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Research Article

INFLUENCE OF THERMAL WATER TYPES ON THE PROPERTIES OF PYROPHILITE PELOIDS

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ABSTRACT

Pelotherapy is the application of thermal muds (peloids) for therapeutic purposes. Artificial peloids were prepared using pyrophilite shale maturated in three different types of thermal water in terms of their pH values. The samples after 30 and 60 days of maturation were examined by X-ray diffraction. No significant variations in the mineralogical composition and diffractograms of pyrophillite peloids were detected after maturation. Only the influence of the maturation process of pyrophillite on the pH value of mineral water with high and low pH value is noticed.

Keywords: Pyrophilite, Peloids, Mineral water.

1. INTRODUCTION

Pelotherapy is the application of thermal muds (peloids) for recovering muscle-bones-skin pathologies [1]. These therapeutic agents have long been used in spas and beauty therapy. In pelotherapy, the application methods of clay mineral-water pastes and dispersions can be used as face masks, cataplasms (also called mud compresses or mud compresses) or mud baths, depending on the area of the body being treated [2-3]. The temperature of application (warm or cold) depends on the therapeutic goals. The maturation process of peloids results in enhancement of the therapeutic properties of the final peloid applied to patients.

Peloids or thermal muds are natural products made up of a mixture of mineral water (sea water and salt-like water included), with organic or inorganic matter generated from biological or geological processes or both which are used for therapeutic purposes in the forms of packaging or baths at temperatures 45-50°C [4]. Alternatively, peloids could be defined as maturated mud or muddy suspension with healing and/or cosmetic properties composed of a complex mixture of fine-grained materials (mineral and/or organic), with mineral water, sea water, salt-like water and commonly organics compounds from biological metabolic activity [3]. The therapeutic effect of peloids is linked with the origin of the peloid, the chemical nature and temperature of the mineral water and the maturation conditions.

Some properties of clays used to prepare peloids that are recommended for most of their use in spas and aesthetic medicine: (i) softness and small particle size, since the application of the clay paste, particularly as face mask, can be unpleasant; (ii) appropriate rheological properties for the formation of a viscous and consistent paste, good plastic properties for easy application and adherence to the skin during treatment; (iii) similarity in pH to that of the skin to avoid irritation or other dermatological problems; (iv) high adsorption capacity allowing clays to eliminate excess grease and toxins from skin, and hence to be effective against dermatological diseases such as boils, acne, ulcers, abscess, and seborrhea; (v) high cationic exchange capacity (CEC), enabling an exchange of nutrients (K^+, Na^+, Ca^{2+}, Mg^{2+}or others) to take place while the clay mineral is in contact with the skin; and (vi) high heat-retention capacity (retentivity), as heat is also a therapeutic agent: clay pastes are mostly applied hot to

treat chronic rheumatic inflammations, sport traumatisms, and dermatological problems.

Peloids should have appropriate properties: hydric degree, consistency, adhesiveness, heat capacity, cooling rate, exchange capacity, ease of handling and pleasant sensation when applied to the skin [5, 6].

Some spas use naturally matured peloids which maturated at the place of their occurrence, while others collect peloids that have the maturated by artificial processes and modifications. During maturation, organic substances with macro- and microelements present in the water are absorbed into the peloids and can be later released during application to the body. The maturation process often helps to improve certain physical properties of the mud such as the heat-retention capacity, rheology and adherence.

The maturation process to create peloid is a complex process that includes physical, chemical, physico-chemical and biological phenomena. The dynamics of the process depends on the nature and initial composition of the water and clay used, on the one hand and on the characteristics of the clay-water mixture after maturation (pH, Eh, biogenic elements, organic matter) on the other hand. Other factors involved in the maturation process are temperature, maturation time and the procedure (continuous mixing, periodically mixing or no mixing) [3]. Furthermore, many of these parameters change during the maturation period (cycling of temperature, light, hydrological regime, mixing time, growth of microorganisms). All these variables decisively affect the properties of the final peloid. Maturation time is a key parameter, along with three main factors controlling the properties of clay-based peloids: raw clay composition, water composition and mixing protocols [1, 6]. The time and method of maturation process for individual clays is determined experimentally.

