2017 International Nuclear Atlantic Conference - INAC 2017
Belo Horizonte, MG, Brazil, October 22-27, 2017
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR – ABEN

Agência Brasileira do ISBN
ISBN 978-85-99141-07-6

BENTONITE MATURATION WITH "ÁGUAS DE LINDÓIA" WATER (SP)

Jefferson K. Torrecilha and Paulo S. C. Silva

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
jeffkoy@usp.br

ABSTRACT

This study aims to characterize the artificial peloid obtained by maturing bentonite with Águas de Lindóia water for periods of three, six and nine months. The pH, moisture, organic matter content, loss on ignition and swelling power of matured and non-matured samples were measured for physicochemical characterization. The elemental concentration was determined by instrumental neutron activation analysis. Results showed that water adsorption capacity, organic matter and swelling power is related to the maturation time and no significant differences occurs in the elemental concentration except for Na.

1. INTRODUCTION

Peloids have been used as thermal therapeutic agents in many spas and thermal centers since ancient times. The term 'peloid' is used to refer to different kinds of sediments or deposits whose compositions include mainly silicates (micas, clays, feldspars, etc.) but also carbonates, sulphates, sulphides and a variable amount of organic substances. When mixed with sea or minero-medicinal waters these elements form pastes or poultices for thermal uses [1]. It can be applied to different parts of the body or on the whole body by means of masks and poultices, or even by partially or totally bathing the body, for therapeutic or cosmetic purposes.

For peloid obtainment, it passes by a maturation process, during which its characteristic greasiness is acquired, due to components mixing and the growth of organic constituents that arise from biological activity [2, 3]. Peloids are formed naturally in a wide range of environments all over the world and in Brazil, only the Peruíbe Black Mud (PBM) had been studied and is well chemically characterized [4]. Nevertheless, the use of these natural peloids in spas and thermal therapeutic centers for cosmetic and medicinal purposes can lead to a depletion of this natural resource over the time [5].

This study proposes to characterize the elemental composition of the peloids artificially obtained by the maturation process of mixing bentonite with minero-medicinal water from Águas de Lindóia (SP). The bentonites have been used as peloid for their high swelling index, high plasticity, water limit and specific heat that improve the quality of the pastes [6].

The Águas de Lindóia water is a low radioactivity, hypo-saline water that emerges at 37 °C and is commonly used for rheumatic and skin affections treatment.

2. METHODOLOGY

The bentonite was acquired in the formal market and for the maturation process, samples were left in contact with running water in the Águas de Lindóia balneary and collected after three, six and nine months (BL3M, BL6M and BL9M, respectively). After collection, the samples were dried, transferred to a mortar, crushed and sieved to a grain size smaller than 150 mesh and irradiated in the IEA-R1 reactor at IPEN, together with certified reference materials, to be analyzed by instrumental neutron activation analysis (INAA). The irradiation occurred at a neutron flux of 10^{12} cm^{-2} s^{-1}, during 8 hours and the induced activity were measured by gamma spectrometry.

For physicochemical characterization, wet samples were treated, sequentially: a) at 105 °C, for 24 h to determine the moisture content; b) at 550 °C, for 4 h, to estimate the organic matter content and c) at 1000 °C, for 2 h, to determine the carbonate and hydroxide mass losses by employing an oven furnace and muffle, as needed [7].

The swelling capacity of bentonites samples was obtain by adding 1 g of dry sample to deionized water in a 100 mL graduated cylinder and recording the volume after 24 h [8].

The pH was determined by mixing 10 mL of the wet mud sample with 25 mL of KCl 1.0 mol L^{-1}. The solutions were stirred for 5 min, let to stand for 1 h and, then, the measurement was done. All the physicochemical parameters were measured in triplicate.

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization

The pH of the bentonite before and after maturation process does not varied (Table 1), being around 7.8 for three, six and nine months. The initial pH of the bentonite (7.8) is also not significantly different from the pH of the used water (7.5, measured in water samples of Águas de Lindóia balneary). Reported values of pH in medicinal muds varies from 6.5 to 8.9 [4, 9-12]. The pH values may influence the availability of the chemical elements adsorbed in the mineral grains composing the mud and a small change in this parameter may affect ionic exchange properties during skin contact.

