Peloids as Thermotherapeutic Agents

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Abstract: The use of peloids as heat-providing therapeutic systems dates back to antiquity. Such systems consist of a liquid phase and an organic or inorganic solid phase. The latter facilitates the handling, preparation and stability of the solid–liquid system, modifying its organoleptic and physicochemical properties, and improves its efficacy and tolerance. Peloids enable the application of heat to very specific zones and the release of heat at a given rate. The aims of this work are to study 16 reference peloids used in medical spa centers as thermo-therapeutic agents as well as to propose nine raw materials as a solid phase for the preparation of peloids. The physical properties studied are the centesimal composition, the instrumental texture and the thermal parameters. In conclusion, the peloids of the medical spas studied are used as thermostherapeutic agents in the treatment of musculoskeletal disorders, especially in knee osteoarthritis and to a lesser extent in back pain and psoriatic arthropathy. The clinical experience in these centers shows that the main effects of the peloids of the medical spas studied are the reduction of pain, an increase in the joint’s functional capacity and an improvement in the quality of life. As thermotherapeutic agents, all the peloids of the medical spas studied and the pastes (raw materials with distilled water) examined showed a heat flow rate of up to four times lower than that shown by the same amount of water. The raw materials studied can be used as solid phases for the preparation of peloids with mineral waters.

Keywords: peloid; thermoderapy; mud therapy; pelotherapy; clay; peat; microcrystalline cellulose; thermal flow; instrumental texture

1. Introduction

Since ancient times, peloids have been used as heat-providing healing systems [1]. Currently, peloid therapy is used in health resort medicine in the form of both balneotherapy and thalassotherapy.

Since the middle of the last century, this technique has been referred to as mud or pelotherapy. A peloid is defined as “a mature mud or mud suspension or dispersion with a solid phase comprised of a mixture of organic and/or inorganic solids, suspended or humidified, with a liquid phase consisting of a solution of ions and molecules of inorganic...
and organic origin whose solvent is water [3]. The term “system” is used to describe the specific proportion of material that contains defined amounts of one or more substances, ordered in one or more phases. The term “phase” refers to a homogeneous and physically different component of a system separated from the other components by defined boundary surfaces [4].

The main properties of peloids recognised are: their applications in thermotherapy [2,3,5,6] manifested by biological effects, metabolic and enzymatic activity, vascular, neuromuscular, analgesic and modifications of the viscoelastic properties of the tissues [7,8]; several other studies have confirmed their anti-inflammatory [9–14], chondroprotective [10,11] and immunological actions [10,14–16] which can be attributed to their chemical composition [17–20] and organic content [21–26].

During the use of peloids in thermotherapy, heat acts as a therapeutic agent. While mainly contained in the liquid phase, this heat is moderated by the solid phases such that it can be applied to very specific zones at a predetermined release rate. In thermodynamic terms, heat transmission is a so-called irreversible phenomenon [27]. Irreversible processes exist whereby there is transport of some physical magnitude from one region to another of a system due to a gradients of different physical magnitudes; such processes are known as transport phenomena and can be expressed through phenomenological laws [28].

Transport phenomena originate from a series of causes, such as the temperature gradient. These magnitudes are designated “forces” in the thermodynamics of irreversible processes. These “forces” give rise to “fluxes” such as heat flow [29].

Several phenomenological equations exist to describe transport phenomena as proportions, such as Fourier’s law, between the thermal flow (Ω) and temperature gradient. The heat equation is a mathematical model that describes the temperature changes that a solid body goes through, which can be summarised as the calorific energy flowing from zones of a greater to lower temperature, and that this energy is proportional to the temperature gradient between the two zones. Accordingly, a greater temperature gradient is needed for a peloid to achieve the best thermotherapeutic effects, provided they are well-tolerated by the patient without producing any undesirable side effects.

This determines the important role of the solid peloid phase that acts as a vehicle or coadjuvant, improving the efficacy of the therapeutic agent. The final goal is the sustained release of heat. The diffusion velocity, together with the biocompatibility, are the most important factors to consider when selecting a predetermined solid phase.

Peloids need to have three qualities: they should have a low cooling speed, should be easy to handle, and should offer a pleasant feeling when applied to the skin. They are used in full or partial baths or applied locally to a given skin zone at a temperature of 42 to 45 °C in 1 to 2 cm layers in 20 to 30 min sessions [30].

