.556X_{42} - 0.1068X_1X_2 - 0.759X_1X_3 - 0.185X_1X_4 - 0.085X_2X_4$;

Table 6.1.2

Main process factors variation levels

№	Factor	Symbol	Variation levels					Δ
			-1.411	-1	0	1	1.414	
1	Air content in pyrolysis gas, %	X_1	50	57.5	65	72.5	80	7.5
2	Air temperature, °C	X_2	140	200	260	320	380	60
3	Particles moister content, %	X_3	6	10	20	30	36	10
4	Pressure drop in the chamber, MPa	X_4	0.06	0.1	0.2	0.3	0.36	0.1

Carbon dioxide: $\grave{Y}_4 = 3.6176 + 0.3238X_1 - 1.1171X_2 + 0.2484X_3 + 0.5341X_4 + 0.9044X_{12} + 0.6544X_{22} + 0.7794X_{32} + 0.7669X_{42} - 0.0844X_1X_2 - 0.0794X_1X_3 - 0.4144X_1X_4 - 0.906X_2X_3 + 0.122X_2X_4 + 356X_3X_4$;

Nitrogen: $\grave{Y}_5 = 0.1997 + 0.0184X_1 - 0.087X_2 + 0.0075X_3 - 0.4082X_4 + 0.56X_{32} + 0.0441X_{42} + 0.016X_1X_3 - 0.018X_1X_4 - 0.017X_3X_4$; *Carbohydrates*: $\grave{Y}_6 = 3.2532 + 0.075X_1 + 0.462X_2 - 0.2996X_3 - 0.331X_4 - 0.6834X_{12} - 0.581X_{22} - 0.284X_1X_2 - 0.044X_1X_3 + 0.094X_1X_4 - 0.1025X_2X_3 - 0.0775X_3X_4$; *Hydrogen sulfide*: $\grave{Y}_7 = 0.4488 + 0.0186X_1 - 0.0071X_2 - 0.0708X_4 + 0.0983X_{22} + 0.129X_{42} - 0.075X_1X_4 - 0.057X_2X_4 - 0.0365X_3X_4$. It was proved that proposed models are adequate with confidence level meaning of 0.95 (Fig. 6.1.3).

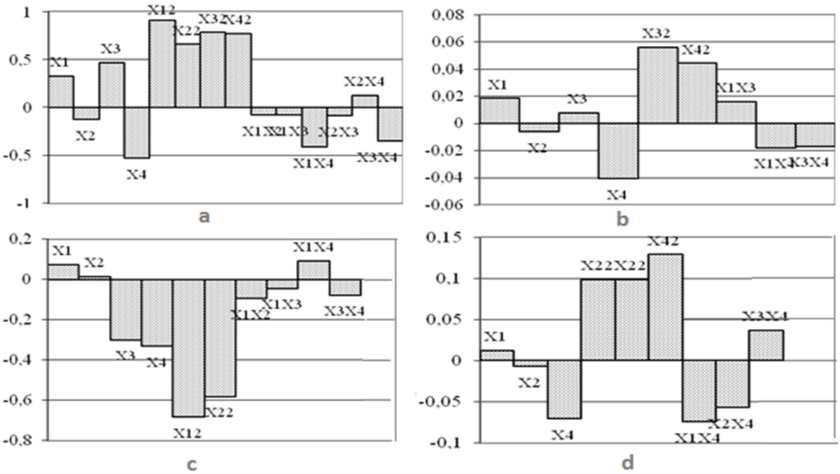

Fig. 6.1.3. Diagrams representing levels of significance of model factors:
a) carbon dioxide; b) nitrogen; c) heavy carbohydrates; d) hydrogen sulfide

It can be used for adjustment of the pyrolysis process and output prognosis for pilot a large scale processes. When the temperature of pyrogas / air mixture is increased, range of conditions when ignition can occur are wider, thus pressure and temperature interaction effects are more complicated. Pressure increase (X_4) for hydrogen (Y_1) narrows down the range where ignition can occur, although for methane and other components of gas mixture (Y_3, Y_5, Y_6, Y_7) the range becomes wider. Thus, an obtained mathematical model proves result obtained in practice i.e. by regulating pressure pulsing, gas composition and temperature at with ignition occur can be controlled. Biomass decomposition process with generation of volatile substances, such as hydrogen (Y_1), methane (Y_2) and partly heavy carbohydrates (Y_6) plays the key role in pyrolysis process. As far other factors (X_1, X_3, X_4) besides temperature also have influence / on yield of volatile substances, it is obvious that all stated factors (X_1, X_2, X_3, X_4) should be considered to control mass transfer which is reflected inbuilt regression equations. Regression dependencies for all given factors appeared to be adequate physical processes, thus can be sued for pyrolysis process control and optimization. The content of gases with highest heating value in the pyrolysis gas was determined as main response function for optimization of the energy yield of the process. The amount of hydrogen Y_1 in the pyrolysis gas was optimized according to obtained optimization model, while numeric limitations accepted after summarizing of average meanings with variance intervals. Considering accepted assumptions the function optimization equations were following:

