UDC 622.2
SCOPUS CODE 2311
https://doi.org/10.36073/1512-0996-2025-2-346-359

A New Method for Destroying Pesticide Waste Using Metal-energy Materials

Iolanta Bieganska University of AGH krakov, Faculty of energy and fuel, krakov, Poland
E-mail: biega@agh.edu.pl
Gela Machaidze Department of Mining technologies, Georgian Technical University, Georgia, 0160, Tbilisi, 75, M. Kostava str.
E-mail: g.machaidze@gtu.ge
Kristop Baranski Universitu of AGH Krakow, Faculty of civil engineering and resource management
E-mail: baranski@agh.edu.pl
Davit Robaqidze Department Mining technology, Georgian Technical University, Georgia, 0160, Tbilisi, 75, M. Kostava str.
E-mail: davitirobaqidze2@gmail.com
Irakli Gachechiladze Department of Mining technology, Georgian Technical University, Georgia, 0160, Tbilisi, 75, M. Kostava str.
E-mail: Irakligachechiladze847@gmail.com

Reviewers:
A. Bezhanishvili, Professor, Faculty of mining and geology, GTU
E-mail: BezhanishviliAleqsandre03@gtu.ge
N. Bochorishvili, PHD doctor, Head of the laboratory of ore processing and mining geotechnics of the G. Tsulukidze mining institute
E-mail: miningnika@yahoo.com

Abstract. The article presents the advantages and disadvantages of conventional methods of pesticide disposal. The characteristics of this group of chemical compounds are made and their impact on the environment is discussed. The assumptions of a conceptual, unconventional method of pesticide disposal using high-energy materials are presented. The applications of computer programs as a tool to support the process of designing research in this area are discussed. Thermodynamic simulations of the effect of the addition of heptachlor (a pesticide) on the thermodynamic properties of a mixed high-energy material of the ANFO type were carried out. The environmental impact of the addition of this chemical compound on the quantitative and qualitative structure of the sub-nitrification products was also evaluated. The calculations showed that at 3.0% pesticide content in the structure of the high-energy material, it is possible to obtain better or comparable energy parameters with respect to the reference ANFO.

Keywords: environmental protection; high energy materials; thermodynamic calculations; utilization; waste pesticides.

Introduction

Pesticides are chemicals used to eliminate pests to protect crops [1]. They are classified according to their chemical structure, purpose, mode and duration of action, method of manufacture, spectrum of action, level of toxicity [2]. The Food and Agriculture Organization (FAO) has defined a pesticide as "a substance intended to prevent, destroy, repel or mitigate any pest in crops before or after harvest to prevent deterioration during storage and transportation." The actual properties are given to the pesticide by the active ingredient (biologically active substance). In addition to this main ingredient, the pesticide contains [3] various types of inert additives (emulsifiers, soluble concentrates, powders, dusts, water-soluble granules, etc.) to facilitate their storage, transportation and application. Pesticides are toxic to all living organisms with carcinogenic, mutagenic, teratogenic and embryotoxic properties [4-6]. Long-term exposure to these substances can cause carcinogenic, endocrine and neurotoxic disorders [6, 7]. The effects of pesticides can appear in future generations. Due to their properties (persistent bioaccumulation and long-distance transportability), they have been termed "Persistent Organic Pollutants - POPs" (POPs). The ingress of these substances into any of the elements of the environment results in a threat to all its elements (contamination of soils, groundwater) [8-10].

According to an assessment by the World Health Organization (WHO), everyone's health depends 25-30% on the state of the surrounding environment. If the trend of environmental pollution does not change, according to the WHO, the cause of one in two deaths in 2050 will be cancer, the primary source of which will be contaminated food, water or

environment. The most common group of POPs is made up of manufactured synthetic chemicals (especially for use in agriculture), which include organochlorine pesticides (OCPs) such as aldrin, dieldrin, dichloro-diphenyl-tetrachloroethane (DDT), heptachlor, mirex, chlordane, toxaphene and endrin. Some of these can also be used in dyes or plastics [11-13]. The use of pesticides widespread in connection with intensive food production, has been associated with the generation of a certain amount of waste. Out-of-date pesticides are mainly stored in 10,000 sites in the former Soviet Union, the southern Balkans and new European Union member states [14, 15]. According to the FAO [16], in Central Europe the largest quantities of outdated pesticides are in the Russian Federation (100,000 tons), Macedonia (38,000 tons), Ukraine (25,000 tons), Uzbekistan (12,000 tons), Kazakhstan (10,000 tons) and Belarus (6,000 tons). In Georgia, past use of pesticides [17, 18] at 30 kg per hectare of arable land has resulted in a large amount of overdue stocks. It was estimated at 3,057 tons, of which the main reserve - at 2,700 tons - was buried at the Iaghluja landfill [19]. A small part of the stockpile (357 tons) was deposited in 214 different small rural warehouses [20].