According to several clinical studies, the most effective indications of this form of therapy are musculoskeletal disorders of the knee [13,31–43], spine [44–50], hand [51–54], as well as fibromyalgia syndrome [55–58], carpal tunnel syndrome and chronic lateral epicondylitis [59,60].

The mechanical and thermal properties of clays and peats that make them useful for thermotherapy have been well described in the literature [30,61–89]. The aims of this study are, firstly, to examine the physical properties, heat and texture, of 16 reference peloids used in medical spas (MSs); secondly, to determine the physical characteristics of nine raw materials (RMs)—six inorganic (clays) and three organic (two peats and a microcrystalline cellulose); and thirdly, to study the properties of the pastes obtained with these nine RMs mixed with distilled water (RM/DW), comparing them with the MSs.

2. Materials and Methods
2.1. Materials
2.1.1. Peloids Used in Medical Spas (MSs)

The origins of the 16 MS samples were Carhué and Copahue (Argentina), Peruíbe and Poço de Caldas (Brazil), Františkovy Lázně (Czechia), Terdax (France), Bad Bayer-
soien (Germany), Héviz (Hungary), Dead Sea (Israel), Polanczyk (Poland) and Archena, Arnedillo, Caldes de Bohí, El Raposo, Lo Pagan and Thalassia (Spain)—see Figure 1.

![Figure 1. Origins of the peloids used in medical spas (MSs).](image)

2. Materials and Methods

2.1. Materials

2.1.1. Peloids Used in Medical Spas (MSs)

The origins of the 16 MS samples were Carhué and Copahue (Argentina), Peruibe and Poço de Caldas (Brazil), Františkovy Lázně (Czechia), Terdax (France), Bad Bayersoien (Germany), Hévíz (Hungary), Dead Sea (Israel), Polanczyk (Poland) and Archena, Arnedillo, Caldes de Bohí, El Raposo, Lo Pagan and Thalassia (Spain)—see Figure 1.

2.1.2. Raw Materials (RMs)

The RMs examined were six inorganic clays lacking carbon chains in their structure and three organic materials—two peats and one microcrystalline cellulose material. These materials and their suppliers were: aluminium bentonite from Süd Chemie Spain (C1), magnesium bentonite from Süd Chemie Spain (C2), kaolin from Avisa (C3), kerolite from Süd Chemie Spain (C4), palygorskite from Tolsa (C5), sepiolite from Tolsa (C6), blonde peat from Plantaflor (P7), milled peat from Turberas del Buyo y del Gistral (P8) and microcrystalline cellulose Avicel PH 101 from FMC Europa (MC9), proposed for the first time as a solid phase.

2.2. Methods

2.2.1. Centesimal Composition

The centesimal composition was quantified by desiccation at 105 °C in an oven until constant weight, and expressed as a percentage relative to the whole peloid. The water content was calculated by the difference with respect to the percentage of solids. Ash is the residue of the solid components left behind after incineration at 850 °C in a muffle furnace until constant weight, expressed as a percentage (weight-to-weight) relative to the whole peloid. The lower the ratio of the percentage of ash to the percentage of solids, the lower the materials’ content of substances that are volatile or removable by high temperatures [3,90]. Knowing the centesimal composition makes it possible to deduce the type of solid phase that constitutes the peloid (inorganic or organic) and calculate its specific heat.

2.2.2. Instrumental Texture

The texture was determined using a Brookfield Texture Analyzer model LRFA 1000 with a round 10 mm stainless steel probe following the Texture Profile Analysis (TPA) method involving two consecutive cycles for each determination. The instrumental texture provides information on hardness, or the force necessary for a given deformation measured in grams (g); adhesiveness, or the work needed to overcome the forces of attraction between the surface of a material and the surfaces in contact with it, measured in grams per second (g.s); and cohesion, defined as the inner bond forces that maintain the shape of
the product. This last parameter is the property of non-consolidated fine-grained materials whereby particles remain joined together due to the surface forces. It is adimensional with high values indicating higher cohesion in the product [91–93]. Hardness conditions the abrasiveness of the peloid responsible for the higher or lower tolerance on the part of the patient, while adhesiveness and cohesion are decisive when choosing the technique of application of the peloid (ilulation, brushing, bathing).