The moisture content, by mass, in the bentonites varied from 6 to 11%. It is possible to note a decrease in the hydration degree in the bentonite samples during the maturation process, occurring mainly from six months to nine months. This results is smaller than in Peruíbe Black Mud [4], that varied from 34 to 73% and some clays used for pharmaceutical propose [13] that varies from 5 to 17%, indicating that the water adsorption capacity is highly dependent of the origin and type of the clay mineral comprising the peloid.

The organic matter content found in medicinal muds may be related to its therapeutic properties [14] and, a peloid is constituted by a geological part composed by the clay and water mixture and an organic part that provides biological metabolic activity. Organic matter content is inversely correlated to the abrasiveness of the mud [15]. The content of organic matter in the bentonite samples varied from 1.6 to 2.8. It is possible to note an increase of organic matter depending on the maturation time. The organic matter increase may be related to the biological activity of microorganisms present in the water or the ones already living in the bentonite that found in the water a good environment for growing. Literature values for organic matter content vary from 0.78 to 20% [3, 4].

Considering the weight % of LOI at 1000 °C values, which stayed around 3.7%, were lower than bentonites from main Sardinia deposits presenting values from 5 to 15% [1, 6]. The bentonite used here presents a low content of coordinated hydroxyl that characterizes clay minerals in its non-matured form and the maturation process with Águas de Lindóia water seems to decrease this amount.

Swelling power, measured in bentonites samples to verify its interaction with a polar media, increased after three months of maturation and, in average, is not significantly different of the starting swelling after six and nine months. Nevertheless, the values measured can be considered high proving the bentonite hydrophilicity [16]. In bentonites from Sardinia deposits the swelling values varied from 6 to 39 mL g^{-1} [6] and literature relates values varying from 15 to 25 mL g^{-1} for some other clays also used to pharmaceutical proposes [4, 13].

Table 1: Physicochemical parameters: pH, swelling values and percentages of moisture, LOI at 550 ºC and LOI at 1000 °C.

	pH	Swelling (mL g^{-1})	Moisture (%)	LOI (%)[a] at 550 °C	LOI (%)[b] at 1000 °C
BENTONITE	7.8	12.2	13.93	1.12	4.53
BL3M	7.8	16.7	11.1	1.6	3.7
BL6M	7.8	12.7	11.19	1.7	3.9
BL9M	7.7	13	6.2	2.8	3.3

[a] Determined by calcination at 550 °C, for 4 h.
[b] Determined by calcination at 1000 °C, for 2 h

3.2. Elemental characterization

For methodology precision and accuracy verification for neutron activation analysis, certified reference materials Syenite Table Mountain (STM-2), from United States Geological Survey (USGS) was analyzed. The results are shown in Table 2 and it can be observed that good precision and accuracy were obtained for the most of the elements with relative standard deviation (RSD) and relative error (RE) generally lower than 10%.

The concentration of trace elements in bentonite non-matured, BL3M, BL6M and BL9M is showed in Table 3, for those elements determined by INAA. As security is always a concern, to be used as therapeutic and cosmetic products, clays have to be completely characterized for impurity content, mainly for the potentially toxic elements, although there is no established official regulation about chemical composition for peloids, either as raw material or as matured form, to be used in pelotherapy. Therefore, the obtained results for bentonites samples were compared to consensus based sediment quality guidelines (SQGs), also showed in Table 3 [17]. The SQG values, the threshold effect concentration (TEC) and probable effect concentration (PEC), provide a reliable basis for assessing sediment quality conditions in aquatic ecosystems for some potentially toxic elements and the results of the bentonite elemental concentrations revealed that none of them is higher than the TEC values.

Table 2: Values obtained in the certified reference materials analysis for quality control of the results, in µg g^{-1}, except were indicated %.

