FERTILIZER BASED ON PYROPHYLLITE IN ACCORDANCE WITH THE REGULATION EU 2019/1009

Milan J. Adamović
Institute for Technology of Nuclear and Other Mineral Raw Materials
Belgrade, Serbia

Jasmina Kustura, Enita Kurtanović, Belma Halilhodžić, Atif Hodžić, Muhamed Harbinja
AD Harbi Ltd.
Sarajevo, B&H

Mirjana D. Stojanović
Engineering Academy of Serbia
Belgrade, Serbia

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ABSTRACT
We are currently witnessing the beginning of the global food crisis and disturbances in the fertilizer market. On the other hand, on July 16, 2022, Regulation (EU) 2019/1009 of the European Parliament and of the Council for laying down rules on the placing on the market of EU fertilizer products establishes strict rules on the safety and quality of fertilizers and repealing Regulation (EC) 2003/2003. The paper presents the modeling of process parameters of multifunctional fertilizer, as a compound inorganic macronutrient fertilizer/liming material/soil improver, based on pyrophyllite shale (pyrophyllite), deposits Parsovići, Konjic, BiH, enriched with dolomite, BiH to achieve the formulation of Product Function Categories (PFC) in terms of the content of secondary macronutrients (CaO and MgO) accordance with Regulation (EU) 2019/1009. The biological efficiency of the newly formulated fertilizer was tested through vegetation trials with beets (Beta vulgaris var. Conditiva).

1. INTRODUCTION
Today, the world is facing a potential food shortage and fertilizers for plant nutrition. Some projections suggest that fertilizer use may have to double to meet the demand for food until 2050. On the other hand, Regulation (EU) 2019/1009 of the European Parliament and of the Council for laying down rules for the placing on the market of EU fertilizer products and amending Regulation (EC) No. 1069/2009 and (EC) No. 1107/2009. The new (EU) Regulation 2019/1009 repeals Regulation (EC) No. 2003/2003, 16th July 2022, and establishes the wide quality, safety, and environmental criteria for "EU" fertilizers [1].
The new regulation provides strict rules on safety contaminants, pathogens, quality (the content of nutrients), and labeling requirements for all fertilizers to be traded freely across the EU. Producers will need to demonstrate that their products meet those requirements before affixing the CE mark. EU fertilizing products are divided into different Product Function Categories (PFC), which should each be subject to specific safety and quality requirements, adapted to their different intended uses. In terms of safety, the new ones are being introduced the limit values for contaminants in fertilizers (Cd, Pb, Ni, Cu, Zn, Hg, As) and other potentially toxic elements and pathogens) [2].

Facing the threatening deficiency of food and fertilizers and the strict requirements of Regulation (EU) 2019/1009, we need fast and comprehensive solutions at the world level. The aim of this paper is to define the parameters of obtaining a natural mineral multifunctional fertilizer based on pyrophyllite from deposits in Parsovići, Konjic, BiH, enriched with dolomite, BiH whose quality and safety are in line with the requirements of new regulations, which will contribute to reduced soil degradation, increasing biodiversity and improving soil quality as a priority for achieving sustainable agriculture. The biological efficiency of the newly formulated fertilizer was tested through vegetation trials with beets *(Beta vulgaris var. Conditiva).*

1.1. Pyrophyllite

Pyrophyllite is a type of phyllosilicate mineral, from the group of layered silicates, based on a combination of two tetrahedral (T) and one octahedral (O) plates, containing no isomorphic substitution and therefore no layer charge. The basic 2:1 structure (T-O-T), with silicon in the tetrahedral layer and aluminum in the octahedral layer, is pyrophyllite ($Al_2Si_4O_{10}(OH)_4$). The basal surfaces where the interlayer space is devoid of the hydrated counterions are hydrophobic, whereas edges resulting from the breaking of the sheets are hydrophilic in aqueous solutions, due to the occurrence of OH groups (essentially silanol). The sheets are held together only by weak van der Waals forces, which result in pyrophyllite's softness (Mohs hardness is between 1 and 1.5). Furthermore, the pyrophyllite has high density (2.7 and 2.9 gcm^{-3}), a relatively high cation exchange capacity (between 50 and 70 meq 100 g^{-1}), and a pH ranging from neutral to slightly alkaline, between 7.5-8.5. Pyrophyllite has a neutral electromagnetic charge [3,4,5,6].