Hydrogen: $L_1 = Y_1 + \lambda_1(Y_3 + X_5 + 20.8) + \lambda_2(Y_4 + X_6 - 19.2) + \lambda_3(Y_5 + X_7 + 15.54)$;

Methane: $L_2 = Y_2 + \lambda_1(Y_3 + X_5 + 20.8) + \lambda_2(Y_4 + X_6 - 19.2) + \lambda_3(Y_5 + X_7 + 15.54)$;

Heavy carbohydrates: $L_3 = У_6 + \lambda_1(Y_3 + X_5 + 20.8) + \lambda_2(Y_4 + X_6 - 19.2) + \lambda_3(Y_5 + X_7 + 15.54)$.

To determine optimal $X_к$ meanings, three systems of equations were resolved. After resolution of given equation system, the stationary point was found where meanings were: (X_1 = 10.44 %, X_2 = 396 °C, X_3 = 3.35 %, X_4 = 0.153). As it can be observed in given equations, it is hard to define Y_1 from Y_2, Y_3, Y_4, Y_5, Y_6, Y_7 thus regression was used to evaluate $У_1$ in the same conditions. Multi collinearity was checked in Farrar-Glauber method for all three equation systems (Farrar & Glauber, 1967). Proposed approach and found mathematical solutions allow controlling mass transfer during pyrolysis process by variation of meaning for (X_1, X_2, X_3, X_4) which can be done for process of any scale. Obtained results gave all sufficient data for process optimization and further up scaling. During the pilot testing of the pyrolysis unit, different types of feedstock (rice and buckwheat husks, sunflower husks and sawdust) with similar physical and chemical properties were used, which gave similar composition of pyrolysis products with not big differences. The pilot scale study was dedicated to establishing of dependencies of the process parameters on the composition of pyrolysis products and finding of the optimal process intensity to obtain certain gaseous products composition. Pilot unit for thermal conversion of biomass into fuel gas was designed to conduct large scale testing and incorporated into boiler house of municipal enterprise. The proposed technology was based on two stage process. The first stage feedstock undergoes thermal decomposition which results in gas production. This gas is burned on the second stage as depicted on the general process flow scheme (fig. 6.1.4).

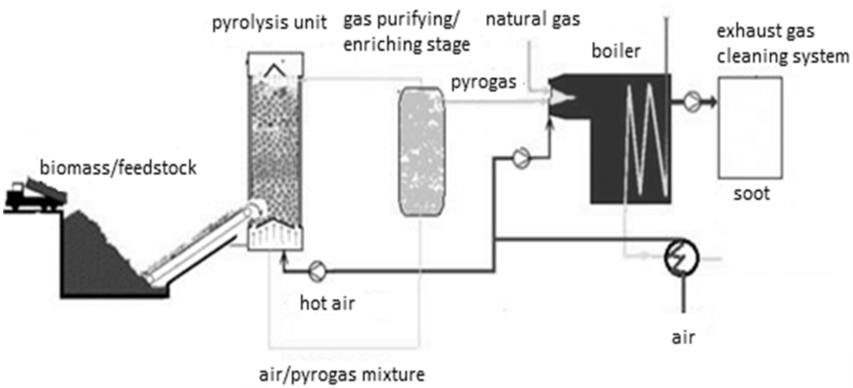

Fig. 6.1.4. General process flow diagram

Pyrolysis gas that was obtained in the process was used as fuel for water boiling system.

Agricultural residue/wastes are promising for producing bioenergy, despite the existing considerations, such as spatial distribution, production costs, and an unstable supply. Availability of the feedstock and regional concentration are good preconditions for local bioenergy generation. However, there is a lack of technologies able to support optimal production limits. Considering both positive and negative impacts of various bioenergy technologies and feedstocks on social economics and ecological challenges, utilization of existing feedstock sources may be the most effective method to develop sustainable, renewable alternative fuel. Experimental methods used and results obtained in this study would be practical to address the challenges in biomass gasification process optimization and adaptation for large-scale implementation.