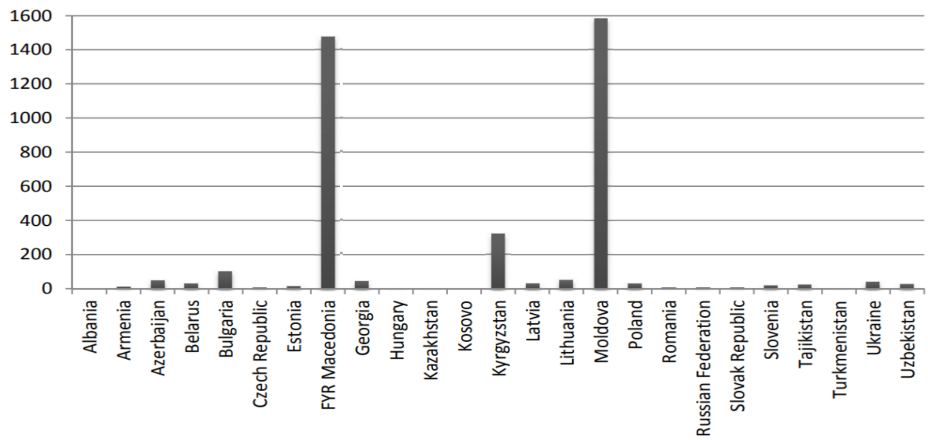


Fig. 1. Amounts of obsolete pesticides (in kg/km^2). Source: study [21] based on [22, 23].

As the volume of stockpiles accumulated in Eastern Europe is huge in relation to the rest of the world, it is important to start solving this problem as soon as possible. Figure 1 shows an estimate of the amount of obsolete pesticides compared to the area of a given Eastern European country.

As mentioned earlier, pesticide waste improperly stored threatens the environment and, above all, negatively affects human health. Numerous scientific works are being undertaken on how to dispose of this waste.

Main Part

1. Overview of methods of pesticide waste disposal

Disposal aims to decompose the biologically active substance leading to the formation of other substances that no longer pose a threat to the environment. A suitable disposal method is selected for each type of pesticide. Many biological, physical, chemical and thermal methods have been developed and patented. The technologies used to dispose of pesticide stocks or remove pesticides from the contaminated environment can be divided into three groups. The first group is where pesticides are destroyed by chemical reactions: dechlorination, photocatalytic oxidation and bioremediation using microorganisms. The second category is that in which contaminants are extracted from specific environments - thermal adsorption. The third category includes curing, stabilization, vitrification and fusion techniques [24-26], whose main goal is to reduce the solubility or mobility of contaminants, usually by physical means rather than chemically. Waste stabilization technologies convert contaminants into less toxic forms by adding a binder to the waste, similar to cement dust or fly ash [24, 25].

2.1. Biodegradation

Biological decomposition processes [27-34] in the environment (surface water, soil) are determined by similar factors: the presence and characteristics of micro-organisms, temperature and pH values. They are time-consuming and require the selection of appropriate conditions, as the aforementioned parameters affect the course of the processes to different degrees and the relationship between them varies.

2.2. Chemical decomposition

The literature describes various chemical processes - mainly oxidation of pesticides [35- 37]. Modern Oxidation Processes - (from English) Advanced Oxidation Processes (AOP) is based on reactions involving OH-hydroxyl radicals and is the most powerful oxidant. Many researchers have taken an interest in this method of pesticide decomposition [38-41].

2.3. Thermal methods - combustion processes

Thermal methods are primarily high-temperature combustion (oxidation) processes, in which pesticides are converted into gases (steam, CO2, volatile acids, metal particles and oxides) and ash [42, 43]. Studies [44] have confirmed destruction efficiencies of 99.99% at temperatures higher than 1000 oC. Attempts have also been made to degrade pesticides in cement kilns [45-47]. The first attempts to burn accumulated pesticide stocks were made in Africa and Pakistan [48]. Old pesticide stocks containing, for example, lead, arsenic or mercury are excluded from the thermal process. Numerous studies have shown that not all technologies are universally effective, and many are designed to work only for a specific group of substances (for example, organochlorines, organophosphates, carbamates, etc.).

Acceptable and inappropriate pesticide waste disposal techniques have been developed [49, 50] (Figure 2).

ISSN 1512-0996
www.shromebi.gtu.ge

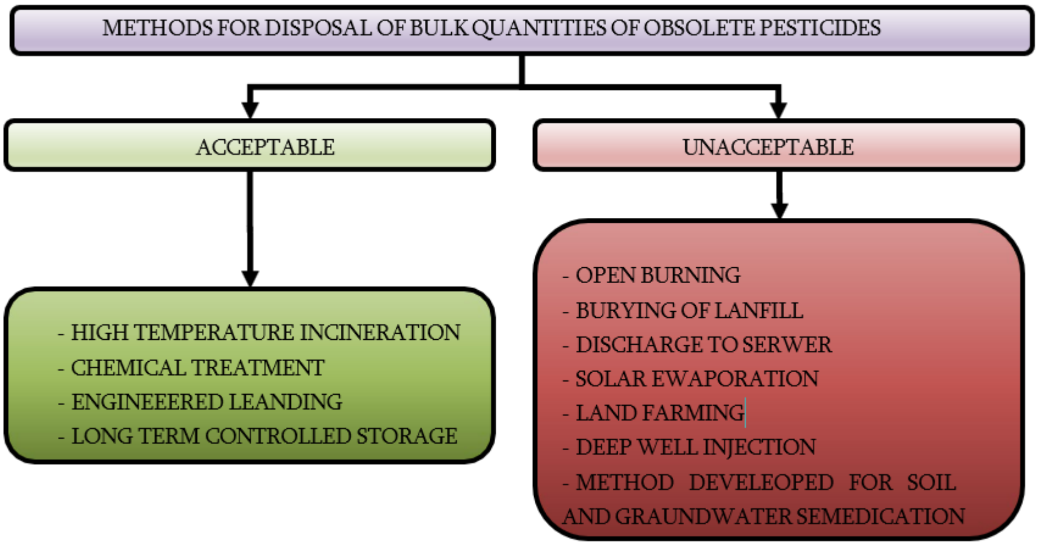


Fig. 2. Acceptable and unsuitable techniques for disposing of large quantities of obsolete pesticides [49, 50].

