PYROPHYLLITE AS AN ECOLOGICAL MINERAL OF THE FUTURE

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ABSTRACT
Pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) is a layered phyllosilicate mineral with a basic 2:1 crystal structure, consisting of an aluminum octahedral layer placed between two silicon tetrahedral layers (T-O-T), connected by weak Van der Waals forces, which results in easy structural disruption. Natural pyrophyllite has an electroneutral surface, which causes a hydrophobic character. Due to its unique properties, such as low thermal and electrical conductivity, high refractive behavior, low coefficient of expansion, rheological properties, low bulk density, low deformation under high temperature, and chemical inertness, pyrophyllite is widely used in various industrial branches: refractory, ceramic, construction, pharmaceutical and cosmetic industry, production of pesticides, fertilizers, paper, paints, plastics, tires. Thanks to its unique properties, pyrophyllite shale from the Parasovići deposit, Konjic, Bosnia and Herzegovina, has shown the possibility of being used in many areas of life. This paper presents the results of research so far, which confirmed the wide application of natural, modified, and enriched pyrophyllite in various industrial branches, agriculture, and environmental protection.

1. INTRODUCTION

Pyrophyllite belongs to the group of aluminosilicate minerals with the chemical formula $Al_2Si_4O_{10}(OH)_2$, and it is found in nature in the form of shale. It got its name from the Greek words *pir*-fire and *phylon*-leaf because it spreads like a fan when heated. It is a part of the isomorphic order of aluminosilicates that contain bound water. It is characterized by a three-layer crystal lattice, which has a tetrahedral structure in the outer layer, and an octahedral structure in the inner layer (Figure 1). The crystals are plate-like, soft, and greasy to the touch. It is electroneutral and not reactive in its natural form. Pyrophyllite is not soluble in water and does not swell. It is thermally stable. Depending on the admixture, the color of pyrophyllite varies from white, and gray to purple.

In previous research, the presence of 34 minerals and over 60 chemical elements have been confirmed in the pyrophyllite schist (hereinafter referred to as pyrophyllite) from the Parsovići deposit, Konjic, Bosnia and Herzegovina (Figure 2) [2-6].

Thanks to its unique properties, pyrophyllite has shown the possibility of use in many areas of life. By crushing pyrophyllite and mechanochemical activation, the structure changes, the bonds of aluminosilicate and OH groups are broken, the specific surface area and porosity of the particles increase, the size of the particles decreases, the solubility and cation exchange capacity increase, all of which contribute to its greater reactivity and surface charging. Due to its electroneutrality in its natural form, pyrophyllite has a lower CEC (cation exchange capacity) compared to other layered minerals, and its reactivity is

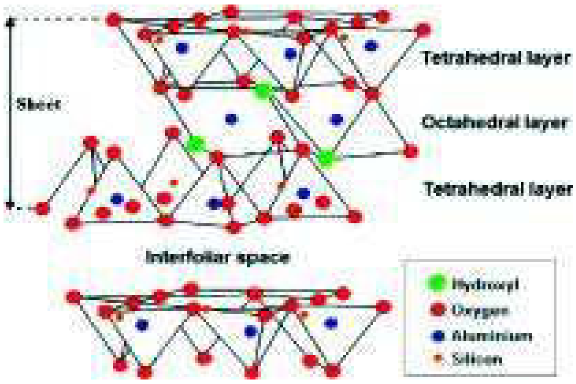

Figure 1. Pyrophyllite structure [1]

Figure 2. Pyrophyllite shale mine, Parsovići

increased by physicochemical, chemical, mechanochemical, and thermochemical treatment. By modifying pyrophyllite with organic, inorganic, polar, and non-polar surfactants, the reactivity and efficiency of pyrophyllite are improved. By modifying pyrophyllite, products with target characteristics of wide industrial-agro-ecological application are obtained. The chemical and mineralogical composition and physical properties of pyrophyllite are tabulated in Table 1, Table 2, and Table 3 [7].