6.2. The role of volatile components in the process of thermal destruction and ignition of the sunflower husk biomass

During last decades sunflower has occupied significant sown areas among industrial crops in Ukraine, which are mainly located in agricultural enterprises of the Steppe and Forest-Steppe (Cherednichenko, 2020). It is known that raw sunflower husk has several disadvantages such as low heating value and bulk density, high moisture, and volatile matter contents (Bala-Litwiniak and Zajemska, 2020). Several case studies have shown that for effective use of biomass as energy, feedstock in thermochemical conversion processes requires pretreatment (Zajemska et al., 2017; Isemin et al., 2017; Islamova et al., 2021).

Crop residues biomass can also be processed in torrefaction, gasification and liquefaction processes (Zolotovska et al., 2016; Kaczynska et al., 2019). The pellets application for heat production allows diminishing the atmospheric burden of greenhouse gases (Kuznetsova, 2012) and creates the conditions for sustainable economic development (Cui et al., 2019). It was shown that in terms of price, sunflower seed husk pellet fuel is 71 % cheaper than natural gas and 75 % cheaper than coal. Meanwhile, there is still uncertainty in the assessment of the impact of pollutant emissions caused by the burning of biomass on air quality caused by the lack of emission factors that would characterize real combustion (Pastorello et al., 2011; Zajqc et al., 2019).

At the same time, biomass contains lower sulfur and ash amount than nonrenewable sources, such as fossil fuels, and, therefore, it generates lower NO_x and SO_x emissions (Klason and Bai, 2007; Perea-Moreno et al., 2018). As a rule, sulfur content in the biomass does not exceed 0.2 % and only certain biomass fuels reach 0.5–0.7 % (for brown coal 0.7–7 %) (Demirbas, 2004; Parmar, 2017). Meanwhile, biomass is characterized by a high proportion of volatile parts and high humidity content (Zolotovska et al., 2016). The amount of ash, active carbon and volatile matter contained in sunflower seed husk briquettes is about 2.4 %, 22.7 % and 72 % accordingly (Spirchez et al., 2019). The content of combustible matter (C, S and H) significantly decreases after thermal processing, while the contents of oxygen (O) and volatile matter significantly rise after drying (Matin et al., 2019).

It is known that the high volatility of the biomass material provides numerous advantages associated with a low ignition temperature and retention of ignition over a longer period of time (Sivabalan et al., 2021). An increase in volatile substances led to increase the heating value of the feedstock. The sunflower husk calorific value is 3500–4000 Cal/kg being supplied through burning (Popescu et al, 2013). The thermal reactivity of the sunflower seed husk is extremely higher than that for the other samples (hazelnut shell, rice husk, and olive refuse) under investigated conditions (Haykiri-Acma & Yaman, 2011). The volatilization stage is characterized by the release of volatiles caused by the decomposition of hemicellulose and cellulose and partial decomposition of lignin (Tibola et al., 2022). This chapter aims was to study the role and composition of volatile components in the process of thermal destruction and ignition of the sunflower seed husk biomass. The thermal analysis of sunflower seed husk biomass was carried out using the derivatograph Q-1500D of the "F. Paulik-J. Paulik-L. Erdey" system. Differential mass loss and heating effects were recorded. Samples of biomass were analyzed dynamically at a heating rate of 10 °C/min in an air atmosphere. The mass of samples was 100 mg. The reference substance was aluminum oxide. The activation energy of thermo-oxidation destruction samples is determined by the method of Broido (Broido, 1969).

The value of the double logarithm for each temperature was calculated using the dependence:

$$\ln\left(\ln\frac{100}{100-\Delta m}\right)=-\frac{E}{R}\cdot\frac{1}{T},$$

where m is the sample mass, %;

E – the activation energy, kJ/kmol;

R – universal gas constant, 8.314 J (mol.K);

T – temperature, K.

High performance capillary gas chromatography was used to separate hydrocarbons in fuel gas using a flame ionization detector. A glassy highly permeable polymer, polytrimethylylpropyne (PTMSP), was chosen as the stationary phase for the separation of hydrocarbon gases. A quartz capillary column with an outer metal protective coating, 10 m long and 0.35 mm in inner diameter, filled with PTMSP was used. The thickness of the adsorption layer was 30 μm. The polymer was dissolved in toluene. The capillary was filled with this solution under pressure. It was removed by heating the column and passing a flow of carrier gas. The following analysis conditions were chosen: column oven temperature 55 °C, evaporator and detector temperatures 130 °C. The carrier gas is nitrogen. The specified flow rate of nitrogen was controlled by a rheometer at a level of 18 cm^3/s. The analysis time was 10 min.

The presence of inorganic components of the pyrolysis gas was determined on a gas chromatograph using a conductometric detector. Separation was carried out at a temperature of 45 °C on two packed columns.