High-temperature incineration is the most effective way to dispose of pesticide waste - often not cost-effective due to cost and availability of the right kind of incinerator.

2.4. Incineration under high pressure and temperature conditions

Despite a lot of past and ongoing work to find an effective method of disposing of various pesticide wastes, it has not been possible to find a universal technology with maximum efficiency. An attempt has been made to burn under high pressure and temperature conditions, which ensures the use of high-energy materials - explosives. The mechanism of decomposition of the pesticide under the conditions produced during the detonation of such a material ensures rapid heating (of the pesticide - chemical compound) to a high temperature, in which the energy of vibration of the bonds causes the breaking of these bonds and the destruction of the chemical compound. Then, by oxidation and rapid cooling

of the oxidation products, recombination is prevented, leading to the formation of new compounds with greater thermodynamic stability.

3. Materials and methods

3.1. Characteristics of heptachlor

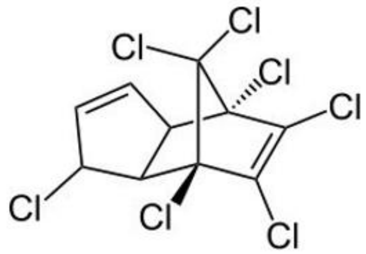
Pesticides are substances used to eradicate unwanted or harmful organisms. In Poland, the number of pesticides approved for marketing is more than 2,500, and they contain several hundred different active substances (data from 2021).

They are divided according to various criteria:

- target application group - e.g. herbicides, fungicides, bactericides, insecticides, plant or insect growth regulators, repellents,
- chemical structure - e.g. organophosphates, polychlorines, urea derivatives, nitrophenols, thiazines or uracil, organo-mercury compounds,
- way of migration and place of action - e.g., surface herbicides, deep herbicides, systemic herbicides,
- selectivity,
- toxicity class and withdrawal period - classes from I (extremely toxic) to VI (potentially harmless),
- effect on plant, vegetable and fruit resistance - preventive and ad hoc.

One of the representatives of insecticides (insecticides) from the group of polychlorine compounds is heptachlor [51]: $C10H5Cl7$ (1,4,5,6,7,8,8-heptachloro-

3a,4,7,7,7a-tetrahydro- 4,7-methane-indene) - used on corn, alfalfa, hay and vegetables, and as a termiticide. It is a persistent organic pollutant (POPs).



Its half-life is ~1.3-4.2 days (air), ~0.03-0.11 years (water) and ~0.11-0.34 years (soil). Like other POPs, heptachlor is lipophilic and poorly soluble in water (0.056 mg/l at 25 °C), so it tends to accumulate in the fatty tissue of humans and animals. Heptachlor is a toxic compound - listed as a probable human carcinogen. [52].

3.2. Characteristics of the explosive

Environmental explosives commonly used in non-coal mining include ANFO and emulsion explosives. ANFO, in which the oxidant is ammonium nitrate (NH_4NO_3) porous, and the fuel is usually diesel, was adopted as the explosive used for modification. More modern mixed explosives are emulsions, which consist of multiple components combined with a so- called matrix. Both materials can be produced mechanically at the blasting site (using MEMUs) or in the form of finished products (bags, cartridges). The open structure of mixing and loading systems makes it possible to expand them in order to use various additional components to refine the explosive.

3.3. Methodology of calculation

The method of pesticide decomposition is that a modified explosive is formed, relative to the one used, where the oxidant or fuel is replaced by the addition of a pesticide. It was assumed that the oxidation reaction would proceed under stoichiometric conditions. In ANFO, which contain 6.0% diesel fuel ($C_{16}H_{34}$), the process of ideal detonation leads to the formation of simple substances according to the reaction:

$$NH_4NO_3 + -CH_2- = N_2 + CO_2 + H_2O \qquad (1)$$

Under unfavorable conditions, nitrogen oxides and/or carbon monoxide can be formed. In modified ANFO, pesticide is substituted in place of oil. The composition of the explosive is designed taking into account thermodynamic parameters. The appropriate selection of the proportions of individual components for designed explosive mixtures should be preceded by calculations of performance parameters. The purpose of these calculations is primarily to determine the temperature of the explosion, whether it is high enough to decompose the pesticide. Also important is the burning speed of the explosive, which increases with pressure, and therefore the best results will be obtained by enclosing such material in a container with a small volume (space).

For thermodynamic calculations, the ZMWCyw computer program developed by the Military University of Technology in Warsaw (Poland) was used, which performs

calculations in the constant volume variant. The algorithm's calculation is based on the European standard PN-EN 13631-15 [53]. The ZMWCyw program uses the chemical potential minimization method described in works [54-56]. The program allows calculating the most important thermodynamic parameters of explosives, such as explosion pressure, explosion temperature, explosion heat, constant volume, explosive strength and gas volume under standard conditions. These parameters provide basic information about the properties of the explosive. It is possible to determine the qualitative and quantitative composition of the resulting substrate, detonation products and their form of aggregation (state: gaseous, solid or liquid).