2.2.3. Thermal Parameters

- Specific heat ($C_p$)

  1. Calculation of the ($C_p$) of the MSs
     The equation proposed by Armijo et al. [80] with which the specific heat of a peloid can be calculated as a function of its ash ($A$) and water ($W$) contents is:

     $C_p = 1.26023 + 0.02926 (W) - 0.00628 (A) + 0.000063 (W) (A)$

  2. Determination of the ($C_p$) of the RMs
     The ($C_p$)'s of the RMs were determined using an air-cooled differential scanning calorimeter DSC1 (Mettler, Toledo). The characteristics of this system include a temperature accuracy of ±0.02 K and a heating rate of 10 K/min. The ($C_p$) capacities of the nine RMs were determined to be between 45 and 36 °C, temperatures that are commonly used for peloid application in spas; the same methods were used to obtain the cooling curves. This takes into account that although the ($C_p$) varies across the temperature range, these variations are so small that the mean values may easily be considered with no appreciable error.

  3. Calculation of the ($C_p$) of the pastes of the raw material–distilled water mixtures (RM/DW)
     For pastes, the ($C_p$) of the system is given by the sum of their components. According to the general equation:

     $$C_p(P) = \left[ \frac{(S_i)C_p(S_i) + (100 - (S_i)) C_p(W)}{100} \right]$$

     where ($S_i$) is the weight percentage of the different solid constituents and $c_p(S_i)$ and $c_p(W)$ are the specific heat capacities of both solid and water. Pastes (RM/DW) were prepared by adding distilled purified water to the RMs and leaving them for 24 h for the water to penetrate, followed by manual mixing. The distilled purified water used to prepare the pastes was obtained using a system consisting of a Fistreen Cyclon distiller fitted to a Water Pro purification system from Labconco and a Synergy UV system from Millipore. The ($C_p$) is used to calculate the amount of heat ($Q$) that a peloid or paste can give off over a range of temperatures.

- Cooling curve test

  Cooling curves were prepared by plotting temperature against time. The thermometer used has a Pt 100 probe to measure the product temperature at 15 s intervals from 45 to 36 °C. The equation best fitting the experimental curve was determined using the program Origin 8 [94]. These curves were then used to obtain the relaxation time ($t_r$) defined as the time needed for the temperature to drop exponentially by 37% of its starting value ($1/e = 0.37$). Accordingly, for a peloid applied at 45 °C and attaining a final temperature of 36 °C, in the first $t_r$, the temperature reached would be $(36 + 9/e) 39.3$ °C. Furthermore, this same time would be required for the temperature to drop to $(36 + 9/e^2)$ 37.2 °C, and in the same time intervals to 36.4 °C and 36.1 °C. Over three times its $t_r$, the temperature reached would be 36.4 °C. This is the normal user body temperature, so the peloid would no longer have a therapeutical effect [80].

  From ($Q$) and ($t_r$), the heat flow ($\Phi$) is obtained; that is, the speed of the passage of heat from the peloid to the patient.
3. Results and Discussion

3.1. Peloids Used in Medical Spas (MSs)

The MSs studied correspond to world-renowned health resort medicine located in nine countries where they are applied as thermotherapeutic agents to more than one hundred thousand patients a year. Table 1 contains the main clinical trials of these MSs published in recent years (Table 1).