	STM Certified Value	Analysis value	RSD	RE
Ba	639 ± 61	657 ± 103	15.61	-2.75
Ca (%)	0.78 ± 0.03	0.53 ± 0.07	12.44	32.63
Ce	256 ± 23	239 ± 2	0.97	5.36
Cs	1.52 ± 0.06	1 ± 0.2	23.16	31.64
Eu	3.45 ± 0.25	2.89 ± 0.04	1.24	16.21
Fe (%)	3.77 ± 0.09	3.97 ± 0.06	1.51	-5.36
Hf	27 ± 0.8	24.5 ± 0.1	0.58	9.11
K (%)	0.38 ± 0.17	4 ± 1	25.51	-23.51
La	154 ± 11	140.7 ± 0.6	0.44	8.63
Lu	0.6 ± 0.04	0.55 ± 0.01	2.74	9.14
Na (%)	6.61 ± 0.68	6.17 ± 0.09	1.39	6.63
Nd	81 ± 4.8	101 ± 13	13.05	-24.82
Rb	114 ± 11	139 ± 9	6.69	-21.50
Sm	12 ± 0.9	14.23 ± 0.04	0.29	-18.59
Ta	16 ± 1.1	24.5 ± 0.1	0.58	-53.38
Tb	1.38	0.99 ± 0.04	4.45	25.42
Th	27 ± 5	32.1 ± 0.4	1.18	-18.98
U	7.6	12 ± 1	8.61	-55.63
Yb	4.2 ± 0.8	3.2 ± 0.1	1.85	23.89
Zn	223 ± 19	193 ± 9	4.90	13.43

Compared with the values for elements found in peloids from European spas and PBM [18] and PBM [4], it is observed that the concentrations of Br, Co, Cr, Cs, Na, and Rb are lower and the concentrations of Ca, Sb, Sm, Ta, Tb, Th and U are higher in these bentonite samples.

Comparing the concentration values determined in non-matured bentonite and the matured ones at three, six and nine months (BL3M, BL6M and BL9M) it was not observed a significant change in the elements concentration except a slightly increase for Co (1.16 to 1.36 $\mu g\ g^{-1}$), K (0.5 to 1.2 %), Rb (14.5 to 17 $\mu g\ g^{-1}$), Se (1.5 to 3.2 $\mu g\ g^{-1}$), Sm (10.3 to 11.6 $\mu g\ g^{-1}$), Ta (2.4 to 3.37 $\mu g\ g^{-1}$) and Yb (1.83 to 3.64 $\mu g\ g^{-1}$) with the maturation time while Na concentration decreased (1.47 to 0.89%). This result must be related to the fact that Águas de Lindóia water, as mentioned before, is an hypo-saline water and only Ba, Ca, Fe, Br, K and Na are found in the order of few mg L^{-1} while all the other elements are found in the order of $\mu g\ L^{-1}$ [19].

4. CONCLUSIONS

This work proposed to characterize the elemental composition of the peloids artificially obtained by the maturation process of mixing bentonite mineral medicinal water from Águas de Lindóia (SP).

The physicochemical parameters pH, moisture, organic matter, loss on ignition and swelling power of the obtained peloid is in good agreement with that observed in literature. No significant variation was observed for the pH between non-matured and matured samples. Moisture and LOI at 1000 °C presented a slightly decrease indicating that the water adsorption may change with the maturation process while swelling power and organic matter presented a trend of increasing with maturation time. As defined in literature, the organic matter content differentiates an ordinary mud from a therapeutic peloid.

Due to the fact that the water used is classified as hypo-saline water the elemental concentrations do not present a significant difference before and after the maturation although it is worth to note that a slightly increase occurs for elements such as Co, K, Rb and Se and a decrease for Na concentration.

Table 3: Trace element concentrations, in µg g^{-1}, except where indicated %, in bentonite samples and the threshold effect concentration (TEC) and probable effect concentration (PEC) values (MacDonald et al., 2000).