For the purpose of the simulation, an ANFO explosive with a composition of 94% ammonium nitrate(V) and 6.0% diesel fuel was assumed. The data of the basic components of ANFO needed to perform the thermodynamics of the calculation were used from the da-

ISSN 1512-0996
www.shromebi.gtu.ge

tabase of the ZMWCyw program. The oxygen balance of individual explosives and compositions were calculated using a worksheet, using the algorithm described in Standard BN-80/6091-42 [57]. Thermodynamic simulations were carried out using the method of changing the composition of the ANFO base recipe by replacing its components with pesticide in appropriate proportions. The basic principle of designing the formulation composition of an explosive - near-zero oxygen balance - was followed. Heptachlor (CAS 76-44-8) was used for the calculations. The pesticide data needed for the simulations were taken from publicly available databases [58-60]. For the purpose of the calculations, taking into account the practical aspects of the preparation of explosives compositions, a minimum step of change in the percentage of components of 0.5% by weight was adopted. Thus, thermodynamic parameters (explosion temperature, explosion pressure, explosion heat, volume of explosion products, explosive strength) were calculated for the designed explosives. The individual explosives were assigned the acronyms given in table 1.

Tab. 1.

Oxygen balance and density of ANFO with pesticide (heptachlor) additive

Ingredients	Density [g/cm^3]	Oxygen Balance [%]	Percentage of Ingredients						
Ammonium Nitrate (V)	0,82	20,00	94,00	93,50	93,00	92,50	92,00	91,50	91,00
Diesel	0,84	-348,25	6,00	5,50	5,00	4,50	4,00	3,50	3,00
Heptachlor	1,59	-81,43	0,00	1,00	2,00	3,00	4,00	5,00	6,00
Density of the explosive			0,821	0,829	0,836	0,844	0,852	0,859	0,867
Oxygen balance of the explosive			-2,095	-1,268	-0,441	0,386	1,213	2,040	2,867
Name of the explosive			ANFO	H/1,0	H/2,0	H/3,0	H/4,0	H/5,0	H/6,0

4. Results and Discussion

The results of thermodynamic calculations for ANFO and explosives with the addition of heptachlor (H/1.0 - H/6.0) are presented in table 2, while in terms of percentage changes in parameter values in table 3.

Tab. 2.

Summary of calculated thermodynamic parameters

Parameter	Unit	ANFO	H/1,0	H/2,0	H/3,0	H/4,0	H/5,0	H/6,0
Explosion pressure	MPa	2 796,85	2 828,47	2 850,46	2 852,82	2 839,44	2 816,70	2 798,40
Explosion temperature	K (°C)	2 663,00 (2389,85)	2 684,00 (2410.85)	2 702,80 (2429,65)	2 683,80 (2410,65)	2 643,20 (2370,05)	2 600,80 (2327,65)	2 557,10 (2283.95)
Constant volume heat of explosion	kJ/kg	3 957,90	3 968,50	3 973,30	3 903,30	3 791,50	3 677,00	3 562,40
Explosive power	kJ/kg	972,80	970,10	966,50	952,30	932,50	912,40	892,00
Gas volume at standard conditions	l/kg	997,40	986,80	976,40	968,90	963,30	957,80	952,40
Density of the explosive	[g/cm^3]	0,821	0,829	0,836	0,844	0,852	0,859	0,867
Oxygen balance of the explosive	[%]	-2,095	-1,268	-0,441	0,386	1,213	2,040	2,867

Tab. 3.

Percentage change in values of individual thermodynamic parameters relative to ANFO

Parameter	Unit	ANFO	H/1,0	H/2,0	H/3,0	H/4,0	H/5,0	H/6,0
Explosion pressure	MPa	0,00	1,13	1,92	2,00	1,52	0,71	0,06
Explosion temperature	K	0,00	0,79	1,49	0,78	-0,74	-2,34	-3,98
Constant volume heat of explosion	kJ/kg	0,00	0,27	0,39	-1,38	-4,20	-7,10	-9,99
Explosive power	kJ/kg	0,00	-0,28	-0,65	-2,11	-4,14	-6,21	-8,31
Gas volume at standard conditions	l/kg	0,00	-1,06	-2,11	-2,86	-3,42	-3,97	-4,51

Changes in the structure of the sub-detonation gas products that predictably will be produced by the detonation of individual explosives are presented in table 4.

Tab. 4.

Summary of changes in the structure of sub-detonation products for individual explosives

Product Name/Explosive	ANFO	H/1,0	H/2,0	H/3,0	H/4,0	H/5,0	H/6,0
NH_3 —Ammonia (gas)	3,61E-02	1,67E-02	3,41E-03	3,41E-04	1,28E-04	6,65E-05	3,87E-05
N_2 — Nitrogen (gas)	1,17E+01	1,17E+01	1,16E+01	1,15E+01	1,14E+01	1,14E+01	1,13E+01
CO_2 — Carbon dioxide (gas)	3,95E+00	3,98E+00	4,01E+00	3,97E+00	3,89E+00	3,81E+00	3,72E+00
CH_4 —Methan (gas)	8,07E-05	1,02E-05	1,45E-07	3,25E-10	2,53E-11	4,75E-12	1,20E-12
O_2 — Oxygen (gas)	2,37E-04	7,68E-04	7,28E-03	1,34E-01	3,54E-01	5,90E-01	8,33E-01
NO — Nitrogen (II) oxide (gas)	3,02E-03	5,60E-03	1,77E-02	7,33E-02	1,11E-01	1,34E-01	1,47E-01
CO — Carbon Monoxide (gas)	2,88E-01	1,75E-01	6,18E-02	1,29E-02	6,37E-03	3,91E-03	2,56E-03
H_2O — Water (gas)	2,70E+01	2,69E+01	2,67E+01	2,64E+01	2,59E+01	2,53E+01	2,48E+01
H_2 — Hydrogen (gas)	9,02E-01	5,38E-01	1,86E-01	3,92E-02	1,98E-02	1,25E-02	8,42E-03
NO_2 — Nitric oxide (IV) (gas)	1,59E-06	5,28E-06	5,11E-05	9,28E-04	2,39E-03	3,87E-03	5,28E-03
N_2O — Nitric oxide (I) (gas)	5,04E-06	9,46E-06	3,02E-05	1,25E-04	1,87E-04	2,22E-04	2,41E-04
Cl — Chlorine ion (gaz)	------	6,73E-06	8,26E-05	8,28E-04	2,55E-03	5,46E-03	9,95E-03
HCl — halogens (gas)	------	1,88E-01	3,75E-01	5,61E-01	7,45E-01	9,27E-01	1,11E+00

