

PROPERTIES OF SPONGILLITE AND PROSPECTIVES OF ITS USAGE

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ABSTRACT

The present work is dedicated to the study of principal features of spongillite from the State of Mato Grosso do Sul (Brazil). It is present in the form of amorphous silica, along with orthosilicic acids of varying composition. Main concomitant elements are titanium and iron. Scanning electronic microscopy showed the presence of hollow needles or microcapillaries and traces of organic detritus. Since the chemical composition of spongillite is that of poorly crystallised silica, it is recommended to be used as inorganic adsorbent and as a bioavailable silicon source. Due to its composition and morphological characteristics it can be blended into one mass with glass waste in the fabrication of lightweight product having a closed-cell structure, ideal as insulating material for oil and gas pipes. Useful materials can be fabricated at minimal expenses by recycling glass waste piled up in Mato Grosso do Sul and neighbouring Brazilian States.

INTRODUCTION

Spongillite or as it is also called spiculite is a product essentially constituted by siliceous needles that are originated from skeleton of sponges and related organisms and accompanied by quartz sand and organic material. In Brazil it basically occurs in peat-bog ponds in the southwestern part of Minas Gerais State, southern Goiás, northeastern Mato Grosso do Sul and São Paulo States [Volkmer-Ribeiro C. et al., 1995, Motta, 1986, Volkmer-Ribeiro, C. et al., 1998]. Siliceous sponges deposit silica in needlelike spicules that support the organisms and provide defense against predation. They were built up by taking up orthosilicic acid from sea water and processing it through complicated biochemical pathways [Kroeger N. et al., 1999]. The gross production of biogenic silica in surface waters was

estimated to amount to 240 ± 40 Tmol of silicon per year [Tacke R., 1999]. The places of spongillite deposits are popularly called in Brazil "mica powder ponds" due to itch and irritation that may demand urgent medical attention. They are caused by microscopic spongillite needles with sharp points. In principle, in a long run it might also lead to the development of chronic lung condition [Rosenberg, D. M., 2000].

The practice of employing this mineral is limited. In Mato Grosso do Sul and Minas Gerais States spongillite is used only as a component in bricks fabrication, in Bahia State it was used for thermal insulators and pigments [Petri and Fúlfaro, 1983]. So far there is no other knowledge of putting it to use. However, taking into account that it is made of nanostructural amorphous silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) one may envisage its use for ion adsorption, as recently proposed [Silva Maia, F., et al., 2000]. Available general bibliography on spongillite concerns exclusively the sponges species producing this material [Volkmer-Ribeiro C. 1995, Motta J.F.M. et al., 1986] and mineralogical characterisation of spongillite from Minas Gerais State [Araújo da Matta Machado, E., 2000]. The present study deals with the physico-chemical properties and morphology of spongillite from Mato Grosso do Sul State in order to ascertain the possibilities of its prospective value.

EXPERIMENTAL

Materials and methods

The spongillite samples provided by the Companhia de Desenvolvimento do Estado de Mato Grosso were taken from the pond Lagoa de Araré, Paranaíba region, MS, where spongillite layer is about 2 m thick [Souza, D.D. et al., 1988]. Raw mineral was washed and mechanically separated using different sieves performed. Density was determined at 25°C in a pycnometer after previous evacuation of the air and

washing with helium, by using an AccuPyc 1330 V2.02 Micromeritics apparatus. Refraction index was measured by immersion technique at 25°C in chloroform and dimethylsulfoxide. Specific area was determined by nitrogen absorption isotherms using CG2000 equipment of CG Instrumentos Científicos (Brazil). X-ray diffraction patterns were registered with a Siemens Kristalloflex diffractometer, CuK α radiation, Ni filter. Phase analysis was carried out by using a set of programs DIFRAC coupled to the diffractometer. Scanning electronic microscopy (SEM) was carried out using a SM 300-TOPCON instrument. The samples were suspended in ethanol and drops of these suspensions were deposited onto a freshly cleaved mica layer, stuck on the stubs. The latter were dried in vacuum desiccator at room temperature and finally sputtered in the SCD 005-BAL-TEC (445 mA, 120 sec) with gold. X-ray Energy Dispersive Analysis (XEDA) was carried out using a Princeton Gamma Tech PGT instrument provided with a SiLi detector. The samples were prepared by placing some mass of spongillite onto adhesive tape of conductive carbon, stuck on the graphite carbon base. No conductive golden film was deposited.