Table 1. Average chemical composition of pyrophyllite

Component	SiO_2	Al_2O_3	Fe_2O_3	FeO	TiO_2	CaO	MgO	CO_2	Na_2O	K_2O	H_20^-	H_20^+	Other elements
Composition [wt. %]	61	23.1	1.1	0.25	0.12	1.85	1.94	4.30	0.61	1.44	0.61	4.66	<0.1

Table 2. Average physical characteristics of pyrophyllite

Characteristic	Value
pH	8.0 - 9.0
Hardness (by Mohs)	1.0 - 1.5
Specific gravity [g/cm^3]	2.6 - 2.8
Volumetric weight without shaking (33 μm) [g/cm^3]	0.38 - 0.42
Volumetric weight with shaking (33 μm) [g/cm^3]	0.525 - 0.55
Volumetric weight without shaking (63 μm) [g/cm^3]	0.508 - 0.53
Volumetric weight with shaking (63 μm) [g/cm^3]	0.75 – 0.82

Table 3. Average mineralogical composition of pyrophyllite

Mineral	Mineralogical composition, [wt.%]
Pyrophyllite	44 - 52 %
Quartz	12 - 18 %
Carbonates	10 - 12 %
Kaolinite	18 - 22 %
Serecite	6 - 12 %
Other minerals in smaller percentages	

2. APPLICATION OF PYROPHYLLITE IN INDUSTRY AND AGRICULTURE

AD Harbi LLC Sarajevo through its own research and research with a team of expert associates and scientific advisors from eminent scientific institutions from the country and the region, has implemented a large number of projects, studies, and scientific works, the results of which result in a wide range of possibilities for using pyrophyllite in various industrial branches, agriculture, and environmental protection. AD Harbi LLC Sarajevo continues to research the possibilities of using pyrophyllite in new, more sophisticated, and profitable industrial branches, and to develop its own products for applied applications, as well as solutions that are environmentally efficient as possible, and innovative and fully functional in the application. Pyrophyllite is used in the following industries: refractory, ceramic, construction, chemical industry, environmental protection, agriculture, and in the cosmetic, pharmaceutical, and medical industries. The subject and goal of this paper are to present the results of previous research, knowledge, and experience in the development of new products based on the mineral pyrophyllite from the Parsovići, Konjic, Bosnia and Herzegovina, deposits in various industrial areas.

2.1 Refractory industry

Due to the property that heat treatment transforms pyrophyllite into mullite, resistant to high temperatures up to 1810 °C, with high electrical resistance, high compressive strength, tensile strength, and impact strength, pyrophyllite is widely used in the refractory industry. By researching the procedures for preparing ceramic fillers based on pyrophyllite for obtaining refractory materials and primarily refractory coatings, it was shown that pyrophyllite occupies an important place either as a final product or as a raw material for various refractory products. As a result of this research, the optimal compositions of Lost foam refractory coatings with micronized (mechanically activated) filler based on pyrophyllite (average particle size between 14 and 16 μm) were determined. Procedures for the preparation of coating suspensions were defined, which achieved predetermined properties of the coating in terms of fire resistance, desired gas permeability, easy application and adhesion to the model surfaces, easy adjustment of the thickness of the coating layers on the surface of the sand molds and cores, without the appearance of bubbles, cracking and rubbing of the dried coating layers. Coating suspensions, the density of 2000 kg/m^3, showed high sedimentation stability (below 4.5 % of precipitated substances in the first 300 min). The application of coatings based on water-based pyrophyllite filler, thinner layers ($0.5x10^{-3}m$), and polystyrene models of lower density (19 kg/m^3) had a positive effect on the surface quality, structural and mechanical properties of aluminum alloy castings obtained by the new casting method with polymer models [8].

2.2 Ceramic industry

Clay minerals are the most important components in traditional ceramic products. Ceramic products can be prepared using different types of clay with different proportions in the mixture, as well as different temperatures. Since pyrophyllite becomes mullite at high firing temperatures, this gives it the possibility of being used as a component in ceramic products [9]. By examining the microstructural and morphological changes of pyrophyllite during thermal treatment at 1050 °C and a pressure of 50 MPa, results were obtained that indicate that pyrophyllite can be used to obtain semipermeable membranes with a homogeneous pore arrangement, for the purpose of purifying pollutants in aqueous solutions [10,11].