	As	Cr	Zn	Ba	Br	Ca	Ce
BENTONITE	9.3 ± 0.1	7.2 ± 0.2	90 ± 1	316 ± 11	7.06 ± 0.08	1.13 ± 0.02	98.6 ± 0.4
BL3M	9.1 ± 0.1	7.1 ± 0.2	85 ± 1	351 ± 11	9.47 ± 0.08	1.08 ± 0.02	112.7 ± 0.4
BL6M	9.8 ± 0.2	6.8 ± 0.3	108 ± 2	475 ± 17	0.66 ± 0.06	1.07 ± 0.03	97.4 ± 0.4
BL9M	7.9 ± 0.2	6.6 ± 0.3	86 ± 3	355 ± 17	2.71 ± 0.08	0.75 ± 0.02	103 ± 2
TEC/PEC	9.79/33	44.3/111	121/459				
	Co	Cs	Eu	Fe (%)	Hf	K (%)	La
BENTONITE	1.16 ± 0.02	0.3 ± 0.1	0.994 ± 0.007	2.23 ± 0.02	7.07 ± 0.03	0.5 ± 0.09	50.6 ± 0.6
BL3M	1.33 ± 0.01	0.5 ± 0.1	0.737 ± 0.007	2.72 ± 0.02	7.98 ± 0.02	0.51 ± 0.09	54.4 ± 0.7
BL6M	1.36 ± 0.02	0.6 ± 0.1	0.648 ± 0.006	2.41 ± 0.02	7.65 ± 0.03	1.2 ± 0.2	47.6 ± 0.9
BL9M	1.36 ± 0.02	0.5 ± 0.1	0.633 ± 0.014	2.68 ± 0.02	8.1 ± 0.06		50 ± 1
	Lu	Na (%)	Nd	Rb	Sb	Sc	Se
BENTONITE	0.521 ± 0.006	1.47 ± 0.02	48 ± 1	14.5 ± 0.4	1.23 ± 0.02	5.49 ± 0.02	1.5 ± 0.1
BL3M	0.611 ± 0.005	1.25 ± 0.02	62 ± 1	13.7 ± 0.4	1.42 ± 0.02	6.3 ± 0.02	1.7 ± 0.1
BL6M	0.563 ± 0.006	1.06 ± 0.02	71 ± 1	16.6 ± 0.5	1.32 ± 0.03	5.23 ± 0.01	2.2 ± 0.1
BL9M	0.56 ± 0.01	0.89 ± 0.01	57 ± 2	17 ± 0.7	1.13 ± 0.06	6.12 ± 0.02	3.2 ± 0.1
	Sm	Ta	Tb	Th	U	Yb	Zr
BENTONITE	10.3 ± 0.3	2.4 ± 0.03	1.5 ± 0.05	37.4 ± 0.1	13 ± 0.2	1.83 ± 0.02	302 ± 14
BL3M	11.3 ± 0.3	2.71 ± 0.03	1.68 ± 0.02	44 ± 0.1	14.5 ± 0.2	3.58 ± 0.02	329 ± 10
BL6M	11.6 ± 0.3	2.16 ± 0.03	1.41 ± 0.05	36.1 ± 0.1	7.3 ± 0.2	3.64 ± 0.04	315 ± 20
BL9M	11.4 ± 0.3	3.37 ± 0.07	1.37 ± 0.04	40 ± 2	13.3 ± 0.4	3.56 ± 0.18	327 ± 10