A column 2 m long and 4 mm in diameter filled with 5A molecular sieves was used to determine H_2, N_2, CO, H_2, O_2. It is noticed that at higher temperatures their crystal structure is destroyed. The second column of the same size with a polymeric sorbent, a copolymer of styrene and divinylbenzene, was used to determine CO_2, and H_2S. The carrier gas, grade A helium, was used for both columns. The temperature of the evaporator and the thermostat of the detector is 110 °C. Gas samples with a volume of 3 cm^3 were introduced through a sampling probe. The ignition temperature was determined by the method of inlet of a pre-prepared gas mixture into an evacuated (residual pressure no more than 0.4 kPa) heated flask, 200 cm^3 in volume, made of quartz glass. The test equipment is shown in figure 6.2.1. The reaction vessel (127 mm long and 127 mm in diameter) was placed in a horizontal steel cylinder of an electric furnace. The stainless-steel cylinder is inserted into the ceramic body. Three Chromel-Alumel thermocouples were used to measure the furnace temperature. The temperature measurement error under static conditions did not exceed 3–6 °C in the range of 220–490 °C. The supplied mixture of gases was prepared in a 3-liter cylinder. The prepared mixture was kept in the cylinder for at least 10 hours before the start of the experiment to complete mixing of the reagents.

The prepared mixture was admitted into the reaction vessel using a 200 cm^3 sealed glass syringe equipped with a three-way valve and connecting tubes (Fig. 6.2.2).

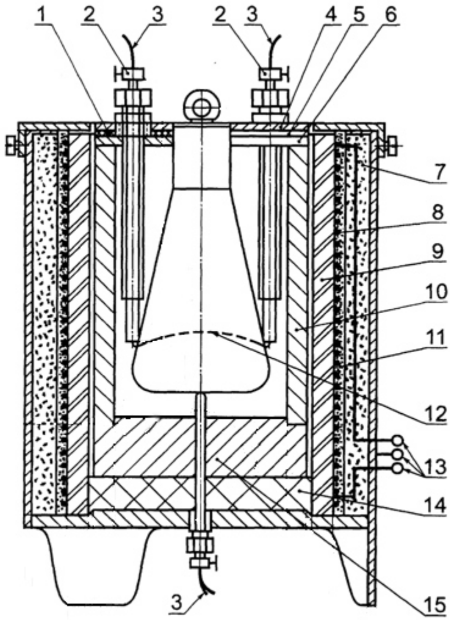

Fig. 6.2.1. Test equipment for determining the ignition temperature of a gas:
1 – high-temperature insulation; 2 – clamping sleeves; 3 – thermocouples; 4 – upper part of the cover; 5 – insulating ring; 6 – lower part of the cover; 7 – thermal insulation; 8 – heater; 9 – ceramic tube; 10 – steel cylinder; 11 – high-temperature mastic; 12 – control points; 13 – heater connection for voltage 220 V; 14 – insulating disk; 15 – metal base

Eight volumetric gaseous samples (20–55 cm^3) were taken in the temperature range of 220–600 °C to be tested at various initial pressures of the mixture (from 100 to 400 kPa).

The pressure of the mixture in the reaction vessel after the inlet was determined by the pressure in the dosing tank before the inlet, taking into account the valve opening time (0.07–1 s).

The pressure in the reactor was recorded by a fast inertia inductive pressure sensor. All the results obtained were treated by statistical methods using the StatGraphics Plus5 software package at significance level of 0.95 % (p-value < 0.05).

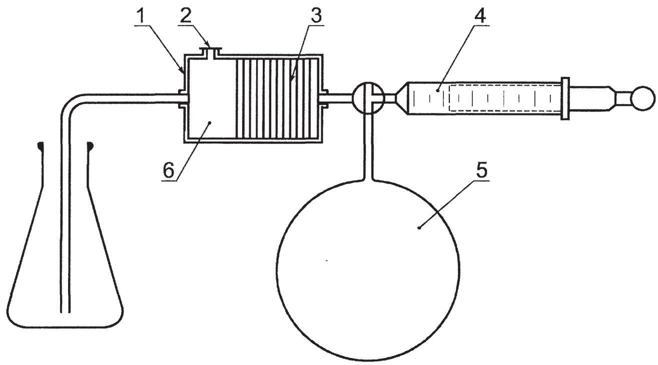

Fig. 6.2.2. Introduction of a gas sample:
1 – flame arrester; 2 – safety membrane; 3 – sintered glass plates; 4 – sealed syringe; 5 – tank with gas; 6 – pre-chamber

Thermal destruction of sunflower husks begins at a temperature of 29–30 °C. The main decomposition of volatile components and evaporation of water occurs in the range of 40–150 °C. The process speed is low, on average 5.5 %/min. The maximum rate (8.7–8.84 %/min) was observed at a temperature of 79–91 °C (Fig. 6.2.3, curve 3). The weight loss at this stage is small and amounts to 8.3 % (Fig. 6.2.3, curve 1). The process of volatile components decomposition is accompanied mainly by endothermic reactions with the most pronounced effects in the temperature range of 61–79 °C (Fig. 6.2.3, curve 2).

