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The Influence of Metal Microelements, Colloids and Organic Phase on Physical-chemical Properties and Processes in Peloids

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ABSTRACT

The main emphasis in this study was on the modification of peloid characteristics through maturation processes, physical-chemical analysis of salty geothermal water and intact geomaterial, content of toxic heavy metals, radionuclides, and microorganisms in matured peloid, and physical-chemical processes that occur in a highly heterogeneous and microheterogeneous system solid-water. Main processes were considered to be mass transfer, colloidal processes, adsorption and surface compounding by macro- and micronutrients from salty mineral water with surface groups of intact geomaterial. This study indicated that inorganic and organic components of peloid could be in the form of colloids, suspended macro- and microparticles, ions and molecules. Colloidal silica had special importance in peloids. Due to low maximum solubility of silica, there were a number of processes in which coagulated and floculated particles were created during maturation, especially in the presence of metal cations (*e.g.*, Fe^{3+} and Al^{3+}) and colloidal metal hydroxides which noticeably reduced the solubility of silica. Single charged alkali metal cations caused coagulation of colloidal silica occupying bridging positions between negatively charged colloidal particles. Colloidal silica in peloid together with other micro- and macro phases, and with the help of numerous microelements, comes in interaction, building a complex surface and occluded compounds. In the multiphase system, very complex organic and inorganic compunds are formed, which are important for therapeutic purposes.

Keywords: Peloid, Macro/micro elements, Thermo mineral water, Colloidal particles.

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Introduction

The term “peloid” usually refers to the natural healing mud, which is a multi-component macro- and micro-heterogeneous system consisting of mineral water, colloidal clay minerals, organic matter, organic-mineral complexes, *etc*. According to The International Society of Medical Hydrology, peloid can be defined as a natural product consisting of a mixture of sea, salt lakes, or mineral-medicinal water (liquid phase), with organic and inorganic material (solid phase) produced by biological action (humus) and geological action (clay minerals). Peloids are used in “pelotherapy” for local or generalized recovering from rheumatism, arthritis, and bone-muscle traumatic damages. The main factors which determine peloid characteristics and its suitability for therapy are: composition, granulometry, geochemistry of mineral water, low-cooling rate, high ion exchange capacity, good adhesivity, ease of handling and pleasant sensation when applied to the skin (Veniale et al., 2004). Today it is known that peloids accelerate blood circulation and metabolism, affect the activity of some endocrine glands, and soothe tension and pain, primarily due to the thermal effect. They also have a beneficial effect on chronic rheumatic diseases, and are used for cosmetic purposes, for example, to remove cellulite. Moreover, some studies have confirmed that peloids possess antimicrobial, antiviral, antineoplastic and anti-inflammatory effects (Suárez et al., 2011).

Primary or secondary mixing of clayey (geo)materials with salty thermo-mineral waters, accompanied by organic materials produced by the metabolic activity of micro-organisms growing during the so-called “maturation” process, is a very common procedure for improving and stabilizing the therapeutic properties of the final product-peloid (Sanchez et al., 2002; Veniale et al., 2007). It is established that the maturation process improves some physical properties of the clay minerals, such as heat retention capacity, rheology, and adhesion. Some studies report that maturation leads to a decrease in grain size, while both mineralogy and chemistry are almost unchanged (Summa and Tateo, 1998).

However, for practical reasons, some studies suggest use of extemporaneous peloids, whose preparation procedure assumes a contact between both phases (clayey material and salty thermo-mineral waters) for around 48 h, instead of several months or up to two years in the case of usual maturation process (Carretero et al., 2006; Gámiz et al., 2009). Organic substances as well as macro- and micronutrient elements present in water are taken up by the peloid during interaction of phases and can be released during application to the human body (Carretero et al., 2010; Gámiz et al., 2009).

Geothermal water from Bujanovačka Spa (south of Serbia) is highly mineralized, hyperthermal (43°C), sodium, hydrogen carbonate, fluoride, sulfate, and carbonic-acid rich (http://bujanovackabanja.org/) . Uniqueness of this spa is in the specific combination of three natural factors: therapeutic thermal waters, peloids and carbon dioxide having a purity of about 98%. During pelotherapy, mud exhibits three effects: mechanical, thermal, and pharmacological. Peloids can be used raw or after passing maturation process, but also as a mixture of mud and paraffin and for preparation of cosmetics (http://bujanovackabanja.org/) .