RESULTS

Spongillite physical constants

The following physical constants were obtained for raw spongillite:

1. Density (average of 5 determinations):
 $2.258 \pm 0,005 \text{ g/cm}^3$
2. Refraction index:
1.444 (in chloroform) and 1.470 (in dimethylsulfoxide)
3. Specific area: lower than $1,0 \text{ m}^2/\text{g}$

Identification by X-ray diffractometry

X-ray patterns of raw and heated spongillite samples are labile confirming amorphous character of the product and the presence of quartz (JCPDF file 33-1161) as a main crystalline phase. Secondary (in intensities) crystalline phases detected after taking extreme care in the consideration of details were polyorthosilicic acids: tetragonal $\text{H}_8\text{Si}_8\text{O}_{20}$ or $\text{H}_8(\text{Si}_2\text{O}_5)_4$ and also tetragonal hydrate $\text{H}_4\text{Si}_8\text{O}_{18} \cdot \text{H}_2\text{O}$ containing tetrahedra SiO_4 sharing faces (JCPDF files 35-0062 and 35-0060). The only difference between the heated and unheated samples were more pronounced reflections of

quartz phase. The presence of the initial phases in the samples of heated spongillite indicates the probability of a reversible equilibrium owing to active rehydration during cooling and storage.

XEDA identification

The results of X ray energy dispersive analysis reported in Figure 1 made possible qualitative characterization of spongillite components. As expected, the only intense peak in both graphics corresponds to the K α line of silicon. Smaller spectrum gives evidence of minor spongillite components, titanium and iron. The presence of titanium in all probability is due to its incorporation into silica matrix forming solid solutions by substitution in SiO_2 . Iron may be a concomitant element from the mineralogical entourage. Ni signal also available in the spectrum comes from detector material. Aluminum may be present in the form of aluminosilicates like kaolinite but not detected in our samples because of its low content ($\leq 5\%$) and sporadic occurrence. It is mentioned however in a recent research dedicated to spongillite coming from Minas Gerais State [Araújo da Matta Machado, E. 2000]

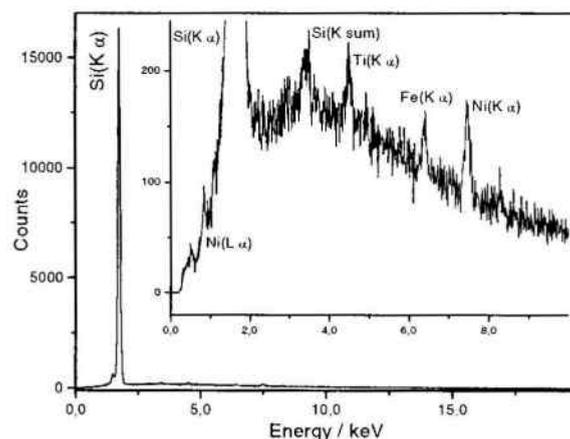


Figure 1. Raw spongillite XED spectrum.

Spongillite micromorphology

The main morphological feature of spongillite is the presence of spicules or needlelike remnants of the dead organisms having silica skeleton. In vision field (Figure 2) spongillite.

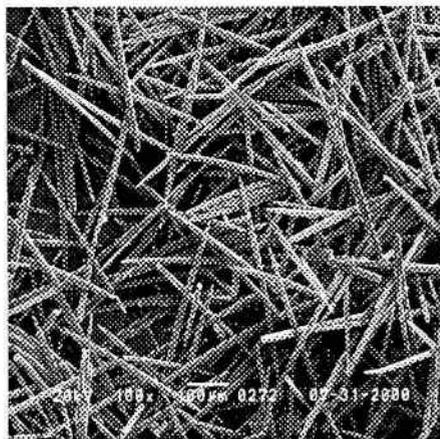


Figure 2. Electronic micrograph of the needles in raw

They are distributed in an irregular way showing an average size of 300 μ m and sometimes broken ends. Intact fossil organisms like sponges which deposited needlelike spicules are also preserved (Figure 3).

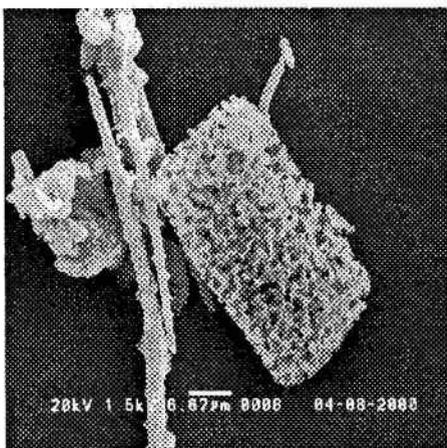


Figure 3. Electronic micrograph of a fossil sponge.

After being reduced to powder by grinding and sieving the needles have an appearance of short hollow rods resembling ceramic insulators (Figure 4). In raw spongillite the inner tunnels are obstructed by small pieces of external origin, such as quartz particles and organic detrite. They contain also gas but its composition was not determined. It may be air, carbon dioxide or methane. Anyway, after calcination there would be only air present. Mineral and organic particles are easily eliminated by washing and calcination at moderate temperatures. Rods surface (Figure 5) is uniform but slightly rough, that is implies points, bristles, ridges or mechanical defects.

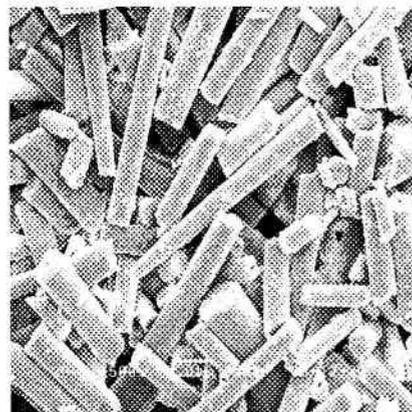


Figure 4. Electronic micrograph of ground spongillite.