The results of thermodynamic simulations indicate that the key parameter affecting the performance of a non-ideal mixed explosive is the oxygen balance. The most favorable value of this parameter, i.e. +0.380%, occurs in the case of H/3.0. The explosive then achieves a higher pressure and explosion temperature compared to the base ANFO. Note that heptachlor has a higher (about 1.59 g/cm3) density than the other components of the explosive (oil and ammonium nitrate about 0.80g/cm3). This causes the adding of larger amounts of pesticide to the ANFO structure to increase the density of the entire mixture, which should increase the detonation velocity. Heptachlor with the chemical formula C10H5Cl7 has an oxygen balance of about -81.43%. This causes the compound to be classified as a flammable component. However, these values are higher than most of the oils used in ANFO production (about -300%). Therefore, the pesticide replacing the oil in appropriate proportions can influence the correction of the oxygen balance and improve the energetics of the explosive. Up to a pesticide content of 3.0% in the structure o the explosive is characterized by comparable or slightly better energetic properties than ANFO. Increasing the pesticide content to 6.0% by weight leads to a decrease in the energetic potential of the explosive by about 4.0-10% relative to the reference. These are already significant decreases. The use of a heptachlor additive to ANFO leads to a change in the qualitative and quantitative structure of the primary gas products formed by detonation. In chemical terms, the pesticide introduces additional amounts of chlorine into the structure of ANFO, which is not formed during the detonation of the reference ANFO. The detonation is predicted to produce additional amounts of chlorine and hydrogen chloride. As the oxygen balances of all analyzed explosives are close to zero, they are gaseous products. A change in the oxygen balance from slightly negative (-2.095% for ANFO) to slightly positive (for 2.867 for H/6.0) results in changes in the quantity of gaseous products produced by the detonation. As the heptachlor increases, the amount of COX (carbon dioxide, carbon monoxide) decreases and

the amount of NOX (nitrogen oxides(IV), nitrogen oxides(I)) increases

Conclusion

The thermodynamic simulations carried out show that the use of computer tools can be very useful in designing new compositions of explosives giving the possibility to estimate the predicted energetic properties. Knowledge of the basic data of individual substrates and their chemical characteristics with the use of appropriate counting algorithms allows a more accurate selection of optimal proportions of components. This makes it possible to reduce the number of time- and cost-intensive field tests and, what is related, allows to achieve optimization of the research methodology. Pesticides are a diverse group of chemical compounds in terms of structure and properties. By evaluating their effect on the explosive, the use of computer programs allows to indirectly predict the potential environmental effects.

References

1. Larramendy, M.L, Soloneski, S. (2022). Pesticides - Updates on Toxicity, Efficacy and Risk Assessment. IntechOpen, p.326., London: United Kingdom ISBN: 1-80356-039-8.
2. Akashe, M.M, Pawade U.V, & Nikam, A.V. (2018). Classification of pesticides: A review. International Journal of Research in Ayurveda and Pharmacy, N9, pp.144-150.
3. Knowles, A. (2008). Recent developments of safer formulations of agrochemicals. The Environmentalist, N 28, pp.35-44.
4. Kowalska, G., Kowalski, R. (2019). Pesticides – scope and risk of use, benefits and hazards. A review. Annales Horticulturae. XXIX (2), pp.5-25. DOI: 10.24326/ah.2019.2.1.
5. Kapka-Skrzypczak, L., Cyranka, M., Kruszewski, M., & Turski, W.A. (2011). Plant protection products and farmers' health –perspectives of the application of biomarkers for evaluation of exposure to pesticides and its

