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Thermal muds: Perspectives of innovations

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Abstract

Pelotherapy is the application of thermal muds ("peloids") for recovering muscle–bone–skin pathologies; more recently such old practice has received applications also for wellness and relax purposes.

Thermal muds are hydrothermal or hydrothermalized pastes produced by primary or secondary mixing of clayey (geo)materials with salty thermo-mineral waters, accompanied by organic materials produced by the biological-metabolic activity of micro-organisms growing during the so-called "maturation" process.

Many spa-centres have been using peloids occurring in-situ, but natural reserves are going exhausted; therefore, thermal muds are currently prepared by maturation of tailored clayey raw ("virgin") materials mixed with salty thermo-mineral waters gushing out in-situ.

Various factors are ruling the quality of a peloid: virgin clay, thermo-mineral water and maturation procedure.

Nowadays pelotherapy is being more-and-more focused on specific pathologies and treatments; such innovative health applications need a "certification" of the peloids suitability. Worse applications of thermal mud could produce non-beneficial effects, or cause relapse.

It is suggested to set up a Network of specialized laboratories for the certification after standard criteria of the quality and suitability of peloid muds, and to appoint an European Master. Degree for assisting the physicians in selecting the peloids in view of treatments focused on different pathologies.

Keywords: Pelotherapy; Muds; Differentiation; Certification; Innovation

1. Introduction

Italy has on old tradition of thermal treatments going back to Romans which used proper buildings called "balnea".

Pelotherapy is the application of thermal muds ("peloids") for recovering muscle–bone–skin pathologies; more recently such old practice has received applications also for wellness and relax purposes.

Thermal muds are hydrothermal or hydrothermalized pastes produced by primary or secondary mixing of clayey (geo) materials with salty thermo-mineral waters, accompanied by organic materials produced by the biological-metabolic activity of micro-organisms growing during the so-called "maturation" process.

The routine applications of thermal muds ("peloids") are: (i) local or total-body cataplasms for recovering chronic rheumatism, myalgias, neuralgias, osteo-arthrosis

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and bone–muscle traumas; (ii) masks for the treatment of cutaneous diseases (acne, seborroea, psoriasis, etc.); (iii) cosmetic and aesthetic cleaning; and (iv) baths against lipo-dystrophies and cellulite.

Usually, peloids have a stimulatory antiphlogistic and analgesic action (Veniale, 1997; Martin-Diaz, 1998; Carretero, 2001; Nappi, 2001; A.A.V.V., 2004; Tateo et al., 2005).

The peloid muds should possess suitable properties: hydric degree, consistency, adhesiveness, heat capacity, cooling rate, exchange capacity, ease of handling and pleasant sensation when applied to the skin.

Nowadays, the "new frontier" of pelotherapy (wellness and relax purposes, focused therapies) is impacting some hindrances: (i) natural occurrences of thermal muds are going exhausted; (ii) focused treatments of specific pathologies need the formulation of peloids possessing suitable properties.

As concerning the exhaustion of natural occurrences, many spa-centres currently prepare the thermal muds by "maturation" of tailored clays mixed with thermo-mineral waters gushing up in-situ.

More difficult is the question concerning the formulation of ad-hoc peloids devised for the treatment of specific pathologies. Their therapeutic suitability is depending upon: (i) granulometry, mineralogy and physico-chemistry of the "virgin" clayey material; (i) geochemistry of the mixed salty thermo-mineral water; and (iii) "maturation" procedure, i.e. (re)mixing practice and lasting time. These factors are ruling the physico-chemical and biological reactions occurring within the clay–water admixture (paste) when lasted to maturate (Curini et al., 1990; Sanchez et al., 2002; A.A.V.V., 2004; Veniale et al., 2004, 2005 and previous references therein).

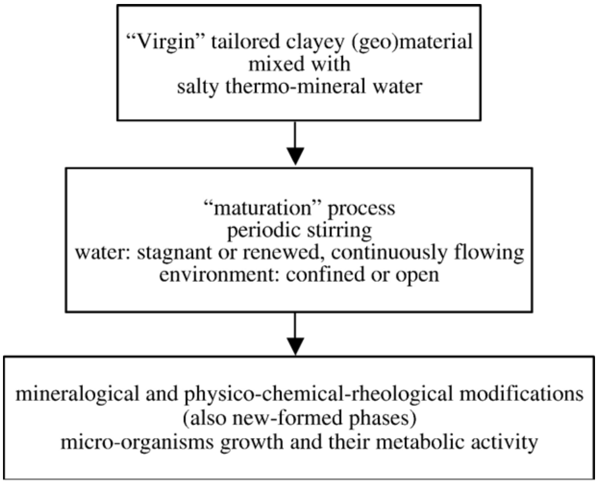
In fact, until the last 10–15 years the scientific literature had only occasional references about the formulation of thermal muds for specific therapies.