In one of the works, the resistance under the effect of cavitation of samples of sintered pyrophyllite was examined. To assess the cavitation resistance, the change in the mass of the sample as a function of the cavitation time was monitored. The ultrasonic vibration method with a stationary sample was applied. Based on the value of the cavitation speed and the analysis of the morphology of the surface damage, the cavitation resistance of the tested samples based on pyrophyllite was determined. The obtained results indicate that samples of sintered pyrophyllite have satisfactory resistance to the effect of cavitation and can be used under conditions of lower cavitation loads [12].

2.3 Construction industry

Instrumental analyzes proved that activated pyrophyllite, which was applied as a mineral additive/cement replacement in cement binders, acts as a pozzolan. Cement-pyrophyllite binders showed a very similar hydration path to Portland cement with a slight acceleration in the early stages of hydration, reduced the hydration energy of cement, and increased the amount of cement mineral alite in the later stages of hydration. The micronized crystalline foil characteristic of pyrophyllite formed a micro-reinforcement inside the voids in the cement microstructure, which could improve the mechanical properties of the cementitious material [13].

The use of pyrophyllite as an ecological material in construction, more precisely as a material for making facades in areas where coal is used as an energy source, has proven to be effective. The research results confirm the possibility of using pyrophyllite with "bare" titanium dioxide as a suitable material for making facades with an air purification effect. Pyrophyllite affects the photocatalytic decomposition of coal combustion products (CO_X, NO_X, SO_X), which contributes to the improvement of air quality in polluted areas, and in this sense is an ecologically very interesting and valuable material [14].

2.4 Electrical industry

Pyrophyllite, as a material with good surface properties, can be used as an electrochemically active component, using this material as a carbon paste electrode. The obtained results open a new field for further research concerning pyrophyllite as a sensor for the detection of pollutants in water. An electroanalytical method was developed for the detection and determination of carbendazim pesticides [15,16].

2.5 Chemical industry

$LiAlH_4$ is a material suitable for hydrogen storage primarily due to the high gravimetric capacity of hydrogen. However, the relatively poor kinetics of the desorption or hydrogen release process limits its commercial use. An improvement in the reaction kinetics and a change in the reaction mechanism of hydrogen desorption from $LiAlH_4$ can occur during the synthesis of composites of this hydride with different catalytically active materials. Within the concept of green chemistry, it is desirable to use as many natural raw materials as possible, including pyrophyllite, and for this reason, the effect of the addition of pyrophyllite, which is known as a good adsorption material, on the desorption and structural characteristics of $LiAlH_4$ as a hydrogen storage material was examined [17].

2.6 Environmental protection

Pyrophyllite has shown great efficiency in the adsorption of heavy metals from contaminated wastewater as well as wastewater from electroplating plants. According to current regulations, the allowed pH value in wastewater from industrial plants before its discharge should be 7, which dictates the need for its neutralization before discharge into waterways. Optimizing the process of adsorption of heavy metals from the wastewater of the electroplating plant, it was concluded that the adsorption of metals is most favorable at a mass of pyrophyllite of 10 g, a fraction size of 0.10 mm, at pH 7 and a contact time of 2 hours [18,19].

The results of the research into the efficiency of the raw and modified pyrophyllite (modified with boric acid) in the adsorption of heavy metals speak of the justification of further research, but also of the practical application of pyrophyllite in the purification of industrial wastewater. Analysis of waste and treated water also found that pyrophyllite treatment reduces: organic carbon; ammonia; total inorganic nitrogen; total phosphorus; total alkalinity. The results showed the additional effectiveness of pyrophyllite on the

reduction of organic compounds, indicating that pyrophyllite can be an effective agent for the treatment of wastewater in mines, the metal industry, and landfill leachate [20].
Chemical stabilization of soil contaminated with heavy metals using natural aluminosilicate materials (pyrophyllite and zeolite) has generally been observed as a very effective measure from the point of view of reducing the accessibility of heavy metals in the soil, and therefore also from the point of view of reducing the possibility of their entering the plant, i.e. into the food chain. The results of this research support the thesis that zeolite, and especially pyrophyllite, have the ability to firmly bind heavy metals to their structure, which, on the one hand, reduces the possibility of their uptake by plants, and on the other hand, contributes to environmental protection, because by immobilizing heavy metals it reduces the possibility of their leaching from the surface layers of the soil into underground water courses. The use of aluminosilicate materials is not demanding from the aspect of performance and cost, so it should be taken very seriously into consideration when making a decision on the method of remediation of land contaminated with heavy metals [21,22].