The unique properties of pyrophyllite, such as its structure it its adsorption capacity, and ion exchange, have led to the use of pyrophyllite in agriculture as a soil regenerator and increased fertility. Pyrophyllite is used as a carrier of fertilizers in agriculture, where it improves the ability of the soil to retain nutrients and reduces leaching, and is an inert pesticide carrier. Improves the efficiency of mineral fertilizers, and has the ability to release tightly bound phosphates that already exist in the soil and make them available to plants. Pyrophyllite has high retention properties which make them very useful in decreasing the bioavailability of heavy metals in soils and preventing their inclusion in the food chain. Pyrophyllite naturally contains micro and macronutrients such as K, Mg, Ca, Si, Fe, Zn, Cu, P, and B essential for plant growth and development. This type of clay has a neutral pH and acts as a buffer in soil conditions and an acidity corrector. Due to the listed characteristics of pyrophyllite, the properties of the soil conditioner (regenerator) are attributed to it. It contributes to the improvement of the physical, chemical, and agrochemical properties of the soil. Improves soil structure, and permeability increases cation exchange capacity, increases soil's ability to retain nutrients and reduces rinsing and motility of heavy metals in the soil, improves the efficiency of mineral fertilizers, acts as a buffer, and regulates soil pH. All of the above justifies the growing global interest in its use to improve and maintain soil productivity in the function of sustainable agricultural production [7,8,9,10].

Also, pyrophyllite application in the amount of 25% of recommended fertilizer rate can reduce the use of mineral fertilizers in lettuce production without adverse effects on its yield and quality [11], pyrophyllite application of 2200 kg/ha in combination with mineral fertilizer NPK 15:15:5 in the amount of 0.8 t/ha confirmed a positive effect on cabbage yield [12]. Watering of onion with the suspension of water and pyrophyllite and suspension of water and enriched pyrophyllite with urea nitrogen compared to the control treatment (H_2O) contributed to the increase in biomass of onion heads by 18.31% and 24.09%, respectively ($p<0.01$) [9]. Pyrophyllite showed antibacterial properties against *Escherichia* coli, *Staphylococcus aureus*, and *Enterococcus faecalis*, and antifungal properties against fungal pathogens (*Fusarium oxysporum, Phoma glomerata,* and *Rhizoctonia solani*). This mineral can also be used for biological control of *F. oxysporum* in the soil for growing potatoes [13]. Tribomechanically activated pyrophyllite converts a part of crystalline SiO_2 into amorphous, which in soil solutions converted to silica acid available to plants that are thought to contribute to plant biotic and abiotic stress tolerance [14].

2. EXPERIMENTAL

This phase included modeling of optimal process parameters required for obtaining a multifunctional fertilizer, PiroFert (working title), based on composite pyrophyllite enriched with dolomite, in order to comply with the requirements of EU regulation 2019/1009.

The starting raw materials are pyrophyllite shale (pyrophyllite) ($Al_2Si_4O_{10}(OH)_4$) from deposit Parsovići, Konjic, BiH and dolomite, BiH ($CaMg(CO_3)_2$).

The content of secondary macronutrients (CaO and MgO) and harmful elements, pH, and neutralization value in pyrophyllite and dolomite composite are shown in Tables 1 and 2, based on a laboratory report of the Faculty of Mining, Geology and Civil Engineering, University of Tuzla.

Table 1. Content of secondary macronutrients CaO and MgO, pH, neutralization value in the composite of pyrophyllite and dolomite

Parameter	MgO %	CaO %	ΣMgO+CaO %	pH (KCl)	NV*eq CaO
Composite	6.82	14.43	21.25	8.60	24.72

neutralizing value

Table 2. Content of hamful elements in composite of pyrophyllite and dolomite

Parameter	Cd mg/kg	Pb mg/kg	Cr^{6+} mg/kg	Cu mg/kg	Zn mg/kg	Ni mg/kg	Hg mg/kg	As mg/kg
Composite	<0.1	2.46	1.12	4.03	18.99	2.55	<1	<1

Investigation of the efficiency of composite PiroFert based on pyrophyllite and dolomite on the neutralization of acidic soil and its influence on the growth and development of beets *(Beta vulgaris var. Conditiva).*

The experiment was carried out at the location of the village of Banja, Aranđelovac, Serbia. The soil on which the beetroot was grown was in the type of oil. At 0-30 cm soil depth, the pH value (H_2O) was 5.1, and it was classified as acidic soil. After the calcification and fertilization of the soil, beetroot (*Beta vulgaris var. Conditiva*) was planted, which belongs to cultures with a weak tolerance to acidic soils (low pH). The experiment was carried out in a 1 m^2 cassette. Table 3 shows the variants of fertilization in the vegetation trial.