| Country | Authors (Year), Location of MS | Diagnosis | Study Design | Modalities | Peloid Application, Duration, Number | Conclusions |
|---------|--------------------------------|-----------|--------------|------------|--------------------------------------|-------------|
| Argentina | Monasterio and Grenovero (2008), Copahue [95] | Osteoarthritis, Knee and Hand | Prospective | Mud packs and/or General mud bath (Chancho), Thermal baths, Steam | 1 or 2 weeks 6 or 12 sessions 20 or 40 min/s | ↓ Pain |
| Brazil | Gouvêa et al. (2021), Peruibe [96] | Osteoarthritis, Knee | Prospective | Muds | 9 weeks 45 sessions 20 min/s | ↑ Joint flexibility |
| | Untura (2008), Poços de Caldas [97] | Osteoarthritis, Knee | Prospective | Muds, Kinesiotherapy, Physical therapy | 4 weeks 20 sessions 30–35 min/s | ↑ Joint flexibility |
| Czechia | Navrátil et al. (2014), Františkovy Lázne [98] | Temporomandibular joint disorders | Prospective | Muds, Pulsed magnetic therapy, Laser therapy, Education | 10–20 weeks 10 sessions 30 min/s | ↓ Pain |
| France | Forestier et al. (2010), Dax * [32] | Osteoarthritis, Knee | RCT | Muds, Massages, Showers, Pool sessions, Exercise therapy | 3 weeks 18 sessions 15 min/s | ↓ Pain |
| | Nguyen et al. (2017), Dax ** [46] | Low back pain | RCT | Muds, Jet showers, Massage, Hot showers, Hydro kinesiotherapy, Education | 5 days 6 sessions 15 min/s | ↑ Opening ability mouth |
| Hungary | Gyarmati et al. (2017), Hévíz [52] | Osteoarthritis, Hand | RCT | Muds | 3 weeks 15 sessions 20 min/s | ↓ Hand-grip strength |
| Israel | Sukenik et al. (1990), Dead Sea [99] | Rheumatoid arthritis | RCT | Mud packs, Sulphur baths | 2 weeks 12 sessions 20 min/ | ↓ Morning stiffness |
| | Sukenik et al. (1992), Dead Sea [100] | Rheumatoid arthritis | RCT | Mud packs | 2 weeks 12 sessions 20 min/ | ↓ Morning stiffness |
| | Sukenik et al. (1994), Dead Sea [101] | Psoriatic arthritis | RCT | Mud packs, Sulphur baths, Dead sea water baths, Climatotherapy | 3 weeks 18 sessions 20 min/ | ↓ Morning stiffness |
| | Elkayam et al. (2000), Dead Sea [102] | Psoriatic arthritis | RCT | Mud packs, Sulphur baths, Dead sea water baths, Climatotherapy | 4 weeks 24 sessions 20 min/ | ↓ Morning stiffness |
| | Sukenik et al. (2001), Dead Sea [103] | Psoriatic arthritis and Fibromyalgia | RCT | Mud packs, Sulphur baths, Dead sea water baths, Climatotherapy | 4 weeks 24 sessions 20 min/ | ↓ Pain threshold points |
| | Abu-Shakra et al. (2014), Dead Sea [105] | Low back pain | RCT | Mud packs | 3 weeks 15 sessions 20 min/ | ↓ Pain |

NSD Pain, NSD Disability, NSD Quality of life.
Table 1. Cont.

| Country | Authors (Year), Location of MS | Diagnosis            | Study Design | Modalities                                                                 | Peloid Application, Duration, Number | Conclusions               |
|---------|--------------------------------|----------------------|--------------|----------------------------------------------------------------------------|--------------------------------------|---------------------------|
| Spain   | Canelas et al. (2010), Archena [106] | Osteoarthritis, Knee | Prospective  | Muds, Sulphur baths, Showers, Massages                                   | 12 days, 12 sessions, 30 min/s        | ↓ Pain                    |
|         |                                 |                      | RCT          | Muds, Baths, Thermal jets                                                | 11 days, 30 min/s                    | ↑ Quality of life          |
|         |                                 |                      | Prospective  | Muds, Baths, Thermal jets                                                | 10 days, 45 min/s                    | ↑ Functional capacity     |
|         |                                 |                      | Prospective  | Muds, Baths, Thermal jets                                                | 10 days, 45 min/s                    | ↑ Quality of life          |
|         |                                 |                      | Prospective  | Muds, Aquatic therapy (Halliwick), Climatotherapy                        | 3 weeks, 30 min/s                    | ↓ Pain                    |
|         |                                 |                      | Prospective  | Muds, Aquatic therapy (Halliwick), Climatotherapy                        | 15 sessions, 2 weeks                 | ↑ Balance                 |
|         |                                 |                      | Prospective  | Muds, Aquatic therapy (Halliwick), Climatotherapy                        | 10 sessions, 30 min/s                | ↑ Balance                 |
|         | Moreo et al. (2017), Thalassia [107] | Post-stroke          |              |                                                                          |                                      |                          |
|         | Morer et al. (2020), Thalassia [108] | Post-stroke          |              |                                                                          |                                      |                          |

RCT: randomized controlled trial; NSD: not significant difference; ADL: Activities daily living; PASI: Psoriasis area severity index; (*) Dax, Balaruc-les Bains, Aix les Bains; (**) Dax, Saint Amand les-Eaux, Royat, Balaruc-les Bains, Aix les Bains.

It may be observed that they are used mostly in the treatment of disorders of the musculoskeletal system, especially in knee osteoarthritis, and, to a lesser extent, for psoriatic arthritis, back pain, rheumatoid arthritis and for the muscle pain of post-stroke patients. These indications are consistent with those of other peloids used in other important medical spas [35,37,38,40,41,47–50].

A study on osteoarthritis with laboratory animals was carried out with Peruibe’s peloid [109].