biological effects. Medycyna Ogólna i Nauki o Zdrowiu, 17(1), pp.28-32.
6. Hernandez, A.F., Lacasana, M., Gil, F., Rodrigez-Barranco, M., Pla, A., Lopez-Guarnido, O. (2013). Evaluation of pesticide-induced oxidative stress from a gene-environment interaction perspective. Toxicology, N307, pp.95-102. https://doi.org/10.1016/j.tox.2012.09.007
7. Nougadere, A., Sirot, V., Kadar, A., Fastier, A., Truchot, E., Vergnet, C., Hommet, F., Bayle, J., Gros, P., & Leblance, J.Ch. (2012). Total diet study on pesticide residues in France: Levels in food as consumed and chronic dietary risk to consumers. Environment International, N45, pp.135-150. https://doi.org/10.1016/j.envint.2012.02.001.
8. Schäfer, R.B., Van den Brink, P.J., & Liess, M. (2011). Impacts of Pesticides on Freshwater Ecosystems. Ecological Impacts of Toxic Chemicals. Chapter 6, pp.111-137.
9. Problem of Obsolete Pesticides in the Republic of Armenia. (2005). In: Forum Book of the 7th International HCH and Pesticides Forum "Towards the Establishment of an Obsolete POPs/Pesticides Stockpile Fund for Central and Eastern European Countries (CEEC) and New Independent States (NIS)". Kiev, pp.41-43.
10. Tiryaki, O., Temur, C. (2010). The Fate of Pesticide in the Environment. Biological and Environmental Science Journal, N4(10), pp.29-38.
11. Manciulea, I., Dumitrescu, L. (2016). Poluanți organici persistenți-Introducere. In Learning Toxicology through Open Educational Resources (TOX–OER); Transilvania University of Braçov. Braçov, Romania. pp.17. Available online: http://moodle.toxoer.com/pluginfile.php/3555/mod_page/content/1/POPs_Introducere_RO.pdf (accessed on 26 October 2022).
12. Reichelt-Brushett, A. (2023). Marine Pollution-Monitoring, Management and Mitigation. p.369. Springer Textbooks In Earth Sciences, Geography and Environment. Southern Cross University, Australia. https://doi.org/10.1007/978-3- 031-10127-4.
13. Ene, A., Bogdevich, O., Sion, A. (2012). Levels and distribution of organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in topsoils from SE Romania. Science of the Total Environment, N 439, pp.76-86.
14. Simeonov, L.I., Macaev, F.Z., Simeonova, B.G. (2013). Environmental Security Assessment and Management of Obsolete Pesticides in Southeast Europe. Springer Science+Business Media Dordrecht, p.470.
15. Vijgen, J., Egenhofer, C. (2009). Obsolete Pesticides. A ticking bomb and why we have to act now. International HCH & Pesticides Association, IHPA, Centre for European Policy Studies, CEPS report, p.19.
16. FAO (2012). http://www.fao.org/agriculture/crops/obsolete-pesticides/where-stocks/en.
17. Lud, D., Schwemm, A., Kalandadze, B., Babaev, E., Simon, M.P., Weller, P., Düring, R.A. (2022). Pesticide handling and waste management: a case study on DDT and HCHs from the Southern Caucasus. SN Applied Sciences, N4(112). p.14. https://doi.org/10.1007/s42452-022-04999-w.
18. Kalandadze, B., Matchavariani, L. (2019). Soil pollution. The soils of Georgia. Springer, Cham. pp. 153-166.
19. Sopadze, G. (2006). Survey of the POPs-related situation in the Republic of Georgia. International POPs Elimination Project - IPEN.

https://ipen.org/sites/default/files/documents/1geo_georgia_country_situation_report-en.pdf. Accessed 26 Jan 2022.

20. Government of Georgia. (2012). Persistent organic pollutants national implementation plan of Georgia 1st edn. Ministry of environment protection of Georgia.
http://chm.pops.int/Countries/CountryProfiles/tabid/4501/Default.aspx. Accessed 26 Jan 2022.
21. Kocur-Bera, K., Dudzińska, M. (2014). Spatial Conditions of Environmental Risk Posed by Obsolete Pesticides – Case Study of the "Green Lungs of Poland" Area. Polish Journal of Environmental Studies, 23(3), pp.763-772. https://www.pjoes.com/Issue-3- 2014,426.
22. FAO (212). Prevention and disposal of obsolete pesticides.
http://www.fao.org/agriculture/crops/obsoletepesticides/where-stocks/europe- stocks/en/ (accessed 20. 08. 2012).
23. Europa.eu.http://europa.eu/about-eu/countries/membercountries/bulgaria/index.pl.htm. (accessed 20. 08. 2012).
24. Jensen, J.K. (1997). Innovative technologies. In Prevention and disposal of obsolete and unwanted pesticide stocks in Africa and the Near East 25. Roma: FAO, p. 48.
25. FAO. (2004). Seventh FAO Consultation on Prevention and Disposal of Obsolete, Banned and Unwanted Pesticide Stocks. No. September.
26. Anastos, G.J., Noland, J.W., Johnson, N.P., & Williams, R. (1988). Innovative technologies for hazardous waste treatment. Nuclear and Chemical Waste Management, N 8(4), pp. 269-281.
https://doi.org/10.1016/0191-815X(88)90053-8.
27. Javaid, M.K., Ashiq, M., & Tahir, M. (2016). Biodegradation and Environmental Impacts of Pesticides. Hindawi Publishing Corporation Scientifica. Article ID 1598325. pp.9.
http://dx.doi.org/10.1155/2016/1598325.
28. Chishti, Z., Hussain, S., Arshad, K.R., Khalid, A., & Arshad, M. (2013). Microbial degradation of chlorpyrifos in liquid media and soil. Journal of Environmental Management, N114, pp. 372-380.
29. Sutherland, T., Russel, R., Selleck, M. (2002). Using Enzymes to Clean Pesticide Residues. Pesticide Outlook, N13, pp.149-151.
30. Barriuso, E., Benoit, P., & Dubus, I.G. (2008). Formation of Pesticide Nonextractable (Bound) Residues in Soil: Magnitude, Controlling Factors and Reversibility. Environmental Science & Technology, N42, pp.1845-1854.
31. Hussain, S., Siddique, T., Arshad, M.,; & Saleem, M. (2009). Bioremediation and Phytoremediation of Pesticides: Recent Advances. Crit. Rev. Environmental Science & Technology, N39, pp.843-907.
32. Rao, M.A., Scelza, R., Scotti, R., & Gianfreda, L. (2010). Role of Enzymes in the Remediation of Polluted Environments. Journal of Soil Science and Plant Nutrition, N10, pp.333-353. Available online:
https://www.researchgate.net/publication/228819276_Role_of_enzymes_in_the_remediation_of_polluted_environments/link/09e4150d0243fdf3fb000000/download. (accessed on 8 August 2022).
33. Chaplain, V., Mamy, L., Vieublé-Gonod, L., Mougin, Ch Benoit, P., Barriuso, E., & Nélieu, S. (2011). Fate of Pesticides in Soils: Toward an Integrated Approach of Influential Factors. In Pesticides in the Modern World-Risks and Benefits; Stoytcheva, M., Ed.; Intech OpenAcess: London, UK. Chapter 29, pp. 535-550.