Experimental

This paper focused on: i) detailed physical-chemical and elemental analysis of salty geothermal water and virgin geomaterial used for peloid maturation process; ii) content of toxic heavy metals, radionuclides, and microorganisms in matured peloid, and iii) processes that took place in a highly heterogeneous and microheterogeneous system solid-water. To date, the latter aspect was very little studied and/or considered in detail.

Virgin clay (native clayey geomaterial for peloid preparation) and thermo-mineral water were the basic ingredients used for the peloid preparation through "maturation" treatment. It was clayey mineral-rich geomaterial of volcanic origin, which was mixed in open air with salty thermo-mineral water, undergoing a maturation process. Already prepared peloid and thermo-mineral water were analyzed without further modifications. All used chemicals were of analytical grade.

Bearing in mind the subject and purpose of this work, program and research methodology included the following:

- ♦ Physical and physical-chemical properties of geothermal mineral water (pH, electrical conductivity, free CO_2, alkalinity, metal cations, anions, *etc.*) were analyzed by the accredited laboratories using the standard methods. These important parameters and factors influenced the ratio of ionic and colloidal states of different ingredients. Details regarding the used analytical methods were provided in Table 1. These analyses were courteously performed at the Institute of Public Health of Serbia "Dr Milan Jovanović Batut", Belgrade, using adequate analytical methods.

- Determination of the chemical composition of mineral water for the dumping of peloids, the content of fluoride, chloride, nitrite and nitrate, phosphate, sulfate, Na, K, Mg, Ca, Fe, Mn, Cu, Zn, Pb, Cr, Cd, Co, Ba, Si, Ni, As, Hg, Se, Sb, Al and Sn;
- Content of the weak electrolyte metasilicicacid (H_2SiO_3) and metaboric (HBO_2) acid.
- Determining the content of radionuclides in appropriate samples.
- EDXRF (Energy Dispersive X-ray Fluorescence) spectrometry technique using radioisotopes ^{241}Am and ^{109}Cd as the excitation sources was employed for determination of chemical compositions of two different samples (184/9V and 183/8V), including macro- and microelements, in salty thermo-mineral water and the virgin clay for peloid preparation. The EDXRF spectra were collected using a modified method EPA 6200. These analyses were courteously performed at the "Vinča" Institute of Nuclear Sciences, Belgrade.
- Macro- and microelements in the virgin clay were determined following the microwave digestion with HNO_3 and H_2O_2. Heavy metals in the samples of the matured peloid were analyzed after their extraction by boiling in the 0.1 M HCl during 15 min (method: AEL M01-05).
- Content of relevant radionuclides in the samples was determined using high-resolution gamma-ray spectroscopy with HPGe detector, according to ISO 10703:1997 and ASTMC1402-98.
- These analyses were courteously performed at the Institute of Chemistry, Technology and Metallurgy – ICTM using adequate analytical methods.

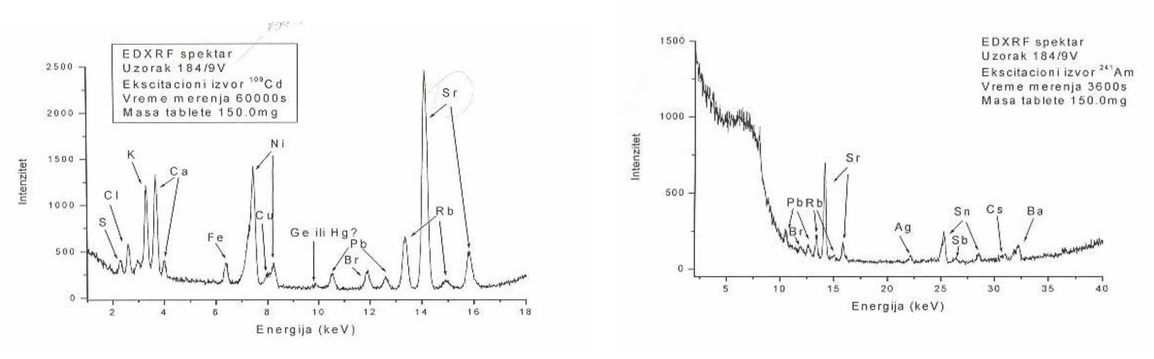
- All samples for testing, indicated by numbers, were taken in accordance with the standards and were taken on the spot by expert of accredited laboratory, therefore, under objective conditions.