On the other hand, and although not as thermo-therapeutic, given the special climatic conditions of the thermal stations of Copahue and the Dead Sea, its peloids are also used in dermatological disorders. [110–115].

Given the importance of these MSs, both the solid and liquid phases of some have been studied, such as Copahue [68,115–118], Peruibe [119], Dax [72] and Archena, Arnedillo, Caldes de Boñí, El Raposo and Lo Pagan [17,74,120–123]; and organic matter, such as Hévíz [124–126] and the Dead Sea [21,127,128].

The centesimal water, solids and ash contents of the 16 MSs are provided along with their ash:solids ratios in Table 2. These ratios indicate that the first four peloids (Františkovy Lázně, Polańczyk, Caldes de Boí and Bad Bayersoien) have peat as their solid phases while the last 10 show the presence of inorganic materials. The peloid from Hévíz originates from the peat base of a lake at a depth of 38 m, which could explain its intermediate ash/solids value [124]. The Copahue peloid shows a reduced ash content due to the presence of sulphur compounds given its volcanic origin. This was confirmed by the odor emitted during the incineration of this peloid [115].

Table 3 lists the values of instrumental texture, hardness, adhesiveness and cohesion of the different spa peloids ordered according to their adhesiveness/hardness ratio.

Those of greater adhesiveness from El Raposo, Lo Pagan, Arnedillo and the Dead Sea could be used for brush applications. Owing to their greater cohesion, the peloids of Poço de Caldas, Thalassia and Carhué would be especially useful for specific body zones. Ge-nerally speaking, those of lower hardness are less abrasive for the patient as there is good correlation between these two parameters [74,121].
### Table 2. Centesimal composition of peloids used in medical spas (MSs) and raw materials (RMs).

| MS and RM                     | Water (%) | Solids (%) | Ash (%) | Ash/Solids |
|-------------------------------|-----------|------------|---------|------------|
| Františkovy Lázně (Czechia)  | 83.0      | 17.0       | 0.6     | 0.03       |
| Polančczyk (Poland)          | 87.1      | 12.9       | 0.6     | 0.04       |
| Caldes Boi (Spain)           | 84.4      | 15.6       | 1.6     | 0.10       |
| Bad Bayersoien (Germany)     | 85.6      | 14.5       | 1.9     | 0.13       |
| Copahue (Argentina)          | 56.2      | 43.8       | 16.0    | 0.36       |
| Hévíz (Hungary)              | 77.7      | 22.3       | 10.0    | 0.45       |
| Dead Sea (Israel)            | 30.1      | 70.0       | 54.2    | 0.77       |
| Lo Pagan (Spain)             | 34.3 *    | 65.7 *     | 56.2 *  | 0.85 *     |
| El Raposo (Spain)            | 39.6 *    | 60.4 *     | 53.2 *  | 0.88 *     |
| Thalassia (Spain)            | 59.9      | 40.1       | 35.8    | 0.88       |
| Carhue (Argentina)           | 44.5      | 55.5       | 40.0    | 0.90       |
| Peruibe (Brazil)             | 58.8      | 41.2       | 37.6    | 0.91       |
| Archenas (Spain)             | 74.6 *    | 25.4 *     | 23.3 *  | 0.92 *     |
| Terdax (France)              | 46.1 **   | 53.9 **    | 50.2 ** | 0.93 **    |
| Arnedillo (Spain)            | 31.4 *    | 68.6 *     | 64.5 *  | 0.94 *     |
| Poços de Caldas (Brazil)     | 52.6      | 49.8       | 47.4    | 0.95       |
| C1                            | 12.55     | 87.45      | 81.46   | 0.93       |
| C2                            | 11.54     | 88.46      | 82.70   | 0.93       |
| C3                            | 1.00      | 99.00      | 88.15   | 0.89       |
| C4                            | 8.3       | 91.70      | 85.93   | 0.94       |
| C5                            | 9.45      | 90.55      | 81.32   | 0.90       |
| C6                            | 10.14     | 89.86      | 82.19   | 0.91       |
| P7                            | 23.89     | 76.11      | 2.31    | 0.03       |
| P8                            | 31.96     | 68.04      | 39.37   | 0.57       |
| MC9                           | 4.07      | 95.93      | 0       | 0          |

* Data from Maraver et al., 2004 [120]; ** Armijo, 2007 [121]. C1 to MC9 are raw materials (RMs).