The process of decomposition of the main components of sunflower husk takes place in the temperature range of 151–400 °C. The degradation ranges of hemicelluloses (220–320 °C) and cellulose (300–380 °C) partially overlap. That is why only one peak is observed on the DTG curve at a temperature of 300 °C. The average speed of the process is 13.7–14.2 %/min, the maximum is 31.7 %/min. The mass loss at this stage is the largest and amounts to 57.8 %. Decomposition reactions of hemicelluloses and cellulose are exothermic with the greatest thermal effects in the temperature range of 280–300 °C.

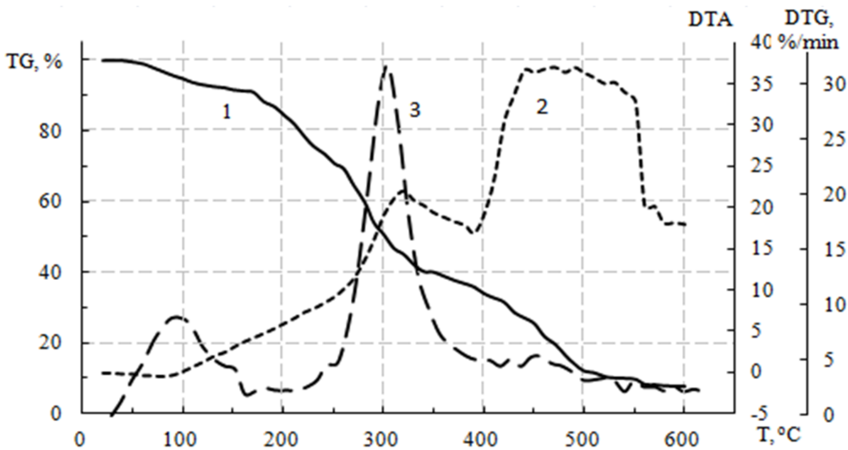

Fig. 6.2.3. Curves of thermogravimetric (1), differential thermal (2) and differential thermogravimetric (3) analysis of sunflower husk

The process of lignin destruction begins at a temperature of 250–280 °C. However, the bulk of lignin decomposes in the range of 400–550 °C. Typically, the decomposition rate is 3.5–4.0 %/min (maximum 5.4 %/min). One small peak is observed at a temperature of 430–440 °C. The weight loss was 26.3 %. Decomposition reactions are exothermic with pronounced thermal effects in the temperature range of 440–500 °C. Combustion of sunflower husk ends in the range of 550–600 °C. The fireproof residue was 7.6 % of the total mass.

According to the activation energy data, the heat resistance of sunflower husks is low (Fig. 6.2.4). The activation energy was 33.7kJ/mol at the initial stage of decomposition. Its value at the stage of destruction of the main components was 32.1 kJ/mol. Low activation energy values are explained by a rather large amount of pentosans (27–28 %) and a relatively small amount of cellulose (31–38 %) in sunflower husk (Yadav et al., 2016). During the process, pyrolysis produces both solid and liquid products (bio-oils, tars, and water), and a gas mixture composed mainly of CO_2, CO, H_2 and CH_4 (Castello et al., 2017; Uddin et al., 2018).

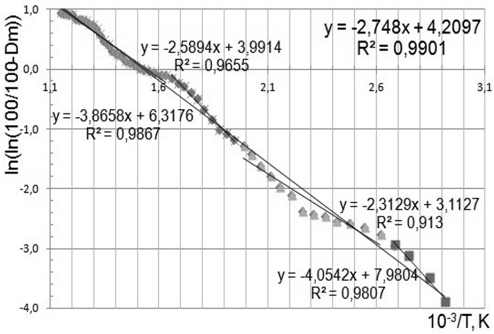

Fig. 6.2.4. Diagram of the process of non-isothermal decomposition of sunflower husk

The results of assessing the release of volatile substances from the particles of sunflower husk biomass are shown in Figures 6.2.5 and 6.2.6.