Results and Discussion

The results of EDXRF spectrometry with the use of radioactive isotopes ^{109}Cd and ^{241}Am, for samples 184 / 9V and sample 183 / 8V

The qualitative analysis of thermo-mineral water (sample 184 / 9V**)** by non-destructive EDXRF spectrometry (Figure 1) showed the presence of the following elements: S, Cl, K, Ca, Fe, Ni, Cu, Pb, Br, Rb, Sr, Ag, Sn, Sb, Cs and Ba. The size of the peaks indicated that K and

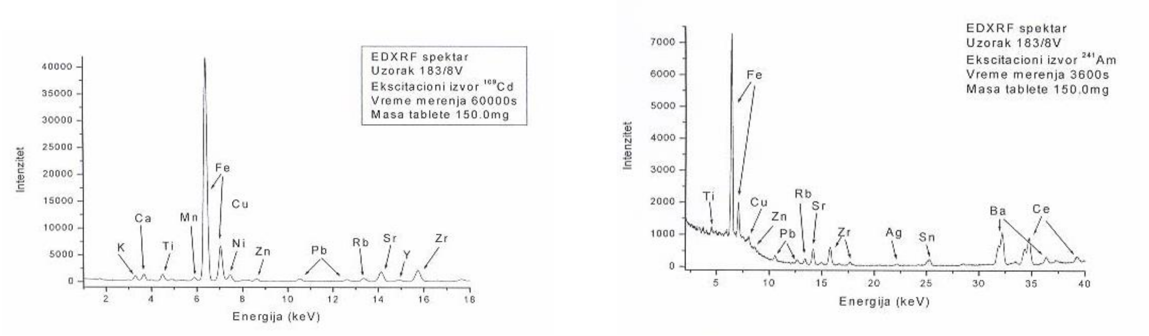
Ca were macroelements, and, besides them, the most common were S and Cl. Other detected elements were present in a smaller proportion, or in trace quantities. Marked small peak, observed in Figure 1a, energetically corresponded to Hg (L line 9.9 keV) or germanium (K line 9.87 keV). Hence, in the absence of other/additional lines, it could not be unambiguously specified which one occurred in water. Moreover, there was a possibility that both of them were simultaneously present or the peak could be the result of some other weaker peaks summation.



a) b)

Figure 1. EDXRF spectra of salty geothermal water acquired by using a) ^{109}Cd and b) ^{241}Am as the excitation sources.

As Figure 2 revealed, the elements detected in the EDXRF spectra of virgin clay (sample 183 / 8V) were as follows: Si, K, Ca, Ti, Mn, Fe, Ni, Zn, Pb, Rb, Sr, Y, Zr, Ag, Sn, Ba and Ce. Moreover, by considering the size of peaks in the spectra, it could be concluded that the most common elements were Si, K, Ca and Fe, while other elements were present in smaller proportion, or in trace amounts. On the other hand, the peaks of Fe, Ni, and Pb (for ^{109}Cd) and Ag, Pb, Sn, and Ba (for ^{241}Am) could be aroused as a result of the influence of background radiation. Therefore, on the basis of EDXRF results, the possible presence of these elements in the sample could not be excluded.



a) b)

Figure 2. EDXRF spectra of virgin clayey geomaterial acquired by using a) ^{109}Cd and b) ^{241}Am as the excitation sources.

The results of sensory, physical, and physical-chemical analysis of water for the sinking of the curative mud, for samples with the identification mark 184 / 9V and sample 183 / 8V

Physical-chemical parameters and quantitative analysis of cations and anions of thermomineral water and virgin clay were summarized in Tables 1 and 2, respectively.

Table 1. Physical and physical-chemical analysis of thermomineral water (sample 184/9V).