### Table 3. Instrumental texture of the peloids used in medical spas (MSs) and the raw material–distilled water mixtures (RM/DW).

| MS and RM/DW          | Hardness (g) | Adhesiveness (g s) | Cohesiveness | Adhesiveness/Hardness |
|-----------------------|--------------|--------------------|--------------|-----------------------|
| Peruibe (Brazil)      | 38           | 1                  | 0.48         | 0.01                  |
| Polančczyk (Poland)   | 924          | 763                | 0.30         | 0.83                  |
| Bad Bayersoien (Germany) | 1163     | 1410               | 0.23         | 1.21                  |
| Copahue (Argentina)   | 200          | 890                | 0.45         | 4.45                  |
| Františkovy Lázně (Czechia) | 105       | 709                | 0.56         | 6.78                  |
| Caldes Boi (Spain)    | 106          | 909                | 0.61         | 8.56                  |
| Dead Sea (Israel)     | 350          | 3097               | 0.86         | 8.84                  |
| Hévíz (Hungary)       | 139          | 1272               | 0.70         | 9.14                  |
| Arnedillo (Spain)     | 462 *        | 4962 *             | 0.50 *       | 10.74                 |
| Carhue (Argentina)    | 65           | 696                | 0.96         | 10.76                 |
| Poços de Caldas (Brazil) | 122        | 1426               | 0.99         | 11.69                 |
| Thalassia (Spain)     | 45           | 548                | 0.96         | 12.10                 |
| Lo Pagan (Spain)      | 461 *        | 6966 *             | 0.50 *       | 15.11                 |
| El Raposo (Spain)     | 394 *        | 7102 *             | 0.80 *       | 18.03                 |
| Archenas (Spain)      | 132 *        | 2491 *             | 0.80 *       | 18.87                 |
| Terdax (France)       | 138 *        | 2646 *             | 0.65 *       | 19.17                 |
| C1                    | 300          | 3672               | 0.96         | 12.24                 |
| C2                    | 300          | 3216               | 0.92         | 10.72                 |
| C3                    | 300          | 2481               | 0.71         | 8.27                  |
| C4                    | 300          | 3317               | 0.88         | 11.06                 |
| C5                    | 300          | 2950               | 0.81         | 9.83                  |
| C6                    | 300          | 3558               | 0.93         | 11.86                 |
| P7                    | 300          | 15                 | 0.38         | 0.05                  |
| P8                    | 300          | 1                  | 0.26         | 0.03                  |
| MC9                   | 300          | 1437               | 0.42         | 4.79                  |

* Data from Armijo, 2007 [121].
As we stated in the introduction and methods, the main therapeutic action of the peloids in rheumatic disorders is due to the action of heat and the way in which they are applied; the most important factor is the amount of water that the peloid contains due to its high values of \( C_p \) heat flow (\( \Phi \)), the amount of heat (\( Q \)) that passes in the unit of time toward the temperature drop.

In Table 4, we provide \( C_p \) data obtained from the analysis of the percentage of water and ash composition of the MSs, along with the \( t_r \) and \( Q \) released by 1 kg of peloid as the temperature drops from 45 to 39.3 °C (\( t_r \) temperature), and \( \Phi \) from the start of the application until the \( t_r \) is reached.

The higher \( t_r \) were recorded for the peloids based on organic material, peat, and those used in the Františkovy Lázně, Polanczyk, Bad Bayersoien and Boi spas, meaning they release their heat more slowly than those prepared with inorganic solid phases. The \( C_p \) values for the peloids based on peat were in line with those reported in the literature [85].

The \( \Phi \) values of MSs ranged from 25.1 J/s for the Poço de Caldas peloid to 33.4 J/s for the Arnedillo and Thalassia peloids.

Table 4. Specific heat (\( C_p \)), relaxation time, heat amount and heat flow recorded for peloids used in medical spas (MSs) and the pastes (RM/DW) with a hardness of 300 g.