The growth of gas emission is directly caused by the rise in the pyrolysis temperature in the range of 200–500 °C. This is due to an increase in the concentration of hydrogen and methane and to a lesser extent it depends on heavy hydrocarbons. The roots of this effect are associated with a more complete decomposition of biomass particles. The volume of pyrolysis gas increases by 1.04; 1.21; 1.3 and 1.61 times at temperatures of 260, 320, 380 and 420 °C, respectively, compared with the volume of the gas mixture at a temperature of 220 °C.

Meanwhile, a noticeable decrease in the yield of carbon dioxide and nitrogen (undesirable impurities in the fuel gas) occurs in the temperature range of 280–500 °C. The amount of hydrocarbons in the resulting gas mixture also increases with increasing temperature and reaches a maximum at a temperature of 420 °C, exceeding this value corresponding to a temperature of 200 °C by 2.1 times. The chemical content of the test gas is shown in Table 6.2.1.

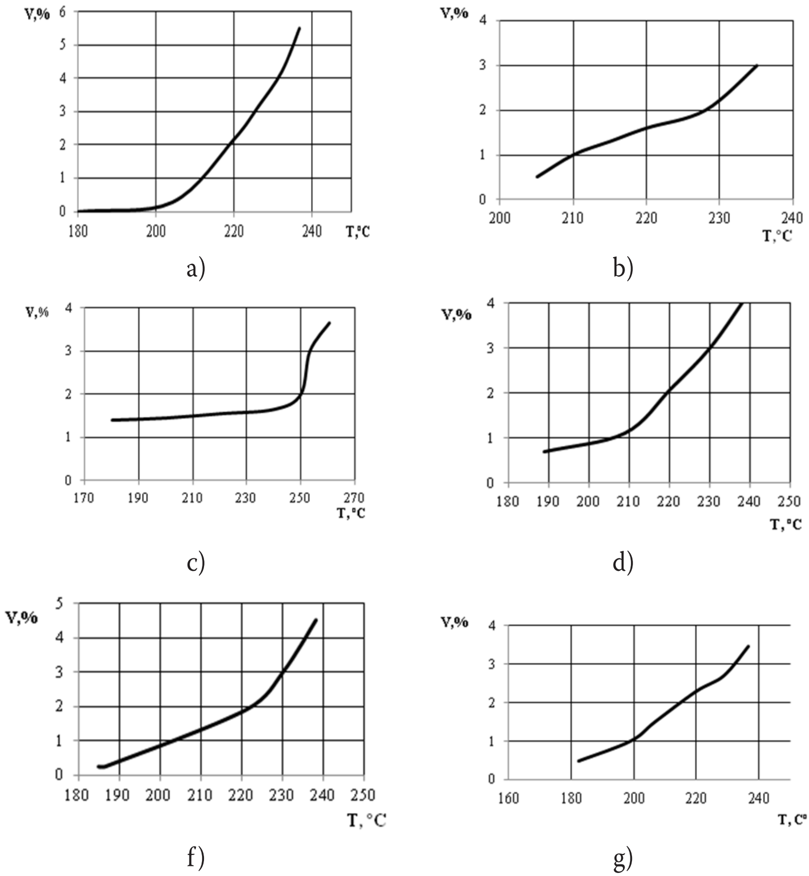

Fig. 6.2.5 – Emission of volatiles from sunflower husk biomass
a) hydrogen; b) methane; c) heavy hydrocarbons; c) carbon monoxide; d) carbon dioxide; f) nitrogen

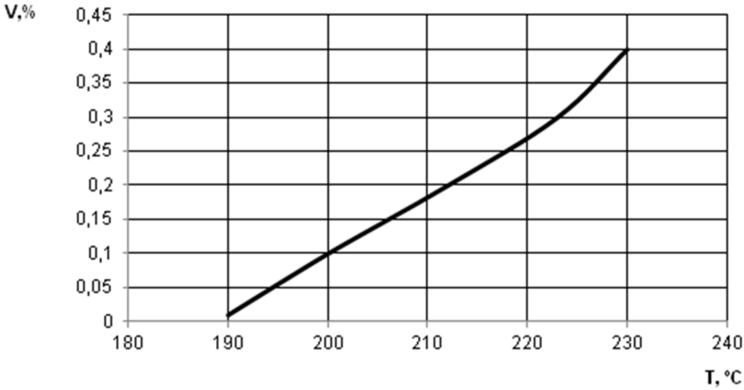

Fig. 6.2.6. Hydrogen sulfide emission from sunflower husk biomass

Table 6.2.1

Chemical content of pyrolysis gas

Components	H_2	CH_4	CO	CO_2	N_2	C_nH_m	H_2S	A
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
Concentration	22.70	16.20	20.80	19.12	2.29	15.54	2.65	0.70