A certain lack of basic research gives the feeling that the practice of thermal mud packing has scarce scientific ground. Some people tend to consider the effect of peloids as simply due to heat or to emphasize it (Berbenni, 1965), but heat is only one factor within a complex mechanism of actions involving many variables.

The Italian Group of AIPEA (now Associazione Italiana per lo Studio delle Argille/AISA) has organized Meetings (Veniale, 1996, 1999) devoted to peloid mud formulation and applications.

During the last decade, our research team has carried out investigations aimed to get insight about the reactions occurring during the "maturation" process (Veniale et al., 1999, 2004), and to put in evidence the need of "certification" of the quality and suitability of peloids devised for specific therapies (Setti et al., 2004; Nicolini et al., 2004).

The *cycle for the preparation of a blended thermal mud* can be schematized as follows:



Suitable properties and active factors of a mature thermal mud are: water retention, consistency, bio-adhesiveness, ease of handling, pleasant sensation while applied onto the skin, cooling kinetics (thermo-insulation and heat-retain) and exchange capacity through mud/skin interface (mobile-soluble chemical elements and organic substances produced by the metabolic activity of growing micro-organisms).

The properties of a blended peloid are related to the granulometry, mineralogy and (physico)chemistry of the *"virgin" tailored clayey (geo)material* used for its formulation.

Granulometry is determining the reactive surface, consequently influencing the interactions between mineral particles, salty water and growing micro-organisms; furthermore, the size and shape of intergrain voids, thus the solution mobility.

Mineralogy, especially the fine "clay" fraction (particle size <2 μm), is influencing some reactions which occur during the maturation process: water uptake, i.e. retention on the external surface of solid particles and trapping within the interlayer space of swelling clay minerals, and ion exchange capacity.

Attention should be paid to abrasive minerals (as quartz and feldspars) and to hazardous constituents, as free silica, asbestos, Fe-oxy-hydroxides. Carbonates, when dissolved, can influence the rheological behaviour of the peloid paste.

Mobile and/or exchangeable toxic elements (as As, Cd, Hg, Pb, Se, Te, Tl, etc.), when scavenged by the skin sweat, become a troubling question (Summa and Tateo, 1998; Summa et al., 2005). Radioactive phases can produce ionising radiations that could be dangerous when exceeding certain levels.

The geochemistry of salty thermo-mineral waters (as source temperature, pH, solid residue, CO_2 and HCO_3^- content, sulphidric degree, sulphate–borate–chloride–bromide–iodide–fluoride and nitrogen amount, and Na^+, K^+, Ca^{2+}, Mg^{2+}, Li^+, Sr^{2+}, Ba^{2+} exchangeable cations) is strongly influencing the characteristics and behaviour of peloids (Veniale et al., 2004, and references therein). For instance, the different mobility of soluble salts contributes to peculiar properties: water retention, swelling index, consistency, adhesiveness, activity and rheological parameters.

Also the growth of micro-organisms (Andreoli and Rascio, 1975; Tolomio et al., 2002, 2004) and their metabolic products depend upon the nature of the clay–water admixture constituting the maturing paste, i.e. kind of clay minerals (swelling or not, ion exchanging) and physico-chemistry of the thermo-mineral waters (for instance: pH, carbonation, soluble salts, mobile and exchangeable ions, etc).

As a matter of fact, the primary reserves of natural thermal muds are going exhausted around the thermal springs; therefore, the peloids used in many spa-centres are prepared by “maturation” of a tailored virgin clayey (geo)material mixed with a salty thermo-mineral water gushing out in-situ.

Maturation is the key of peloid preparation and its procedure makes each peloid peculiar. Unfortunately, (re)mixing–shacking and lasting time are rather empirical in many spa-centres and left to the judgement of practitioners; consequently, the factors ruling the physico-chemical and biological reactions occurring during the maturation process are out of scientific control and not repeatable for different spa-centres.

The maturation process is very complex: it is modifying the water–clay paste environment (pH, Eh, temperature, light exposure, hydrologic regime, confined–open) and developing the new-growth of micro-flora and fauna, as well as their metabolic products.