2.7 Agriculture

The production of health-safe food has become a priority task for food manufacturers, thanks to the increase in consumer standards. Because of this, they operate in a split between two conflicting requirements, to produce as much food as possible while its quality is as good as possible. At the same time, the application of artificial fertilizers in agricultural production resulted in the gradual degradation of the soil as well as numerous other processes such as depletion, leaching, and soil pollution with dangerous substances from the industry. For this reason, in recent years there has been an increasing interest in the use of natural aluminosilicates in order to maintain and improve soil productivity. One such solution is pyrophyllite. Pyrophyllite is one of the best detoxifying clays, partly because it has a balanced mineral composition, and partly because it can be reduced to extremely small particle size. The smaller the particle size, the greater the specific active surface area for removing toxins. It is rich in electrolytes and exchanges a lot of free ions in the cation exchange, which makes it an excellent soil conditioner [19]. Pyrophyllite has the ability to quickly neutralize acidic solutions in dynamic conditions, as well as the ability to buffer them [23].
The two-year research carried out on cabbage of the Bravo variety confirmed the effectiveness of pyrophyllite as a bio-stabilizer and soil conditioner, its effect on increasing the pH value of the soil, on the absorption and firm cross-linking of heavy metals, and its stimulating effect on the growth and development of plants, increasing the yield and components of the nutritional value of the head Cabbage of the Bravo variety [24]. Based on a two-year study on the effect of pyrophyllite on the vitamin C content found in the Bravo F1 cabbage hybrid (*Brassica oleraceae var. Capitata*), it can be concluded that pyrophyllite has a positive effect on the vitamin C content [25].
It was established that the natural mineral pyrophyllite can be used in the production of pepper and cabbage seedlings in a protected area as an addition to the commercial substrate (pyrophyllite was used in a concentration of 20%). To continue further research, it would be best to use the following substrate mixtures: soil + earthworm + pyrophyllite, soil + earthworm + manure + peat + pyrophyllite, peat + manure + pyrophyllite, peat + manure [26].
The positive effect of pyrophyllite in the open space on the following cultivated crops was determined: vegetable crops - pepper (*Capsicum annuum*), tomato (*Solanum lycopersicum*), fruit crops - pomegranate (*Punica granatum)*, aronia (*Aronia melanocarpa)*, fig (*Ficus carica)* and medicinal cultures - lavender (*Lavandula angustifolija*), immortelle (*Helichrysum italicum*) and lemon balm plant (*Mellisa officinalis*). The changes recorded in the cultures are

vegetative - increase in plant growth and green mass (because of the silicon content in it, it affects the better habitus of the plant), strengthening of the plant stem, and generative - increase in yield, earlier ripening of fruits, better quality fruits. The results of the analyzes for the fruits, which were carried out in the laboratory of the Federal Institute of Agriculture, showed that pyrophyllite influenced the increase of dry matter and ash in the fruit, and the content of micro and macro elements. The end result was a fruit without heavy metals and pesticide residues and with an increase in nutritional value [27].

After conducting a research experiment, multiple effects of pyrophyllite on soil, yield, and quality of cabbage (fruit size, organoleptic properties, and appearance) were observed [28]. Pyrophyllite showed a positive effect on selected physiological and biochemical parameters, such as a reduction of oxidative stress in selected field crops (two varieties of wheat, Brkulja, and Spelt) and vegetable crops (salads and endives), an increase in protein concentration and, to a certain extent, an increase in chlorophyll concentration [29,30].

The use of pyrophyllite reduces the use of mineral fertilizers without negative effects on yield and quality, which ultimately enables significant material savings because it is a cheaper product than mineral fertilizers. At the same time, its application also makes an immeasurable contribution to environmental protection, because the same agrotechnical measure reduces the possibility of leaching of nutrients from the zone of the root system of cultivated culture (lettuce) into the lower layers of soil and groundwater. The fertilizer variant, in which the ratio of fertilizer and pyrophyllite was 75%:25%, proved to be the most effective combination in order to achieve the highest yield. All fertilization variants in which pyrophyllite was used showed a positive effect on increasing the plant's antioxidant capacity, especially the variant in which pyrophyllite with finer granulation was used in relation to the 25%:75% with fertilizer. The above data point to the conclusion that the use of pyrophyllite as a substitute for part of the fertilizer can significantly contribute to the increase of the antioxidant capacity of the plant, and therefore to its greater health value. Since pyrophyllite also affects the reduction of uptake and accumulation of heavy metals, the conclusion follows that its application can influence the creation of an agricultural product of greater health value. Namely, the high content of heavy metals in the edible parts of the plant is undesirable for the reason that it can negatively affect the physiological processes in the human body, on his health, and even have a carcinogenic effect [31].