N^o	Analyzed parameter	Unit	Result	Analytical method
1.	Smell	-	no	/
2.	pH	-	7.55	SRPS H.Z1.111.:1987
3.	Electrical conductivity	µS/cm	4500	EPA 120.1:1982
4.	Dry residue at 105°C	mg/dm^3	3180	Handbook$^{1)}$ P-IV-7
5.	Hydrogen sulphide (H_2S)	mg/dm^3	-	/
6.	Free CO_2	mg/dm^3	55.3	/
7.	$KMnO_4$ consumption	mg/dm^3	0.69	SRPS EN ISO 8467:2007
8.	Alkalinity (p-alkalinity)	meq/dm^3	0	SRPS EN ISO 9963-1:2007
9.	Alkalinity (m-alkalinity)	meq/dm^3	50.2	SRPS EN ISO 9963-1:2007
10.	Fluoride (F^-)	mg/dm^3	< 1.0	EN ISO 10304-1:1995

11.	Chloride (Cl^-)	mg/dm^3	55.2	SRPS-ISO 9297:1997 SRPS-ISO 9297:2007
12.	Nitrite (NO_2^-)	mg/dm^3	0.016	APHA-Method 4500-NO_2^-
13.	Nitrate (NO_3^-)	mg/dm^3	5.8	EN ISO 10304-1:1995
14.	Phosphate (PO_4^{3-})	mg/dm^3	0.046	Handbook$^{1)}$ P-V-16/A
15.	Sulphate (SO_4^{2-})	mg/dm^3	200	EN ISO 10304-1:1995
16.	Sodium (Na^+)	mg/dm^3	726	APHA-Method 3111-B, 1999
17.	Potassium (K^+)	mg/dm^3	49	APHA-Method 3111-B, 1999
18.	Magnesium (Mg^{2+})	mg/dm^3	8.02	SRPS H.Z1.181:1985
19.	Calcium (Ca^{2+})	mg/dm^3	41.6	SRPS H.Z1.181:1985
20	Strontium	mg/dm^3	1.5	/
21.	Total hardness as $CaCO_3$	mg/dm^3	156	AEL M02-01
22.	Iron (Fe)	mg/dm^3	0.36	APHA-Method 311-B, 1999
23.	Manganese (Mn)	mg/dm^3	0.05	APHA-Method 311-B, 1999
24.	Copper (Cu)	mg/dm^3	< 0.03	APHA-Method 311-B, 1999
25.	Zinc (Zn)	mg/dm^3	0.018	APHA-Method 311-B, 1999
26.	Lead (Pb)	mg/dm^3	< 0.19	APHA-Method 311-B, 1999
27.	Chromium (Cr)	mg/dm^3	< 0.13	EPA-Method 218.1, 1978
28.	Cadmium (Cd)	mg/dm^3	< 0.014	APHA-Method 311-B, 1999
29.	Cobalt (Co)	mg/dm^3	< 0.05	APHA-Method 311-B, 1999
30.	Barium (Ba)	mg/dm^3	< 1.0	EPA-Method 208.1, 1974
31.	Nickel (Ni)	mg/dm^3	< 0.06	APHA-Method 311-B, 1999
32.	Silicon (Si)	mg/dm^3	57.5	Handbook P-V-40/A
33.	Arsenic (As)	µg/dm^3	72	SRPS ISO 11969:2002

34.	Mercury (Hg)	μg/dm^3	< 1.0	BS EN 1483:2007
35.	Selenium (Se)	μg/dm^3	< 0.3	APHA-Method 3114-B, 1999
36.	Antimony (Sb)	μg/dm^3	2.5	AEL M-02
37.	Aluminum (Al)	mg/dm^3	< 1.5	/
38.	Tin (Sn)	μg/dm^3	< 0.5	AEL M02-03
30.	Metasilicic acid	mg/dm^3	118.00	/
31.	Metaboric acid	mg/dm^3	17.00	/
32.	Total dissolved solids	mg/dm^3	4983.60	/

Peloids acted as ionic mediators on human skin. The pathway of incorporation of exchangeable ions and other compounds existing in peloids in the human body, applied for therapeutic and cosmetic purposes, was the absorption through skin (dermal absorption). For this reason, concentration of toxic heavy metals and other harmful components in peloids should be at the level that does not cause damage to human health (Gerencsér et al., 2010; Vreca and Dolenec, 2005). To date, only the maximum acceptable concentrations established for soils and cosmetics could be used as guidelines for healing mud and peloids. For example, in December 2008, Health Canada released Draft Guidance on Heavy Metal Impurities in Cosmetics, which outlined recommended impurity limits in cosmetic products for lead (10 ppm), arsenic (3 ppm), cadmium (3 ppm), mercury (3 ppm), and antimony (5 ppm) (https://www.canada.ca/en/health-canada/consumer-product-safety/reports-producations/industry-professionals/guidance-heavy-metal-impurities-cosmetics.html).