In many spa-centres the thermal muds are recycled, i.e. after application on the patient, the “exhausted” peloid is matured again to loose possible hazardous features acquired from the previous therapeutic application; for instance, toxic chemical elements leached by the patient sweat.

Such situation highlights the importance of a scientific documentation (protocol) to certificate the quality of peloids (Kleinschmidt, 1992; Setti et al., 2004; Nicolini et al., 2004).

The increasing success of such health and wellness remedies is somewhat jeopardizing: not all that does glitter is gold !

Previous investigations (Curini et al., 1990; Galzigna et al., 1995, 1996; Yvon and Ferrand, 1996; Veniale et al., 1999, 2004, 2005; Galzigna et al., 1999; Bertelli, 2000; Sanchez et al., 2000, 2002; Salvagno, 2002; Galzigna et al., 2004) have evidenced the importance of determining variability and evolution of the interacting factors acting during the maturation process, which in turn are influencing properties and behaviour of the peloids when applied for curative treatments.

In fact, the treatment of bone–muscle damages, rheumatic and arthrosis pathologies, skin diseases (the most common applications of pelotherapy) and new treatments concerning cosmetic, aesthetic, wellness and relax purposes should require thermal muds with different peculiar characteristics.

Noteworthy, the Centro Studi Termali “Pietro d’Abano” (Abano Terme–Montegrotto thermal district, Padua—northern Italy) is using a small-scale prototype maturation plant for controlling and standardizing the evolution of the mud paste under variable conditions (A.A.V.V., 2004).

The formulation of peculiar peloids for differentiated therapies and/or treatments is the “new frontier”!

2. Results and discussion

Reviews on the curative effects of peloids for the human health have been published by Veniale (1996, 1997), Carretero (2001) and Tateo et al. (2005).

Investigations of clayey raw geomaterials used in Italian spas for the formulation of peloids have been carried out by Magrini (1974), Bertolani and Loschi-Ghittoni (1996), Summa and Tateo (1998), Veniale (1998), Gorgoni et al. (1999), Jobstraibizer (1999), Minguzzi et al. (1999), Cara et al. (2000): see reference review therein.

During the last decade relevant contributions have been performed by our research team with the aim of getting insight on the behaviour of peloids, and to formulate innovative muds especially devised for the specific treatment of different pathologies (Veniale et al., 1999; Bertelli, 2000; Veniale et al., 2004; A.A.V.V., 2004).

Specific parameters have been tested to verify the effects of various maturation procedures.

The *granulometric profile* can still undergo changes not appreciable, but in some cases the clay (<2 μm) fraction of the virgin clayey material resulted decreased due to clay particle agglomeration (Sanchez et al., 2002; Veniale et al., 2004).

Mineralogical changes are mainly concerning the degradation of illite and feldspars, partly transformed into mixed-layer illite/smectite and smectite. Also the crystallinity degree of pristine smectite was lowered. Subordinately, dissolution of carbonates has been detected.

On the other hand, an important event is the precipitation-growth of new mineral phases as gypsum (Sanchez et al., 2002), halite (Veniale et al., 2004), pyrite and silica (Jobstraibizer, 2002). For instance, pyrite occurring in the thermal muds of the "Euganeo" basin (northern Italy) mainly shows framboidal aggregates, and its genesis is correlated to the nature of mineral waters and solid matrix; furthermore, with the geothermic gradient (Jobstraibizer, 2002). Precipitation kinetics of amorphous silica is ruled by the solution ionic strength and possibly also related to the amount of organic matter. Experiments carried out on blended muds (Bertelli, 2000) at variable Eh, pH and geothermic gradient put in evidence a trend of increasing Fe^{2+}/decreasing Fe^{3+}, a behaviour congruent with a reducing environment. Simultaneously, the sulphur content (including organic ones) increases; this condition is also to be referred to the action of thio-bacteria (see Galzigna et al., 2004).

Cation exchange capacity (CEC), soluble salts, water retention, swelling index, activity, consistency parameters (WL, WP and PI), heat capacity and cooling kinetics resulted influenced by the geochemistry of mineral waters used for the maturation treatment, but some opposite trends for Br–I salty and sulphureous, Ca-sulphate waters, respectively, have been recognized; noteworthy, the influence of pH value (Veniale et al., 2004).