34. Uqab, B., Mudasir, S., & Nazir, R. (2016). Review on Bioremediation of Pesticides. Journal of ioremediation and Biodegradation, N7, p.343. Available online: https://www.omicsonline.org/open-access-pdfs/review-on-bioremediation-of- pesticides-2155-6199-1000343.pdf. (accessed on 9 August 2022).
35. Salvestrini, S., Cerbo, P.D., & Capasso, S. (2002). Kinetics of the chemical degradation of diuron. Chemosphere. N48(1), pp.69-73. DOI:10.1016/S0045-6535(02)00043-7.
36. Mahamuni, N.N., Adewuyi, Y.G. (2010). Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation. Ultrasonics Sonochemistry, N17(6), pp.990-1003. https://doi.org/10.1016/j.ultsonch.2009.09.005.
37. Kim, K., Tsay, O.G., Atwood, D.A., & Churchill, D.G. (2011). Destruction and detection of chemical warfare agents. Chemical Reviews. 111(9), pp.5345-5403. https://doi.org/10.1021/cr100193y.
38. Ijpelaar, G.F., Groenendijk, M., Hopman, R., Kruithof Joop, C. (2002). Advanced oxidation technologies for the degradation of pesticides in ground water and surface water. Water Supply. 2(1), pp.129-138. https://doi.org/10.2166/ws.2002.0017.
39. Ribeiro, Ana R., Nunes, Olga C., Pereira, Manuel, F.R., Silva Adrián, M.T. (2015). An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environment International. 75, pp.33-51. http://dx.doi.org/10.1016/j.envint.2014.10.027.
40. Kudlek, E. (2019). Identification of degradation by-products of selected pesticides during oxidation and chlorination processes. Ecological Chemistry and Engineering, 26(3), pp.571-581. https://sciendo.com/journal/ECES.
41. Malakootian, M., Shahesmaeili, A., Faraji, M., Amiri, H., Martinez Susana, S. (2020). Advanced oxidation processes for the removal of organophosphorus pesticides in aqueous matrices: A systematic review and meta-analysis. Process Safety and Environmental Protection, 134, pp.292-307. https://doi.org/10.1016/j.psep.2019.12.004.
42. Felsot, A.S., Racke, K.D., Hamilton, D.J. (2003). Disposal and Degradation of Pesticide Waste. Reviews of Environmental Contamination and Toxicology, 177, pp. 123-200. DOI:10.1007/0-387-21725-8-3.
43. Al Hattab, M.T., Ghaly, A.E. (2012). Disposal and Treatment Methods for Pesticide Containing Wastewaters: Critical Review and Comparative Analysis. Journal of Environmental Protection, N 3, pp.431-453. http://dx.doi.org/10.4236/jep.2012.35054.
44. Ferguson, T.L., Wilkinson, R.R. (1984). Incineration of pesticide wastes. In: Krueger RF, Seiber JN (eds) Treatment and Disposal of Pesticide Wastes. ACS Symposium Series. Washington. N259, pp. 181-191. https://doi.org/10.1021/bk-1984-0259.ch011.
45. Stobiecki, S., Cieszkowski, J., Siłowiecki, A., Stobiecki, T. (2001). Disposal of Pesticides as an Alternative Fuel in Cement Kiln. In Proceedings of the Project Outline 6th International HCH and Pesticides Forum. Poznań, Poland, 20-22 March 2001. pp.285-289. Available online: http://www.hchforum.com/6th/forum_book/A.5.8.pdf. (accessed on 11 August 2022).

46. `Cement, Kilns. (2022). Center for Health, Environment & Justice. Available online: https://chej.org/wp-content/uploads/Cement-Kilns-PUB-0401.pdf. (accessed on 11 August 2022).
47. Karstensen, K.H., Justnes, H. (2007). Environmentally Sound Management of Hazardous and Industrial Wastes in Cement Kilns in China. Conference: International Conference on Sustainability in the Cement and Concrete Industry At: Lillehammer, Norway. N1, pp.334-342. https://www.researchgate.net/publication/283349851.
48. Huden, G.H. (1990). Pesticide Disposal in a Cement Kiln in Pakistan. Report of a Pilot Project. Agency for International Development. USA, Washington. pp.159. https://pdf.usaid.gov/pdf_docs/PNABS355.pdf.
49. FAO. (1997). Pesticide Disposal Series 4. Disposal of bulk quantities of obsolete pesticides in developing countries. FAO Pesticide Disposal Series N26(4), p. 44. Accessed: Jan. 09, 2023. [Online]. Available: https://agris.fao.org/agris-search/search.do?recordID=XF9767671.
50. Mohafrash Samia, M.M., Mossa Abdel-Tawab, H. (2024). Disposal of expired empty containers and waste from pesticides. Egyptian Journal of Chemistry, N67(4), pp.65-85. DOI: https://doi.org/10.21608/ejchem.2023.222647.8249.
51. Metcalf, R.L. (2002). Insect Control in: Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, Weinheim. doi:10.1002/14356007.a14_263.
52. IARC. (1991). Occupational Exposures in Insecticide Application, and Some Pesticides Monographs on the Evaluation of Carcinogenic Risks to Humans, Lyon, France, 53, p.621.
53. PN-EN 13631-15. (2007). Materiały wybuchowe do użytku cywilnego. Materiały wybuchowe kruszące. Część 15: Obliczanie właściwości termodynamicznych. In Explosives for Civil Uses. High Explosives. Calculation of Thermodynamic Properties. Polish Committee for Standardization: Warsaw, Poland.
54. Grys, S., Trzciński, W.A. (2010). Termodynamiczne modelowanie procesów spalania, wybuchu i detonacji nieidealnych układów wysokoenergetycznych (Thermodynamic modeling of combustion, explosion and detonation processes of non-ideal high- energy systems). Biuletyn WAT, 59(3), pp.71-118.
55. Mader, C.H. (1979). Numerical Modeling of Detonations; University of California, Berkley: Berkley, CA, USA, 1979.
56. White, W.B., Johnson, S.M., Danzig, G.B. (1958). Chemical equilibrium in complex mixtures. Journal Chemical Physics, N28(5), pp.751-755. https://doi.org/10.1063/1.1744264.
57. BN 80 6091 42. (1980). Górnicze Materiały Wybuchowe. Obliczanie parametrów użytkowych. In Mining Explosives. Calculation of Utilities Parameters. Polish Committee for Standardization: Warsaw, Poland.
58. Chemeo portal website: https://www.chemeo.com/cid/46-676-1/Heptachlor (accessed on 27.03.2023).
59. NIST Chemistry WebBook site: https://webbook.nist.gov/cgi/cbook.cgi?ID=C76448&Units=SI (Accessed on 27.03.2023).
60. PubChem National Library of Medicine site: https://pubchem.ncbi.nlm.nih.gov/compound/Heptachlor (Accessed on 27.03.2023).