In Europe there was no specific legislation and regulation regarding maximum acceptable concentrations of potential toxic elements in peloids. The European Cosmetics Directive (76/768) and the new Cosmetics Products Regulation (1223/2009) allowed "the non-intended presence of small quantities of a prohibited substance, stemming from impurities of natural or synthetic ingredients, the manufacturing process, storage, migration from packaging, which was technically unavoidable in good manufacturing practice, provided that such presence did not cause damage to human health when the product was applied under normal or reasonably foreseeable conditions of use" (European Union, 2009).

Table 2. Chemical analysis of raw/virgin clayey geomaterial for peloid formulation (sample 183/8V).

N°	Analyzed parameter	Unit	Result	Guideline value[1]
	Microwave digestion with HNO_3 and H_2O_2			
1	Lead, Pb	mg/kg	69.1	< 30.0
2	Cadmium, Cd	mg/kg	2.20	< 5.0
3	Chromium, Cr	mg/kg	49.8	< 50.0
4	Arsenic, As	mg/kg	9.2	< 5.0
5	Mercury, Hg	mg/kg	2.98	< 10.0
6	Nickel, Ni	mg/kg	42.5	< 50.0
7	Manganese, Mn	mg/kg	562	-
8	Cobalt, Co	mg/kg	13.7	-
9	Zinc, Zn	mg/kg	184.5	-
10	Sodium, Na	mg/kg	22900	-
11	Potassium, K	mg/kg	2770	-
12	Magnesium, Mg	mg/kg	4500	-
13	Calcium, Ca	mg/kg	347.5	-
14	Iron, Fe	mg/kg	2100	-
15	Copper, Cu	mg/kg	59.2	-
16	Tin, Sn	mg/kg	< 0.02	-
17	Selenium, Se	mg/kg	< 0.02	-
18	Antimony, Sb	mg/kg	1.35	-

(1) Mark * refers to the non-accredited method

As Tables 1 and 2 described the amount of heavy metal cations in the matured peloid mud was lower with respect to virgin. When geothermal water was mixed with the virgin clayey geomaterial, content of heavy metals decreased due to ion exchange, hydrolysis, partial dissolution of minerals and other phenomena that will be discussed in detail. The importance of ion exchange mainly refers to major elements, such as alkaline or alkaline earth metal cations (Ca^{2+}, Mg^{2+}, K^{+} and Na^{+}), between geothermal water and the clay. Due to their high concentrations in geothermal water, major elements could replace potentially toxic cations in virgin geomaterial, resulting in the final peloid with significantly lower content of heavy metals.

The results of chemical analysis of thermal mineral water, referring to the characteristic cations, anions, and weak electrolytes

The water temperature at the source was 42 °C, its pH was 7.2, specific mass 1.002, and belongs to category of sodium hydrocarbonate water, fluoride, sulfide and carbonic acid hyperthermia. Dry residue at 180°C was 3.2, and the total mineralization 4.996 g/dm^3 in its composition was given in Table 3.

Table 3. The results of chemical analysis of thermal mineral water, referring to the characteristic cations, anions and weak electrolytes.

Cations	**Content (mg/dm^3)**
Sodium	1132.00
Potassium	66.00
Calcium	42.00
Magnesium	11.00
Strontium	1.50
Iron	0.70

Anions	
Hydrocarbonate	3355.00
Chloride	56.00
Fluoride	0.70
Sulphate	183.70
Weak electrolytes	
Metasilicic acid	118.00
Metaboric acid	17.00
The sum of all soluble ingredients	4983.60

The results of radiological tests

Radioactive phases could produce ionising radiations that could be dangerous when exceeding certain levels. Results of radiological study of thermomineral water, virgin clay and peloid samples were comparatively shown in Table 4. The content of radionuclides in the samples was below the limits of radioactive contamination, established for medicinal and cosmetics products based on natural raw materials.

Table 4. The results of radiological examination of mineral water.