Table 3. Variants of fertilization in the vegetation trial

Variant of fertilizer	Control	Experiment with PiroFert
NPK (15:15:15), g/m^2	30 g	30 g
Compost from vegetable waste, g/m^2	5000 g	5000 g
PiroFert g/m^2	-	500 g

At the end of the vegetation trial, the length and mass of beet plant organs (roots and leaves) were measured on 5 selected plants (on the basis of pairs). The trial lasted five months.

3. RESULTS AND DISCUSSION

3.1. Formulation of multifunctional fertilizer based on pyrophyllite

Formulation of multifunctional fertilizer, based on quality and safety parameters for Product Function Categories PFC1, PFC2, and PFC3, defined in the Regulation EU 2019/1009:

1. **Category PFC1 (C, b):** Compound solid inorganic macronutrient fertilizer with more than one secondary macronutrient (calcium (Ca), magnesium (Mg), sodium (Na), sulphur (S)) and no primary macronutrients (nitrogen (N), phosphorus (P), potassium (K)) and must contain at least 1,5 % by mass of total magnesium oxide (MgO) and 1,5 % by mass of total calcium oxide. The sum of all declared macronutrient contents shall be at least 18 % by mass.
2. **Category PFC2:** Liming material: shall be an EU fertilizing product the function of which is to correct soil acidity and shall contain oxides, hydroxides, carbonates, or silicates of the nutrients calcium (Ca) or magnesium (Mg); minimum neutralizing value: 15 (equivalent CaO), minimum grain size: at least 70 % < 1 mm,
3. **Category PFC3 (B):** Inorganic soil improver, Soil improver is an EU fertilizer product whose function is to maintain, improve or protect the physical or chemical properties, structure, or biological activity of the soil to which it is added.

According to Directive EU 2019/1009, contaminants in fertilizer must not exceed the following limit values shown in Table 4.

Table 4. Content of harmful components in fertilizers according to the Directive EU 2019/1009) [2]

Category	Cd (mg/kg)	Cr(VI) (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Ni (mg/kg)	Hg (mg/kg)	As (mg/kg)
PFC1	3	2	120	<600	<1500	100	1	40
PFC2	2	2	120	<300	<800	90	1	40
PFC3	1.5	2	120	<300	<800	100	1	40

Based on the content of secondary macronutrients CaO and MgO and the content of harmful components in the composite of pyrophyllite and dolomite, PiroFert, (Table 1 and 2), the product formulation was defined, mass fraction, based on pyrophyllite and a small part of dolomite where the sum of active components is above 18%, which is the minimum for registration (Σ CaO +MgO = 21.25%) which in terms of quality and safety meets the criteria of three categories PFC1, PFC2, and PFC3, EU directive 2019/1009, and can be registered as multifunctional fertilizers, as a compound inorganic macronutrient fertilizer/liming material/soil improver. The product must meet product-specific labeling requirements, obtaining the CE mark in order to be ready for the EU market. With dolomite content in the composite, the requirements of the regulation for regenerators (inorganic soil improver) and/or means for adjusting the pH value of the plastering material are met. It should be emphasized that pure pyrophyllite meets the requirements of registration as a conditioner (inorganic soil improver).

3.2. Results of the vegetation experiment with beetroot

The measurement of the length of the beet parts and the diameter of the root as well as the mass of the plant parts, at the end of the experiment (5 months after sowing), was carried out on 5 selected plants (on the principle of pairs) of each treatment. The results are shown in Table 5 and the appearance of the beets at the end of the experiment is shown in Figure 1.

Table 5. Average length and diameter of beet roots at the end of the experiment, cm

Parameters	Control	Experiment PiroFert	Index Control 100 %
Leaf	32.8	36.6	111.58
Root	14.2	18.2	128.17
Total	47.0	54.8	116.59
Root diameter, cm	4.0	5.3	132.50

The lengths of the main parts of the plant, leaves, and roots (Table 5) including the diameter of the roots indicate their more intensive development compared to the development of plants in the control treatment. Leaf length was greater by 11.58%, root by 28.17%, and root diameter by 32.50%.