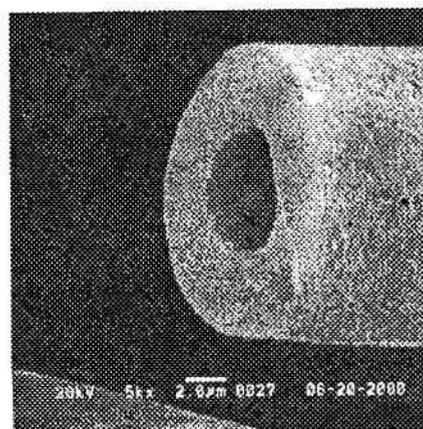


Figure 5. Electronic micrograph of a typical rod surface.

The size of the central cavity having form of a regular tunnel is around 1/10 to 1/2 of the cylinder's diameter or even more. A section of a typical rod is reported in Figure 6.

DISCUSSION

As ensues from the above characterisation, main features of spongillite are: 1. it is composed of active hydrated silica; 2 it is present in the form of hollow rods; 3. The rods, along with the air, probably, contain gas in their inner recesses. These can indicate at least three possible fields of application. The first is the use of spongillite for the adsorption of inorganic and/or organic compounds owing to the presence of orthosilicic acids with free protons and water covering the surface. Actually, raw formulae $H_8Si_8O_{20}$ and $H_4Si_8O_{18} \cdot H_2O$ of the hydrates mentioned above do not mean that spongillite over the whole volume is characterised by this composition, since it is only an average value given by chemical analysis of a block with no NMR

measurements performed. So in fact the superficial area is much richer in hydrated silica containing a stratum capable of fixing charged particles due to the orientation of its dipoles within double electric layer [Schukin, E.D. et al., 1988]. That is why spongillite may be envisaged as a material with activated surface and therefore be recommended as a potent absorbent.

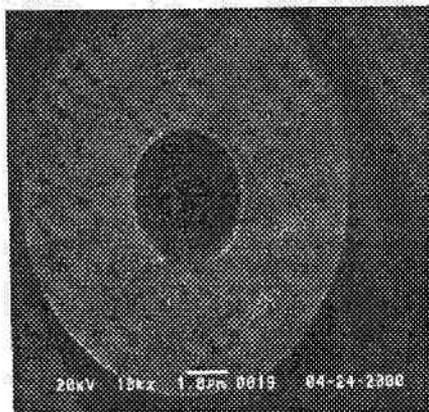


Figure 6. Electronic micrograph of rod's transversal section.

The second recommendation concerns silicon as bioactive trace element. It is concentrated in connective tissue and is thought to play a rôle in cross-linking tissue structures, the by helping to create tough but flexible strength. A lack of silicon is known to reduce normal growth and repair of the skin, hair and nails [Jugdaohsingh, R. et al., 2000]. However, direct silicon supplementation has delivered few benefits. The reason for this in most cases is that a nonbioavailable silicon source has been used [Reffitt, D. M. and Jugdaohsingh, R., 1999]. Therefore, stabilised orthosilicic acid is the only form of supplemental silicon that has been shown bioavailable to humans [Calomme, M. R., 1998]. That is exactly the composition found present on the surface of spongillite. So it may be used as a precursor for medical preparations fulfilling physiological requirements and as well for beauty products.

The third and more promissory possibility of using spongillite even in its partially purified form is to take advantage of both the composition (silica, no matter hydrated or not) and gas closed up within the remnants of biological structures. It is evident that the evolution of this gas into a liquid medium will produce bubbles making the product to look "foamy", as it is customary in the fabrication of cellular glass. This material is widely used for industrial insulators protecting oil and gas pipes, refinery columns and even as a high strength sound absorber [Godeke, H. and Fichs H.V., 1998]. The process of fabrication of cellular glass implies, as a rule, the usage of gas-forming additives, such as CaCO_3 or

graphite providing carbon dioxide as a result of carbonate decomposition or incineration of organic matter. Not long ago, diatomite minerals closely related to spongillite were mentioned as a source of self glass supply making these additives unnecessary [Saakian, E.R., 1991]. Recent research showed that cellular glass preparation allows the recycling of glass waste in industrial scale [Auadi, A. et al., 1997; Eslinger, J.M., 1980].

At present, the installations providing Bolivian oil to Brazil will have to deal with the problems of pipes overheating and large amount of low cost insulators may be needed for their protection. Since the properties of raw glass (colour, transparency, composition, etc) do not interfere with cell formation and thermal conductivity, good insulators can be fabricated at minimal expenses by recycling glass waste piled up in Mato Grosso do Sul and neighbouring Brazilian States. So spongillite, locally occurring natural cell-forming material may be recommended for the production of these insulators. In this way two problems – deactivating of an irritant and preparation of a valuable product - will be resolved.

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