Sample	^{40}K (Bq/kg)	^{232}Th (Bq/kg)	^{226}Ra (Bq/kg)	^{137}Cs (Bq/kg)	^{238}U (Bq/kg)	^{235}U (Bq/kg)
Mineral water	1.4±0.1	< 0.2	< 1.1	< 0.1	< 0.8	< 0.4
Virgin geomaterial	276±8	22±1	20±2	< 0.1	12±4	< 0.6
Peloid	388±11	29±1	27±2	< 0.1	18±4	< 0.9

Diagnostic criteria established on the basis of the analysis of obtained results

By the analysis of the research results, and bearing in mind the review of literature and theoretical knowledge in the field of colloids and colloidal state, as an important prerequisite for the necessary physical-chemical and medicinal properties of the curative mud, the following diagnostic criteria were achieved:

- Medicinal waters, by definition, belonged to the category of sodium hydrocarbonate, fluoride, sulfate and carbonic acid hypothermia, with a temperature of 42ºC;
- Thermomineral waters had a very high value of dry residue of 3.2 g/dm^3, at 180°C and high mineralization value in an amount of 4.983 g/dm^3;
- According to the content of cations, anions and weak electrolytes (Table 3) and total chemical composition of mineral water for peloid sinking (Table 1), it could be seen that water contained predominantly sodium and potassium, followed by calcium and magnesium, as macrocomponents;
- Concerning the anions present, the water was rich with HCO_3^- ions (3355 mg/dm^3), which was mainly related to the alkali and alkaline earth metals;
- The presence of Cl^- and SO_4^{2-} ions was noted, and F^- ion in very small quantities of 70 g/dm^3;
- Metasilicic and metaboric acid were found in high quantity, far above the solubility limit;
- Thermal water contained very small quantities of aluminum (Al) 1500 mg/dm^3, arsenic (As) 72 mg/dm^3 and silicon (Si) 57.5 mg/dm^3;
- Wet mud contained a number of heavy metals and others; some in traces (Cd, As, Hg, Ni, Sn, and Se), others in microquantities (Pb, Cr, Mn, Co, Sb, and Zn), as well as macrocomponents (Na, K, Mg, Ca and Fe);
- EDXRF spectra of geothermal water for the peloid preparation (Figure 1) revealed the following elements: S, Cl, K, Ca, Fe, Ni, Cu, Pb, Br, Rb, Sr, Ag, Sn, Sb, Cs and Ba;
- Based on the size of the peaks of EDXRF spectra for geothermal water, it was concluded that the most common elements were K, Ca, Ni, Cu, Sr, Cl and S, while the other detected elements were present in a smaller share or trace;
- In EDXRF spectrum of geothermal water a small peak was detected, which corresponded to the Hg (L line 9.9 keV) or germanium (K line 9.87 keV), which in

this case, due to the lack of other lines, could not be determined with certainty (Figure 1);

- In the EDXRF spectra related to crude mud, which did not undergo the process of ripening, the following elements were detected: Si, K, Ca, Ti, Mn, Fe, Ni, Zn, Pb, Rb, Sr, Y, Zr, Ag, Sn, Ba and Ce (Figure 2);
- Due to the size of the peaks on EDXRF spectra for raw peloid, it could be concluded that in this sample the most frequent elements were Si, K, Ca and Fe, while the other elements were present in a smaller proportion, *i.e.*, in traces, as microelements;
- On the other hand, peaks Ni, Pb, Ag, Sn and Ba in the spectra of raw peloid occurred because of the influence of background from the instrument, so the possible presence of these elements in the sample could not be ruled out.

Discussion of possible chemical interactions and processes in heterogeneous systems of peloid

Previous research on peloids primarly focused on their curative and ion-exchange characteristics, paying no attention to other physical-chemical processes and colloidal phenomena in the peloid, and even ignoring a number of microcomponents which had considerable influence on the consistency of peloids. Physico-chemical processes that most likely occurred in peloid during the maturation process were as follows:

- Water retention, *i.e.*, retention on the external surface of solid particles and within the interlayer space of swelling clay minerals as well as hydration and dehydration of the surface groups on solid surfaces;
- Adsorption and absorption of ions and molecules on solid surfaces and within pores;
- Coagulation - floculation processes;
- Ion exchange process between mineral water and aluminosilicates;
- Reactions between adsorbates and adsorbents in which surface complexes were formed;
- Polymerization of silica aid monomers;
- Biochemical decomposition of organic phase and its mineralization;
- Generation of metabolites of some colonizing organisms;
- Creating inorganic and organic sols and gels;
- Processes of mass exchange;
- Formation of crystallization centers and solid phases of new deposits;

- Oxido-reduction processes.