Natural pyrophyllite enriched with the nitrogen of non-protein origin (NPN) from urea has shown effective application in agriculture, primarily in crop production (farming and vegetable growing, fruit growing, and viticulture) and feeding ruminants. Namely, it is concluded that the pyrophyllite-urea composite (with minor corrections by the addition of sulfur as a building block in the synthesis of essential amino acids, methionine, and cystine) can be used in the diet of ruminants as a source of nitrogen that bacteria in the rumen use for the synthesis of their own high-quality protein of microbial origin, which it is then digested in the digestive tract and used as a source of nitrogen and amino acids for the maintenance of the body and the production of meat and milk. Also, this composite in which pyrophyllite is a carrier of urea, i.e. NPN, can, with certain supplements and corrections with other minerals (P, K, etc.), be used in a process of feeding plants [32].

The use of a multifunctional fertilizer (as a complex solid inorganic fertilizer/liming material/soil improver), based on pyrophyllite and dolomite in the conditions of growing beetroot (*Beta vulgaris var. Conditiva*) had a positive effect on the formation of plant biomass (leaf length, root length, and root diameter) and an increase in root yield, which was higher by 48.97 % compared to the control treatment (CT). Fertilizing the soil with multifunctional fertilizer also had a positive effect on the chemical properties and nutritional value of beets expressed on 100 % dry matter. The pH value of the soil where beets were grown (ET) increased from 5.06 (H_2O) and 4.04 (KCl) before sowing, to 6.40 (H_2O) and 5.73 (KCl), respectively, after harvesting the beets [33].

As part of research in agriculture, the possibility of obtaining pellets based on pyrophyllite and organic fertilizer obtained during poultry farming was investigated. Among the chemical characteristics, the pH factor was examined as an interesting indicator for the use of the product thus obtained in agriculture, especially in acidic soils. This indicator, although it is a small sample, points to the attitude that increasing the fertilizer content increases the basicity of the obtained pellets [34].

Experimental testing confirmed that pyrophyllite can be used as an effective adsorbent for the adsorption of nitrates and phosphates from artificial fertilizers, and thus can be used for the process of fertilizing plants [35,36].

Examining the effect of pyrophyllite on the quality of silage of corn plants, seven weeks after ensiling, the results showed that the presence of *Salmonella spp*. has not been proven, while the presence of *Staphylococcus aureus, Clostridium perfringens, and Clostridium spp.* was <10 cfu/g, below detection limits [37].

Pyrophyllite also showed efficiency in the adsorption of aflatoxin B1, zearalenone, and ochratoxin. In in vitro test conditions on a liquid chromatography (HPLC) instrument, it was determined that the adsorption index was better on the finer granulation sample. The researchers assume that the better adsorption index on finer-grained pyrophyllite could be the result of a larger contact surface, i.e. a higher content of pyrophyllite in the sample, which was 75 to 80 % for the finer-grained sample and 50 % for the larger-grained pyrophyllite sample. These results indicate that the finer granulation of pyrophyllite had aflatoxin B1 adsorption efficiency similar to or at the level of adsorption of this mycotoxin by other aluminosilicate minerals such as zeolite, bentonite, and similar adsorbents [38].

It was found that pyrophyllite can inhibit the development of gram-negative bacteria *Escherichia coli* (67.20 - 84.80 %) and gram-positive bacteria *Enterococcus faecalis* (74.42 - 81.33 %). Better results were achieved by using finer granulation of pyrophyllite. In contrast, no inhibition of the development of *Staphylococcus aureus* was found, probably due to the pronounced defense mechanism of this bacteria [39,40].