| MS and RM/DW                      | \( C_p \) (J/gK) | \( t_r \) (s) | \( Q \) (J) | \( \Phi \) (J/s) |
|-----------------------------------|-----------------|--------------|------------|---------------|
| Dead Sea (Israel)                | 1.9             | 400          | 10,830     | 27.1          |
| Arnedillo (Spain)                | 1.9             | 324          | 10,830     | 33.4          |
| Lo Pagán (Spain)                 | 2.0             | 400          | 11,571     | 28.9          |
| El Raposo (Spain)                | 2.2             | 468          | 12,654     | 27.0          |
| Terdax (France)                  | 2.4             | 456          | 13,908     | 30.5          |
| Poços de Caldas (Brazil)         | 2.5             | 564          | 14,136     | 25.1          |
| Carhue (Argentina)               | 2.8             | 578          | 15,789     | 27.3          |
| Copahue (Argentina)              | 2.9             | 648          | 16,302     | 25.2          |
| Peruíbe (Brazil)                 | 2.9             | 534          | 16,416     | 30.7          |
| Thalassia (Spain)                | 2.9             | 498          | 16,644     | 33.4          |
| Archena (Spain)                  | 3.4             | 708          | 19,437     | 27.5          |
| Hévíz (Hungary)                  | 3.5             | 624          | 20,064     | 32.2          |
| Františkovy Lázně (Czechia)      | 3.7             | 744          | 21,033     | 28.3          |
| Caldes Boi (Spain)               | 3.7             | 684          | 21,204     | 31.0          |
| Bad Bayersoien (Germany)         | 3.8             | 696          | 21,432     | 30.8          |
| Polańczyk (Poland)               | 3.8             | 726          | 21,717     | 29.9          |
| C1                                | 2.6             | 486          | 15,039     | 30.9          |
| C2                                | 2.9             | 528          | 16,638     | 31.5          |
| C3                                | 2.1             | 330          | 12,176     | 36.9          |
| C4                                | 2.6             | 462          | 14,710     | 31.8          |
| C5                                | 3.0             | 468          | 16,814     | 35.9          |
| C6                                | 3.2             | 522          | 18,199     | 34.9          |
| P7                                | 3.6             | 624          | 20,675     | 33.1          |
| P8                                | 2.4             | 468          | 13,834     | 29.6          |
| MC9                               | 3.1             | 600          | 17,906     | 29.8          |

3.2. Raw Materials (RMs) and the Pastes (RM/DW)

As we have indicated previously, another of the objectives of this work is to study and proposed RMs that make the elaboration of pastes (RM/DW) possible with mechanical and thermal properties similar to MSs for use as a solid phase for the preparation of peloids as thermotherapeutic agents. We followed the same criteria as for the MSs to achieve this; that is to say, we studied the centesimal composition, instrumental texture and thermal parameters.

Table 2 also shows the centesimal water, solids and ash contents of the RMs. When calculating the ash-to-solids ratio of the solid phase, values close to unity indicate an inorganic product while those approaching zero reflect an organic product, just as for the MSs.
Regarding the instrumental texture of the pastes (RM/DW), the hardness diminishes as their water content rises, following a negative exponential curve. This was not the case for the pastes (RM/DW) based on peat that reached a maximum hardness value. It should be noted that the product MC9, as it is organic, behaved in this regard like a clay, as can be seen in Figure 2. In this figure, we have limited ourselves to including only three inorganic RMs—C1, C3 and C6—and two organic ones—P8 and MC9—for clarity [91].

![Figure 2](https://via.placeholder.com/150)

**Figure 2.** Plots of hardness of the pastes against % water content.

Table 3 also shows the values of instrumental texture, hardness, adhesiveness, cohesion and the adhesiveness/hardness ratio of the pastes (RM/DW). The pastes (RM/DW) prepared with materials C1 to C6 and MC9 with a hardness of 300 g (we adopted this value because it is the average value of the Spanish peloids we have already studied) previously presented an adhesiveness that ranged from 2481 g in the formulation with C3 to 3672 g for the C1-based formulation, and a hardness of only 1437 g was observed for the organic material MC9. This indicates that the pastes would, overall, show good adhesive properties for the user and pastes (RM/DW) prepared with C3 and MC9 will be more easily removed after their use. The pastes (RM/DW) based on inorganic materials showed much higher ratios than those containing organic materials in the solid phase, as occurs in the MSs. Cohesiveness values are provided for the pastes. The pastes (RM/DW) prepared with inorganic materials showed much higher cohesiveness values than those recorded for the pastes (RM/DW) containing organic materials in their solid phase, as occurs in the MSs [74].

When water is added to a clay, it arranges itself around the clay particles. If little water is added, clays become coated with water layers, giving rise to a mass with some cohesion. This weak cohesive force between aggregates determines that the clay particles do not slide over each other. This property is made use of when the peloid is applied to the skin for therapeutic purposes [129]. If the water concentrations present in peloids and pastes are reduced, this leads to a lower mobility of bonds and to the products breaking up. As the proportion of water increases, the greater distance between particles causes cohesion loss and the product behaves more or less like a viscous liquid [130].