The different CEC behaviour and soluble salt content observed in peloids formulated with sulphureous versus Br–I-salty waters could be discriminating for either dermathological masks (Torresani, 1990; Lotti and Ghersetich, 1999; Veniale et al., 1999) or body cataplasms for the treatment of bone–muscle damages.

Nissenbaum et al. (2002) have evidenced that the beneficial curative effects for the treatment of psoriasis by the black clayey sediments from the Dead Sea are to be ascribed to their content of reduced sulphur species, present as poorly crystallized iron sulphides.

Leaching tests have shown that the release–exchange of mobile elements (ions) between the skin sweat and peloid mud is depending on the amount of swelling clay minerals (Summa and Tateo, 1998).

Pastes reach in smectitic clays (bentonites) are considered suitable materials for the formulation of pelotherapic muds due to the ability of smectite to retain large water amounts (Yvon and Ferrand, 1996; Morandi, 1999). In fact, a high-moisture content is an important factor for high heat capacity of the peloid when applied to the patient's body at 40–45 °C for 20–30 min.

The temperature reached by the peloid mud after 20 min of application (calculated after a simple innovative mathematical model: Cara et al., 1999) is influenced by the water retention. Such an information is also important for the spa-management, especially when high energy-costs have to be met for the peloid heating.

The heat retention–dissipation is also depending on the granulometry (specific surface) of the solid phase (Ferrand and Yvon, 1991).

The effect due to interactions of different kind of water molecules ("dense", "ice-like", "diffuse double layer" located on and/or around the clay particle surface) on the mobility-diffusion of unbound water through the pore spaces have already been discussed (Veniale et al., 2004).

Furthermore, smectites possess high amount of exchangeable cations which can widely range in hydration degree, thus influencing moisture content and water diffusion.

An increase in plasticity and a slow cooling are considered to improve the quality of peloids.

The interactions between skin and peloid mud are influenced by the rheological and tensiometric properties of the latter which are driving the chemical and heat transfer (Bettero et al., 2004). The rheological behaviour of a peloid is correlated to its physico-chemical and visco-elastic properties before and after application on the skin. It has been evidenced that the induced modifications can be used for evaluating the epidermal barrier function (Bettero et al., 1999). A protocol has been developed for testing the bio-adhesiveness of peloid muds, thus for evaluating the effectiveness of peloid applications. It is based on innovative tensiometric approaches concerning the superficial skin free energy and the related polar and dispersed components which are measured in-vivo and in-vitro. The model is suitable for direct topical non-invasive evaluations (performed by contact angle measurement) of the skin bio-adhesiveness, i.e. expressing the tensiometric affinity of a topical system for the skin. It is called TVS (Tensiometric Versus Skin) index of bio-adhesiveness; in other words, the functional epidermal states before and after topical application of a peloid. It can also be used to devise peloids with peculiar functional properties (Bettero et al., 2005). A preliminary study has been carried out by the Permanent Thermal Observatory (OTP) of Padua University for testing peloid muds used in spa-centres of the Abano Terme and Montegrotto district. The results (Table 1) show that the TVS mud index is mainly within the range of 55–65; several muds

Table 1
Average values of TVS mud index of thermal muds from the Abano–Montegrotto spa-district (Padua, Italy); unpublished data from an Interior Report of the Permanent Thermal Observatory of the University of Padua

	TVS mud index (mN/m)		
N=90	Reference range 55–65	Several muds 65–75	Few muds 85–90

have values between 65 and 75, and only a few reach the 85–90 range (Bettero et al., 2006).

Among the beneficial effects of a thermal mud, the new-growth of living species (algae, mainly diatoms and cyanophyceae, bacteria, protozoa, and the biomaterials produced by their metabolic activity and degradation) plays an important role (Galzigna et al., 2004).

The thermophylic micro-organisms that progressively colonize the maturing mud (Andreoli and Rascio, 1975; Tolomio et al., 2002, 2004) usually concentrate within several upper centimetres and their type and cell density depend on the lasting time, confined–open environment, sunlight exposure and remixing–shacking operations.

For instance, diatoms can move while secreting metabolic products and migrate through the interstitial spaces of the moistened paste, adapting their nutritional and metabolic level to the lack of light.

Noteworthy, the muds with the highest content in smectite (bentonitic virgin materials) show the lowest growth of micro-organisms during the maturation process (Andreoli, personal communication); in such circumstances, a clay–water paste too rich in smectite could create an "asphyxic" environment hindering the micro-organism growth.

Diatoms alive within the thermal mud are able to produce proteins and lipids as the result of biotransformation by thio-bacteria.