One of the types of peloids known so far are phyllo-peloids in which phyllosilicates are the main ingredient [7]. Pyrophyllite as minerals is classified as phyllosilicates. Pyrophyllite and other aluminosilicates have wide applications in medicine due to their antiseptic, antitoxic and antibacterial properties [8]. Physical-chemical properties of pyrophylliteshale from the "Parsovići" deposit fulfil many of the requirements for use in pelotherapy [9, 10].

The aim of this study was to analyze the main mineralogical related changes during the maturation process of pyrophyllite in four different mineral waters from Bosnia and Herzegovina and to determine the physicochemical properties of maturated peloids. Artificial peloids were prepared using pyrophilite maturated in three different types of thermal water in terms of their chemical compositions and pH values. To our knowledge, this is the first time that the pyrophilite and mineral water from Bosnia and Herzegovina spas was studied for peloid preparation.

2. MATERIAL AND METHODS

Pyrophyllite shale from the "Parsovici" Konjic, Bosnia and Herzegovina deposit (granulation up to 50 μm) was used as mineral for preparation of peloids. The pyrophyllite samples were mechanically treated before research to up to 0-100 μm particle size.

For maturation process, three types of thermal waters from Bosnia and Herzegovina were sampled from spa center Kulasi-Prnjavor (pH 11.8), spa center Guber-Srebrenica (pH 4.2) and spa center Slavinovici-Tuzla (pH 9.9).

Samples with a concentration of 500 g/l were prepared. The samples were stored in cubic plastic containers with a volume of 3 l semi-covered to avoid contamination by atmospheric dust at around 20°C. All samples were periodically stirred and homogenized during their maturation time. To control the physico-chemical changes during the maturation process, three control points were chosen (0 days, 30 days and 60 days). After the corresponding maturation period, 50 g of each sample was dryed and solid was analysed.

For the mineralogical study, the samples were examined by X-ray diffraction analysis with a Bruker D4 Endeavor equipment and Diffract plus software. Powdered whole samples were X-rayed from 2° to 65° 2θ using CuKα radiation with a scanning speed of 1° 2θ/min. The pH was measured by means of a Mettler Toledo FE 20.

3. RESULTS AND DISCUSSION

The pyrophyllite, $Al_2Si_4O_{10}(OH)_2$, is an aluminosilicate mineral, which posses 2:1 layer silicate structures that is composed of individual Al-O octahedral layer sandwiched between two SiO_4 tetrahedral layer [11].

Fig.1 shows diffractograms of pyrophyllite samples before and after maturation. It can be seen that no new phases were detected after maturation process and the intensities of the existing phases were only slightly shifted.

Chemical analysis revealed a predominant composition of Si and Al, with Ca, Fe and K in percentages lower than 5%. Also, Mg, Na, S and Ti are presented in percentages

lower than 1%. The mineralogical composition of the pyrophilite sample before and after 30 and 60 days of maturation process is shown in Table 1.

No significant changes in chemical composition of pyrophilite after 90 days of maturation process in Kulasi and Guberthermal waters were observed. Regarding Slavinovici thermal water, a decrease of potassium ion content and an increase of sodium ion content was registered.