In vitro, testing of the effect of fractions of micro gelled and mechanically micronized pyrophyllite of different granulations added in different concentrations to the PDA nutrient medium on the growth of the fungal phytopathogens *Fusarium oxysporum, Phoma glomerata,* and *Rhizoctonia solani* showed the best result in limiting the growth of *P. glomerate* (micro gelled granulation < 100 μm and mechanically modified granulation < 45 μm) [40,41].

It was observed that pyrophyllite, and especially the mechanically modified fraction 0 - 2 mm, significantly reduces the wilting symptoms of plants and thus reduces the loss of potato yield in soil contaminated with *F. oxysporum.* The obtained results indicated the possibility of using pyrophyllite in the biological control of soil contaminated with *F. oxysporum*, which would greatly contribute to the production [40,42,43].

Since plants produce electrical signals (weak negative electric fields), electropositive dusting agent during treatment not only adhere better to plant parts but also their distribution is much more uniform than is the case with electronegative dusting agents Electropositive dusting agents can cover 2 - 3 times larger plant area than the same amount of electronegative dusting agent. In addition, these dusting agent cover well both the face and the back of the leaf and are also distributed around the bud, flowers, and lower parts of the plants. Talc, kaolin, bentonite, and diatomite have a negative electrostatic potential, and pyrophyllite, carbonates, and gypsum have a positive electrostatic potential [44].

Based on the physical properties of pyrophyllite, especially its granulometric content, particle shape, and its ability to disperse, and then electrostatic nature, as well as the results of chemical compatibility, pyrophyllite can be used without unreservedly for dusting agent formulation, for dusting tested fungicides and insecticides [45].
Pyrophyllite proved to be a good adsorbent for glyphosate (organophosphorus herbicide), so in the future, it could be used as a filter in many experiments where it is necessary to examine the possibility and efficiency of adsorption, with fact that when examining the effect of pH on the efficiency of glyphosate adsorption, the basic medium proved to be more effective. The pH value of 13.47 proved to be the most effective in terms of glyphosate adsorption [46,47].

2.8 Pharmaceutical industry

The unique physical and chemical properties of pyrophyllite make this mineral special and suitable for use in many industries and as a substitute for talc [48]. Recent research into nanocomposites as potential carriers in pharmacy is focused on the use of inorganic substances with a layered structure that are part of bioactive molecules/medicines. One such promising inorganic material with a layered structure is clay, which is also a common component in pharmaceutical products, and as a secondary or active substance. Clay is not only an "inert ingredient", it can also be used to reduce or increase dissolution rate, delay and/or target drug release, stop side effects, camouflage taste or increase stability. On the basis of testing the stability of pyrophyllite and bioactive molecule/drug using methods of thermal analysis (differential thermal analysis/thermogravimetric analysis-TGA/DTA) and Fourier transform infrared spectroscopy (FTIR), it was concluded that pyrophyllite retained good thermal stability in the powder mixture. The thermal stability and inertness of pyrophyllite are a very good basis for its potential use as a pharmaceutical carrier. Based on the value of the pre-exponential factor, it was assumed that both pyrophyllite and talc do not interact with other ingredients in the mixture [49].
Pyrophyllite clay proved to be very thermally stable. The process of thermal transformation includes the reaction of evaporation, dehydroxylation, and the formation of a new phase, mullite. Antimicrobial tests have shown that both PYRO and PYRO/Ag have antibacterial activity. Pyrophyllite has great potential for development in pharmaceutical and medical applications as a filler and can serve as an alternative to talc, as it does not contain associated toxic minerals such as asbestos [9,50].

3. CONCLUSION

Aluminosilicate natural mineral raw material pyrophyllite from the Parsovići deposit, Konjic, Bosnia and Herzegovina, thanks to its physical and chemical characteristics, in natural or modified form, is widely used in industry, through a diverse range of the above-mentioned branches. From this comes the conclusion that it is worth continuing the research in new, more sophisticated, and profitable industrial branches, in order to eventually reach the product of applied application. The results of the research should serve as a critical review of the path traveled and as a basis for defining a new direction of research and development of new products based on the mineral pyrophyllite. From the wide range of possibilities of using pyrophyllite in different industrial branches, a whole series of products will result, which will contribute to meeting the needs of the market with products of this type based on domestic raw materials, which will reduce the need for imports and increase exports.

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