UDC 622.2
SCOPUS CODE 2311
https://doi.org/10.36073/1512-0996-2025-2-346-359

პესტიციდების ნარჩენების განადგურების ახალი მეთოდი მაღალენერგეტიკული მასალების გამოყენებით

იოლანტა ბიეგანსკა	ენერგეტიკისა და საწვავის ფაკულტეტი, კრაკოვის AGH უნივერსიტეტი, პოლონეთი, კრაკოვი E-mail: biega@agh.edu.pl
გელა მაჩაიძე	სამთო ტექნოლოგიების დეპარტამენტი, საქართველოს ტექნიკური უნივერსიტეტი, საქართველო, 0160, თბილისი, მ. კოსტავას 75 E-mail: g.machaidze@gtu.ge
კრისტოფ ბარანსკი	სამოქალაქო ინჟინერიისა და რესურსების მენეჯმენტის ფაკულტეტი, კრაკოვის AGH უნივერსიტეტი, პოლონეთი, კრაკოვი E-mail: baranski@agh.edu.pl
დავით რობაქიძე	სამთო ტექნოლოგიების დეპარტამენტი, საქართველოს ტექნიკური უნივერსიტეტი, საქართველო, 0160, თბილისი, მ. კოსტავას 75 E-mail: davitirobaqidze2@gmail.com
ირაკლი გაჩეჩილაძე	სამთო ტექნოლოგიების დეპარტამენტი, საქართველოს ტექნიკური უნივერსიტეტი, საქართველო, 0160, თბილისი, მ. კოსტავას 75 E-mail: Irakligachechiladze847@gmail.com

რეცენზენტები:

ა. ბეჟანიშვილი, სტუ-ის სამთო-გეოლოგიური ფაკულტეტის პროფესორი

E-mail: BezhanishviliAleqsandre03@gtu.ge

ნ. ბოჭორიშვილი, გ. წულუკიძის სამთო ინსტიტუტის საბადოთა დამუშავების და სამთო გეოტექნიკის ლაბორატორიის უფროსი, აკადემიური დოქტორი

E-mail: miningnika@yahoo.com

ანოტაცია. მნიშვნელოვანია პესტიციდების განადგურების ჩვეულებრივი მეთოდების დადებითი და უარყოფითი მხარეები. მზადდება ამ ჯგუფის ქიმიური ნაერთების მახასიათებლები და განხილულია მათი გავლენა გარემოზე. მაღალენერგეტიკული მასალების გამოყენებით წარმოდგენილია პესტიციდების განადგურების კონცეპტუალური, არატრადიციული მეთოდის დაშვება; კომპიუტერული პროგრამების გამოყენება, როგორც ინსტრუმენტი ამ სფეროში კვლევის დიზაინის პროცესის მხარდასაჭერად. განხორციელდა ჰეპტაქლორის (პესტიციდის) დამატების ეფექტის თერმოდინამიკური სიმულაციები ANFO

ტიპის შერეული მაღალენერგეტიკული მასალის თერმოდინამიკურ თვისებებზე. ასევე შეფასდა ამ ქიმიური ნაერთის დამატების გარემოზე ზემოქმედება ქვენიტრიფიკაციის პროდუქტების რაოდენობრივ და ხარისხობრივ სტრუქტურაზე. გამოთვლებმა აჩვენა, რომ მაღალენერგეტიკული მასალის სტრუქტურაში 3.0% პესტიციდის შემცველობით შესაძლებელია უკეთესი ან შესადარებელი ენერგეტიკული პარამეტრების მიღება, საცნობარო ANFO-სთან დამოკიდებულებით.

საკვანძო სიტყვები: გარემოს დაცვა; თერმოდინამიკური გამოთვლები; მაღალი ენერგიის მასალები; ნარჩენები პესტიციდები; უტილიზაცია.

The date of review 28.10.2024
The date of submission 23.12.2024
Signed for publishing 16.06.2025