REFERENCES

1. J. L. Legido, C. Medina, M. L. Mourelle, M. I. Carretero, M. Pozo, "Comparative study of the cooling rates of bentonite, sepiolite and common clays for their use in pelotherapy", *Applied Clay Science*, **36**, pp.148–160 (2007).
2. M. Mosso, M. De la Rosa, M. Díaz, "Microbiología del manantial de águas minero medicinales y de los lodos del balneario de Arnedillo", *Anales de la Real Academia Nacional de Farmacia*, **14**, pp.23–28 (1988).
3. M. V. Fernández-González, J. M. Martín-García, G. Delgado, J. Párraga, M. I. Carretero, R. Delgado, "Physical properties of peloids prepared with medicinal mineral waters from Lanjarón Spa (Granada, Spain)", *Applied Clay Science*, **135**, pp.465–474 (2017).
4. P. S. C. Silva, J. K. Torrecilha, P. F. M. Gouvea, M. F. Máduar, S. M. B. Oliveira, M. A. Scapin, "Chemical and radiological characterization of Peruíbe Black Mud", *Applied Clay Science,* **118**, pp.221-230 (2015).
5. F. Veniale, E. Barberis, G. Carcangiu, N. Morandi, M. Setti, D. Tessier, "Formulation of muds for pelotherapy: effects of "maduration" by different mineral waters", *Appl. Clay Sci.* **25**, pp. 135–148 (2004).
6. S. Cara, G. Carcangiu, G. Padalino, M. Palomb, M. Tamanini, M, "The bentonites in pelotherapy: chemical, mineralogical and technological properties of materials from Sardinia deposits (Italy)", *Applied Clay Science*, **16**, pp.117–124 (2000).
7. W. E. Dean, 1974. "Determination of carbonate and organicmatter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods", *Journal of Sedimentary Petrology*. **44**, pp.242–248 (1974).
8. M. D. Foster, U. S. G. Survery, D. C. Washington, "Geochemical studies of clay minerals: II — relation between ionic substitution and swelling in montmorillonites", *American Mineralogist*, **38**, pp.994–1006 (1953).
9. M. C. Karakaya, N. Karakaya, S. Sarıoğlan, M. Koral "Some properties of thermal muds of some spas in Turkey". *Applied Clay Science*, **48**, pp.531–537 (2010).
10. A. Knorst-Fouran, L. M. Casás, J. L. Legido, C. Coussine, D. Bessières, F. Plantier, J. Lagière, K. Dubourg, "Influence of dilution on the thermophysical properties of Dax peloid (TERDAX®)", *Thermochimica Acta*, **539** (10), pp.34–38 (2012).
11. M. I. Carretero, M. Pozo, J. L. Legido, M. V. Fernández-González, R. Delgado, I. Gómez, F. Armijo, F. Maraver, "Assessment of three Spanish clays for their use in pelotherapy", *Applied Clay Science*, **99**, pp.131–143 (2014).
12. M. S. Muñoz, C. M. Rodríguez, A. G. Rudnikas, O. D. Rizo, M. Martínez-Santos, E. Ruiz-Romera, J. R. F. Castillo, A. Pérez-Gramatges, N. V. Martínez-Villegas, D. B. Padilla, R. H. Díaz, P. González-Hernández, "Physicochemical characterization, elemental speciation and hydrogeochemical modeling of river and peloid sediments used for therapeutic uses", *Applied Clay Science*, **104**, pp.36–47 (2015).
13. A. López-Galindo, C. Viseras, P. Cerezo, "Compositional, technical and safety specifications of clays to be used as pharmaceutical and cosmetic products", *Applied Clay Science*, **36**, pp.51–63 (2007).
14. C. Gomes, M. I. Carretero, M. Pozo, F. Maraver, P. Cantista, F. Armijo, J. L. Legido, F. Teixeira, M. Rautureau, R. Delgado, "Peloids and pelotherapy: historical evolution, classification and glossary". *Applied Clay Science*. **75–76**, pp.28–38 (2013).
15. M. Pozo, M. I. Carretero, F. Maraver, E. Pozo, I. Gómez, F. Armijo, J. M. A. Rubí, "Composition and physico-chemical properties of peloids used in Spanish spas: a comparative study", *Applied Clay Science*. **83–84**, pp.270–279 (2013).

16. M. M. G. R. Vianna, C. L. V. José, C. A. Pinto, P. M. Büchler, F. R. Valenzuela Díaz, “Preparação de duas argilas organofílicas visando seu uso como sorventes de hidrocarbonetos”, *Anais do 46º Congresso Brasileiro de Cerâmica (CD-Rom)*, São Paulo, 1860-1871 (2002).
17. D. D MacDonald, G. Ingersoll, T. A. Berger, “Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems”, *Archives of Environmental Contamination and Toxicology*, **39**, pp.20–31 (2000).
18. A. Quintela, D. Terroso, E. Ferreira d Silva, F. Rocha, “Certification and quality criteria of peloids used for therapeutic purposes”, *Clay Minerals*, **47**, pp.441–451 (2012).
19. P. S. C. Silva, C. H. R. Saueia, J. P. Oliveira and F. T. Lazzerini, “Effective dose assessment due to Águas de Lindóia water ingestion”, *International Conference Environmental Radioactivity*, Greece (2015).