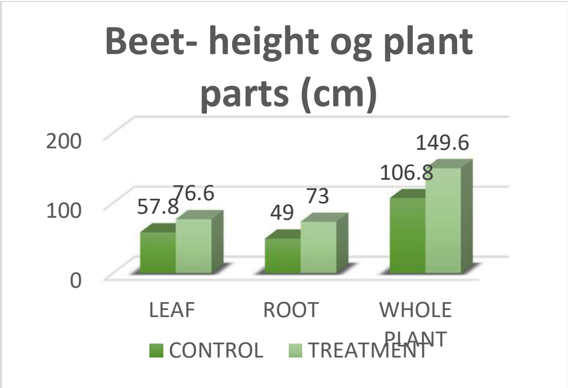
Figure 1. The appearance of beets at the end of the experiment (whole plant, root, and section)

The average mass of the basic parts of the plant, leaves, and roots (Table 6), similar to the length of the same parts of the beet, was higher in the experimental treatment with PiroFert. The average mass of the leaf in this treatment was greater than the control treatment by 32.55%, the root by 48.97%, and the total mass of the plant by 40.07%.

Table 6. The average weight of the beet parts at the end of the experiment, g

Parameters	Control	Experiment PiroFert	Index Contol 100 %
Leaf	57.8	76.6	132.52
Root	49.0	73.0	148.97
Total	106.8	149.6	140.07

The results of the height and mass of beet plant organs are illustrated in Figure 2.



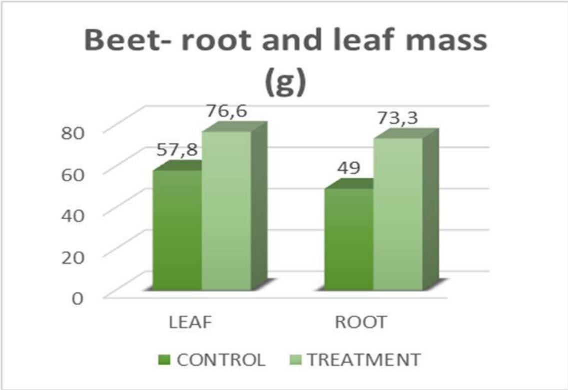


Figure 2. Experiment with beet, (composite – pyrophyllite/dolomite) and effects on height and mass of roots and leaves of the plant

Five months after the calcification and extraction of the beets, the pH value of the soil in the trial treatment (PiroFert) increased from 5.9 to 6.4, which indicates that the calcification with pyrophyllite and dolomite-based fertilizer, already in the first year, gave good and desired results.
As this is the first year of testing the PiroFert composite, it is necessary to repeat the test in order to determine the biological efficiency of the fertilizer.

4. CONCLUSION

The new Fertilizer Products Regulation (EU) 2019/1009 will apply from 16th July 2022 and establishes EU-wide quality, safety, and environmental criteria for fertilizers. In accordance with that, the paper promotes multifunctional fertilizer, as a compound inorganic macronutrient fertilizer/liming material/soil improver, based on pyrophyllite, deposits Parsovići, Konjic, BiH, enriched with dolomite to achieve the defined formulation of Product Function Categories (PFC), according to the new regulations. The new EU soil strategy for 2030 sets out a framework and concrete measures to protect and restore soils and ensure that they are used sustainably with the aim of reduced degradation and increased soil fertility, emphasizing the advantage of natural fertilizers over industrial ones. The aim of this paper is to promote the use of pyrophyllite as one of the most promising natural aluminosilicate materials, environmentally friendly and economically viable materials whose application meets the stringent requirements of sustainable agricultural production, the requirements of the new EU soil strategy for 2030 and new Fertilizer Products Regulation (EU) 2019/1009.
The use of pyrophyllite-based fertilizers with the addition of dolomite (PiroFert product AD Harbi Ltd. Sarajevo, Bosnia and Herzegovina) to neutralize acidic soil in beet growing conditions (*Beta vulgaris var. Conditiva*) had a positive effect on the correction-increase of soil pH as well as the formation of plant biomass (leaf and root length as well as root diameter). Analogously, in the treatment with the addition of PiroFert fertilizer to the soil, there was an increase in root yield, which was higher by 48.97% compared to the control treatment.
The same research should be continued in the second year with the aim of a more comprehensive overview of the effects of soil neutralization and its stabilization after calcification.

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