The adhesiveness/hardness ratios of the pastes (RM/DW) prepared from the inorganic and organic materials and distilled water are shown in Table 3. The inorganic pastes had higher ratios than the pastes made from organic materials, as occurs in the MSs.
Regarding the thermal parameters, the \((C_p)\) measured from the RM given in J/gK were C1 = 0.859, C2 = 0.981, C3 = 0.972, C4 = 0.870, C5 = 0.765, C6 = 1.253, P7 = 1.291, P8 = 1.148 and MC9 = 1.420 [80].

We also provide the mean \((C_p)\) data obtained from the pastes (RM/DW) prepared with the inorganic and organic materials in Table 4. These results are in line with those obtained in prior work and, overall, the \((C_p)\) values of the organic materials were higher than those of the inorganic materials [61,66,71,73,77,81,82,86,131,132].

The highest \((C_p)\) (expressed in J/gK) was recorded for a paste prepared with the palygorskite clay (C6) and the lowest for a paste prepared with kaolin (C3). The elevated \((C_p)\) of the preparation based on P7 can be attributed to the large amount of water needed for its preparation (Figure 3).

Table 4 also provides the \((C_p)\) in J/gK, \(t_r\) in seconds, the Q in J lost by 1 kg of the MSs and pastes (RM/DW) as it cools from 45 to 39.3 °C, the \(t_r\) temperature, and the \(\Phi\) as the J/s reached that temperature range for the MSs and pastes (RM/DW) examined here.

Other works carried out with pastes made with different solid (organic and inorganic) and liquid (DW, natural mineral water and sea water) phases determine the heat transfer curves with temperature ranges that are different from those used [61,66,70,75,83,89,132].

For distilled water, the \(t_r\) determined under the same conditions as for the MSs and pastes (RM/DW) was 230 s, much lower than the values observed for the MSs and pastes (RM/DW).

According to the \(t_r\) values in seconds calculated from the heat loss curves for the different pastes, the preparation containing C3 was the fastest at releasing heat, while the slowest in doing so were the C2-based pastes. The pastes containing the organic products P7 and MC9 also released heat slowly.

Corresponding values for the pastes RM/DW were between 29.6 J/s for P8 and 36.9 J/s for the C3-based ones, similar to the values recorded for the MSs.

If we compare the heat-releasing capacity of the MSs and pastes (RM/DW) to that of water, 1 kg of water with a mean \((C_p)\) of 4.1788 J/kg K cooling in the same conditions as the MSs and pastes (RM/DW) has a \(t_r\) of 230 s and would release a Q of 23,819 J at a \(\Phi\) of 103.56 J/s. This means that the solid phases of MSs and pastes (RM/DW) cause the heat to

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**Figure 3.** Specific heats of the raw materials (RMs), and specific heats and relaxation times of the raw material–distilled water (RM/DW) formulations.
be released three to four times slower than if we applied water directly, which indicates that they can be used on the skin for a thermotherapeutic effect without undesirable effects. Thus, compared to water, the MSs and pastes (RM/DW) enable the application of a large amount of heat over a longer time period in a more localized manner (Figure 4).

**Figure 4.** Heat flows recorded for the RM/DW formulations, distilled water and MS.

### 4. Conclusions

The peloids of the MSs studied, according to the literature cited, are used as thermotherapeutic agents in the treatment of musculoskeletal disorders, especially in knee osteoarthritis and, to a lesser extent, in back pain and psoriatic arthropathy.

The main effects of the application of the MSs studied are the reduction of pain, the increase in the functional capacity of the joint and an improvement in the quality of life.

Considering the centesimal composition of these products, it can be concluded that the ash:solids ratio of the peloids used in the medical spas (MSs) studied, just like the RMs proposed, indicates that a value close to zero corresponds to the organic solid phases, while values close to one correspond to the inorganic phases.

The behavior of the instrumental texture of the pastes (RM/DW) prepared with clays and microcrystalline cellulose is similar to that of the peloids used in medical spas (MSs) with an inorganic solid phase, highlighting that microcrystalline cellulose is an organic product.

As thermotherapeutic agents, all the medical spas (MSs) studied and the pastes examined, both organic and inorganic, showed a heat flow rate of up to four times lower than that shown by the same amount of water. The raw materials studied can be used as solid phases for the preparation of peloids with mineral waters.

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