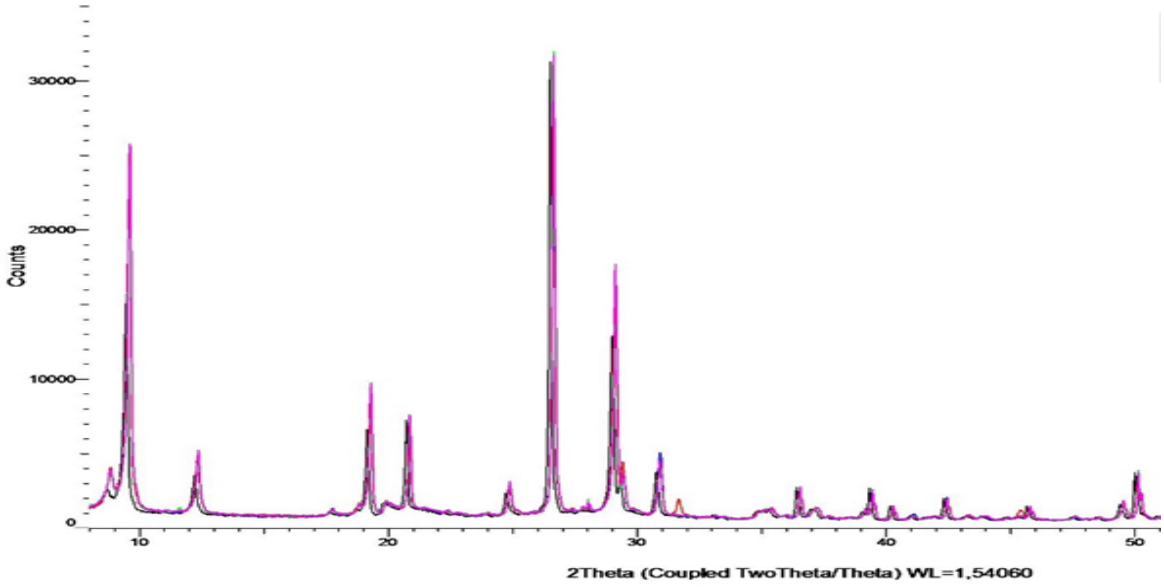

Fig. 1: XRD of pyrophyllite samples before and after 90 days of maturation

Table 1: The mineralogical composition of the pyrophilite sample before maturation process, after 30 and 60 days maturation in tested thermal waters

XRF	Raw pyrophillite (%)	Peloid after 30 days (%)			Peloid after 60 days (%)		
		Kulasi	Guber	Slavinovici	Kulasi	Guber	Slavinovici
SiO_2	63.08	63.70	64.33	60.91	64.56	62.06	60.50
Al_2O_3	27.42	26.28	25.53	26.82	26.93	29.04	27.41
CaO	4.44	5.09	5.36	5.88	4.35	4.42	4.23
Fe_2O_3	1.54	1.62	1.59	1.67	1.45	1.60	1.45
K_2O	1.24	1.04	1.12	1.20	1.26	1.31	0.80
MgO	0.79	0.90	0.94	1.02	0.74	0.84	0.80
Na_2O	0.63	0.65	0.60	1.53	0.66	0.65	2.96
SO_3	0.27	0.15	0	0.17	0.16	0.25	0.20
TiO_2	0.21	0.24	0.21	0.23	0.22	0.21	0.19
ZnO	0.05	0.04	0.03	0.06	0.05	0.06	0.07
SrO	0.04	0.03	0.03	0.03	0.03	0.03	0.04
MnO	0.03	0.03	0.03	0.02	0.02	0.02	0.03
ZrO_2	0.03	0.02	0.01	0	0.02	0.03	0.03

Table 2: pH values of thermal water before and after maturation process

sample	pH of thermal water	pH after 60 days of maturation
Kulasi	11.75	7.81
Guber	4.23	7.89
Slavinovici	9.85	9.75

The maturation process of pyrophilite was performed in three thermal waters that differ in pH value (Table 2). The influence of the virgin clay on the pH value of mineral water is noticeable. The thermal water from spa Kulasi was highly alkaline with a pH value 11.8, from spa Guber was acidic with pH 4.2 and from spa Salvinovici the water was slightly alkaline with pH 9.9.

The pH values of peloid sample Kulasi was altered during the experiment, with a decrease from 11.8 to 7.8. The pH value of the sample from Guber increased from 4.2 to 7.9. The pH value for sample from Slavinovici remained almost constant during the experiment.

4. CONCLUSION

No significant variations in the mineralogical composition were detected in peloids of pyrophillite after maturation for 30 and 60 days in three different thermal waters. A maturation time of 30 and 60 days would be enough for the clay to achieve the optimum properties for its use as a peloid. Higher maturation times would not result in marked mineralogical changes, although the development of microorganisms in later stages might influence the therapeutic properties of the peloids. Therefore, further research concerning growth of micro-organisms during maturation of pyrophillite should be necessary.

Conflict of interest

Authors declare that they do not have any conflict of interest.

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