It is known that the thermal decomposition of xylan produces furfural, which quickly ignites and causes a sharp increase in temperature and self-heating of biomass (Zaichenko et al., 2020). An ignition risk ranking is estimated using both kinetic parameters and characteristic temperatures (Jones et al., 2015). Some crop residues, olive cake and sunflower husk are predicted to have a high risk of low temperature ignition. The determination of the critical condition for self-ignition was carried out at a constant temperature of 490 °C and various initial pressures of the mixture (100–300 kPa). Typical barograms are shown in figure 6.2.7. The analysis of thermo-barograms showed that the heating of the gas mixture occurs mainly in the process of puffing. Insufficient heating of the gas to the level of the reactor temperature at the moment of closing the valve was 1–2 % and depended both on the pressure and the diameter of the reactor. The completion time of gas heating after closing the valve did not exceed the ignition delay in the entire studied temperature range of 200–600 °C (Fig. 6.2.7 and 6.2.8).

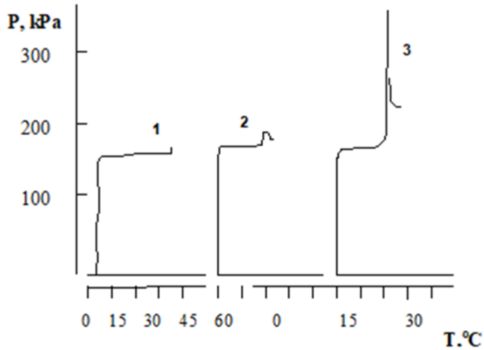

Fig. 6.2.7. Barograms of studies at a temperature of 490 °C with O_2 = 42.3 %: *1 – no ignition; 2 – degenerate ignition; 3 – self-ignition*

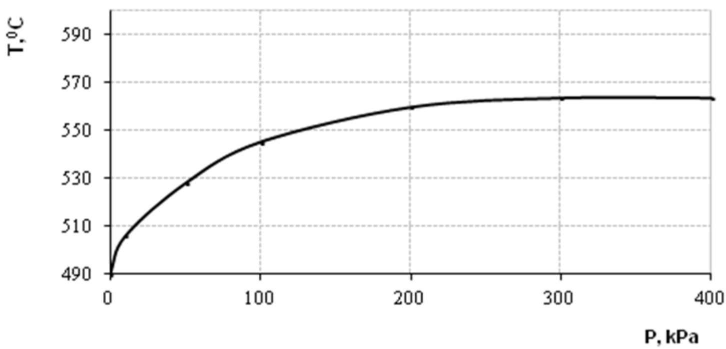

Fig. 6.2.8. Dependence of the autoignition temperature on pressure

The transition from a smooth increase in pressure of 90 kPa to an explosive one (in the range of 300–400 kPa) occurred when the initial pressure of the mixture after the injection into the reactor changed by

1–10 %. This transition depends on the chemical content and temperature of the gas mixture. The composition of the gas can be controlled by adjusting the pressure pulsations and the ignition temperature of the gas mixture. The flash point changes with increasing pressure (Fig. 6.2.8 and 6.2.9).

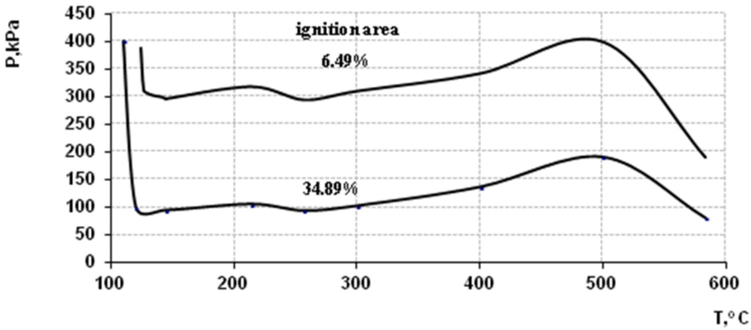

Fig. 6.2.9. Dependence of the autoignition temperature on pressure for a gas mixture with air

A change in pressure from 100 to 200 kPa leads to an increase in the flash point to 300–500 °C. As can be seen, the pyrolysis process occurs at varying pressure. Ignition of pyrolysis gas is possible when the limit temperature is reached.