The peloid was extremely macro and micro heterogeneous solid-water system which contained soluble inorganic and organic components in the form of colloids, suspended particles, ions and molecules. Dominant constituents of the peloid were clay minerals, coagulated inorganic and organic sols, complexes of heavy metals with organic ligands, chelates, aqua complexes, hydroxide gels and various metal species (Al, Mg, Ca, Fe); a number of suspended solid particles of silicates, carbonates, sulphates and silica; soluble ions of many cations and anions; chemical compounds in the form of inorganic and organic molecules and polymeric forms of silica. The structures of the most probable colloidal micelles in peloid could be shown as follows.

$$\{m[(SiO_2)]nSiO_3^{2-} \cdot 2(n-x)Na^+\}\ 2xNa^+ \qquad \text{(I)}$$

$$\{m[M_2(SiO_3)_p]nSiO_3^{2-} \cdot (2/p)(n-x)M^{p+}\}\ (2/p)xM^{p+} \qquad \text{(II)}$$

where M^{p+} was general symbol for the cations (*e.g.*, Fe^{3+}, Al^{3+}, Ca^{2+}, Mg^{2+}, *etc.*). Cations adsorbed on the surface of colloidal silica species acted as cristalization centers for carbonates, sulphates of calcium and other deposits that could be formed in water.

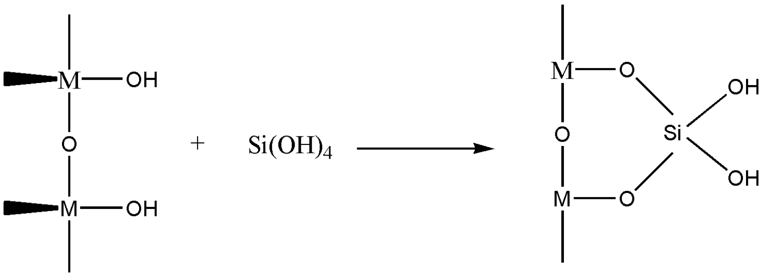
This complex system, with dominant interfacial mass exchange, was out of equilibrium and unstable. For this reason, colloids tended to be destabilized through coagulation-floculation process, forming precipitate or gelatinous state. Due to low maximum solubility of silica, there were a number of processes in which coagulated and floculated particles were created, especially in the presence of metal cations (*e.g.*, Fe^{3+} and Al^{3+}) and colloidal hydroxides which noticeably reduced the solubility of silica. Research in this work focused precisely on the impact of colloidal silica on a number of phenomena and processes in peloids. Depending on the crystallographic modification of crystalline SiO_2, solubility in water was in the range of from 70 to 120 mg/dm^3. Thus, for example, at extremely low concentrations of Fe and Al, the solubility of silica was drastically reduced.

For instance, the addition of Fe^{3+} ions in a solution of $Si(OH)_4$ significantly delayed the polymerization process.

$$(\text{-}SiOH)_m + Fe^{3+} \rightarrow (\text{-}SiOH)_{m-n}(\text{-}SiO)_nFe^{3-n} + nH^+ \qquad \text{(III)}$$

$$2Si(OH)_4 + 2Al^{3+} + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 6H^+ \qquad \text{(IV)}$$

Within the peloid, interaction of monomer $Si(OH)_4$ with metal hydroxides or oxides could not be avoided. This interaction may be depicted by the following equation:



(V)

Deposition of colloidal silica was influenced by floculating ions and it was significantly diminished if metal cations were previously complexed with the chelate ligands.

The presence of Cl^- ions in geothermal water could significantly stabilize colloidal state, acting as an anticoagulant. On the other hand, the F^- ion had a major impact on the creation and structure of numerous suspended particles and easily transformed ortosilicic acid into H_2SiF_6 in accordance with the following mechanism:

$$Si(OH)_4 + 6HF \rightarrow 2H^+ + SiF_6^- + 4H_2O \qquad (VI)$$

Since it was not possible to avoid the presence of the organic phase in the structure of peloids, and this was not desirable, its presence ensured the creation of molecular solution and organic sols, and in interactions with other micro and macro components chelate a number of organic complexes could be formed, as well as silica-organic compounds.