Usually, maturation is going on for a few months up to 1–2 years depending on the spa-tradition, but Galzigna et al. (1995) reported the development of a sulphoglycolipid (considered a powerful anti-inflammatory product) just after 50–60 days of maturation in sulphate–Br–I water, a reaction coinciding with the drop of chlorofilla-α.

The nature of the lipid fraction can change as consequence of mud recycling (Ferrara et al., 1999); on the other hand, the re-maturation of "exhausted" peloids eliminates pathogen micro-organisms, yielding again a sterile mud.

3. Summary and conclusions

Pelotherapy is being more-and-more focused on specific pathologies and wellness–relax treatments. Such differentiated health applications need a certification (after standard criteria) of the thermal mud suitability for peculiar and specific curative applications (Setti et al., 2004; Nicolini et al., 2004).

The maturation procedure for the formulation of blended thermal muds is influencing their properties and behaviour during the therapeutic treatments (A.A.V.V., 2004; Veniale et al., 2004).

The various and heterogeneous variables playing a role during the maturation process should be controlled and ruled by protocol procedures to certificate their quality. Depending upon such differences, it could also be possible to discriminate among peculiar peloids: for instance, for body cataplasms, dermatological masks, wellness–relax baths; furthermore, for specific therapies of rheumatism, arthrosis, muscle–bone traumas, skin diseases, lipo-dystrophies, etc.

Currently, there is a lack of normative regulation about the quality standard of peloid mud. After a Workshop held on the occasion of Euroclay 2003 (Modena, Italy), the factors and parameters to be surveyed for qualifying virgin clays and mature peloid muds are:

Granulometry: clay fraction <2 µm (at least 70–80%) is determining the specific surface area (reactivity) and influencing the ease of handling and pleasant sensation when the peloid mud is applied onto the skin of patients (care should also be paid to abrasive minerals as quartz and feldspars).

Specific surface area is ruling the interactions between solid/liquid constituents and the thermal behaviour of peloid muds.

Mineralogy of the bulk sample and clay fraction: the content of swelling–exchanging clay minerals (at least 60–70%) is leading: (i) the rate of water retention–release: the heat capacity is improved and the cooling kinetics slowed by high mixture content; (ii) the exchange mechanisms of mobile ions between peloid and skin sweat. Some risks can arise by the presence of asbestos minerals, free silica and Fe-oxy-hydroxides; it is to notice that Fe content between 5–8% can favour a low heat release.

Hazardous chemical elements (as As, Cd, Hg, Pb, Se, Tl, etc.) need attention for their toxicity when scavenged by maturing waters and liberated by the body sweat leaching exerted during the pelotherapic application. Radioactive elements can produce dangerous ionising radiations (also volatile) that could remain in the lung tissues for a long time; a risk enhanced when the thermal mud is recycled, a common praxis in many spa-centres.

pH value can influence consistency and activity of the peloids; an alkaline environment due to carbonate dissolution will influence the mud plasticity and activity and, on the other hand, decrease bacteria and germ activity.

Fundamental for determining quality and behaviour of the peloid muds is their *biological activity*: i.e. living micro-organisms growing during the maturation process and their metabolic products (De Bernardi and Pedrinazzi, 1996).

Innovative methodologies and protocols have been developed for testing *cooling rate* and *bio-adhesiveness* (Cara et al., 1999; Bettero et al., 1999, respectively), important parameters for the evaluation of the effectiveness of peloid muds.

Investigations are in progress to qualify peloids for peculiar therapies.

4. Suggestions

The above considerations point out the need to realize a NETWORK of specialized laboratories for the control and certification of the quality and suitability of peloid muds (like the Permanent Thermal Observatory existing in the Abano and Montegrotto spa district, northern Italy), also with the aim to focus their formulation for the specific therapy of different pathologies and treatments (Setti et al., 2004; Nicolini et al., 2004).

Our research team, in collaboration with the Centro Studi Termali “Pietro d’Abano” (Abano Terme, Padua) is also projecting a maturation plant for standardizing the procedure of peloid formulation–maturation.

A new professional figure able to tailor and control the quality of thermal muds, and to assist physician specialists (rheumatologist, traumatologist, orthopaedist, physiotherapist, dermatologist, etc.) in selecting the suitable peloids as requested for a correct treatment of peculiar and different pathologies and purposes, is suggested.

The opportunity to appoint a European Master Degree ad-hoc could be considered.

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