Decomposition reactions of hemicelluloses and cellulose are exothermic with the greatest thermal effects in the temperature range of 280–300 °C. The process of lignin destruction begins at a temperature of 250–280 °C. However, the bulk of lignin decomposes in the range of 400–550 °C. Combustion of sunflower husk ends in the range of 550–600 °C. The fireproof residue was 7.6 % of the total mass. The activation energy value at the stage of destruction of the main components was 32.1 kJ/mol. Gas emission increases with an increase in the pyrolysis temperature in the range of 200–500 °C due to an increase in the composition of hydrogen, methane and slightly from heavy hydrocarbons. The amount of pyrolysis gas in the gas mixture increases with increasing temperature. The amount of hydrocarbons in the resulting gas mixture also increases with increasing temperature and reaches a maximum at a temperature of 420 °C. The analysis of thermo-barograms showed that the heating of the gas mixture occurs mainly in the process of puffing. Insufficient heating of the gas to the level of the reactor temperature at the moment of closing the valve was 1–2 % and depended both on the pressure and the diameter of the reactor. The completion time of gas heating after closing the valve did not exceed the ignition delay in the entire studied temperature range of 200–600 °C. The composition of the gas can be controlled by adjusting the pressure and the gas mixture temperature of the ignition. A change in pressure from 100 to 200 kPa leads to an increase in the flash point to 300–500 °C.

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CONCLUSION

The demand for biomass is expected to increase significantly in the coming decades and contribute to the development of the world's bio-based economy. Numerous forecasts indicate that the cultivation of energy crops and trees of the second generation on marginal lands will be able to satisfy the great demand for bio-raw materials.

Depending on the type of minerals and methods of their extraction, technosols formed in this process have their own specific features. Thus, the composition and properties of the edaphic constructions of the technosols of the Nikopol manganese deposit are transformed at various stages of biological development and use. Initially, these substrates have somewhat negative indicators. In the first years, there and over densification and a decrease in porosity, a low supply of basic nutrients, and an increased content of easily soluble salts. As a result of biological development, the dynamics of changes in the properties and nutritional regimes of the phytomeliorated rocks acquires a positive movement towards the level of zonal soils. As a result of the functioning of the root systems of plants and various physiological groups of microorganisms, enzymes are accumulated, which are accumulated by the organic-mineral part of edaphotopes. Artificial edaphotopes almost always approach zonal black soils in terms of their main indicators of biological activity.

The study of the accumulation of energy with the biomass of agricultural crops in crop rotation on marginal lands in Western Donbas proved that the greatest positive impact is made by the full application of all reclamation factors.

However, the leading of these factors is the creation of a screen of loess loam, and the most productive crop is corn for grain on black steam. In general, the distribution of crops according to the decrease in the amount of straw biomass looks like this: in the first place is corn, placed in pairs; on the second – corn for winter wheat; on the third – corn for corn for grain; on the fourth – winter wheat in pairs; on the fifth – spring barley on the stubble. The largest output of energy with straw biomass was recorded when growing corn, winter wheat was second, and alfalfa was third.

Most of the mining substrates of the Nikopol manganese ore deposit are suitable for the creation of industrial plantations of energy crops and trees. Loess loam, red-brown clay and their mixture are most favorable for growing miscanthus. Dark grey schist clay is not suitable for growing miscanthus as an energy crop due to low productivity. The best substrates for switchgrass are red-brown clay, loess and red-brown loam, as well as grey-green clay. Options with black soil and dark grey schist clay are the worst in yield. Nevertheless, the productivity of switchgrass on dark grey schist clay is higher than that of miscanthus, so using this substrate to obtain switchgrass raw materials is quite reasonable.

The use of soil amendments is expedient to increase the energy yield with the biomass of fast-growing perennial herbaceous crops on low-productivity reclaimed lands. Thus, the use of mineral fertilizers on plantations with miscanthus can increase the energy output of miscanthus up to 360–370 GJ/ha, switchgrass – up to 310–320 GJ/ha. The use of sewage sludge allows you to get the best result and increase the energy output up to 370–560 GJ/ha (miscanthus) and up to 300–400 GJ/ha (switchgrass).

The prospects of creating plantations of fast-growing tree with a short growing cycle (poplar, ailanthus, elaeagnus, robinia, paulownia, etc.) on reclaimed land are obvious. At the same time, special attention should be paid to the selection of species and cultivars.

The specific properties of technosols have a certain influence on the thermal characteristics of the biomass of herbaceous and woody plants. The duration of thermolysis changes, there is a shift in the decomposition intervals of hemicellulose and cellulose, and variations in the fractions of the residual mass after the combustion of raw materials. Small changes in activation energy indicators are also possible. Volatile components of biomass are mainly affected as substances most sensitive to environmental conditions. They, in turn, affect the speed of reactions and the thermal stability of wood and grassy biomass.

The wide variety of biomass by-products of processing of agricultural products for food or feed production can also be used as an essential resource for the supply of bio-feedstock. The pilot unit for thermal conversion of biomass into fuel gas was designed to conduct large-scale testing and incorporated into the boiler house of a municipal enterprise.

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