Water used in the preparation of peloid had a high concentration of sodium, which was available not only for the above reaction, but also for the formation of new phases, such as trona ($Na_3H(CO_3)_2 \cdot 2H_2O$), seen in Figure 3. Previous processes which lead to formation of solid deposits caused a considerable change in the chemical composition of geothermal water (a liquid phase in peloid).

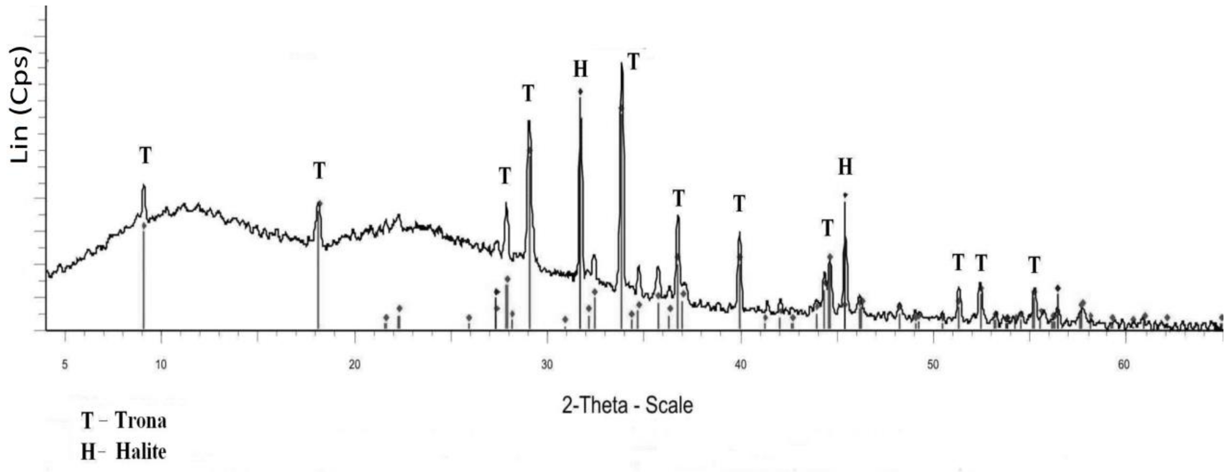


Figure 3. XRD pattern of salty geothermal water.

The main clay minerals in peloid were smectites and minerals based on metal oxides and hydroxides. Smectite was a very good absorber of water, whereby it swelled ensuring high water retention capacity (Cara et al., 2001). Noteworthy, smectite possessed high content of variable exchangeable cations, which could largely vary in hydration degree (Sparks, 2002), thus influencing moisture and water diffusion. A multicomponent mixture in the form of pulp, saturated with H_2S from geothermal waters, upon the occurrence of redox processes of ripening (biochemical processes), could create peloid of strongly mineralized structure, which had good healing and plastic qualities, important for its implementation.

Conclusion

Peloids were considered as highly complex and heterogeneous systems, composed of minerals, amorphous inorganic materials, and organic matter. Therapeutic and curative characteristics of peloid were realized through thermal effects and ion exchange properties in contact with human skin. Due to the potential human toxicity or radiation risks during pelotherapy, this study has involved detailed physical-chemical and radiological analysis of mineral water, virgin geomaterial and final peloid from Bujanovačka Spa. All tested parameters have fulfilled the requirements, according to Serbian regulations.

High mineralized water was extraordinarily suitable for the preparation of peloids. Presence of silicic acid, as well as Al^{3+}, Fe^{3+}, F^- and trace elements, were reflected in the extraordinary process within the peloid at phase boundaries solid-water. Moreover, clay minerals and silicic acid had a key role in processes of hydration and dehydration. Polymer form of silicic acid significantly affected the formation of solid phase and deposits in the form of layers or clusters within the peloids and mediated mass exchange processes between human body and peloids.

The presence of metal cations and hydroxides, anions, clayey material, and organics in ionic, molecular, or colloidal state gave rise to many processes and interactions between all mentioned constituents, forming chelates, organosols, organic complexes with metal cations and polymeric forms of various inorganic and organic compounds.

Peloids should be active, but stable colloidal systems, so, in that sense, a harmonious correlation between the added macro and micro elements and the process of creating peloids was established in this paper.

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Conflict-of-Interest Statement

None.

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