An investigation of the chemical composition and acid corrosion of *pedra sabão* (soapstone)

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Abstract: In this paper the results of a basic study of the chemical composition and structure of soapstone are reported. An investigation of the effects of aqueous sulfuric acid solutions on the physical integrity of the stone was also performed. The studied soapstone samples had a lamellar nanostructure as verified by DRX data. Furthermore, they contained isolated silanol (Si–OH) groups, as indicated by FTIR data, and the majority of the silicon atoms were bonded to OH groups, as shown by $^{29}$Si CP MAS NMR analysis. It was also shown that a low resistance to acid attack is associated with a large amount of magnesium and/or iron in the stone.

Keywords: soapstone, acid rain, chemical composition, baroque art.

INTRODUCTION

So-called *pedra sabão* ("soapstone") was extensively employed in the nineteenth century for the production of many artistic artifacts in Brazil, such as the statues of the prophets in Congonhas city, in Minas Gerais State, which are an example of baroque art in South America. The statues were made by a Brazilian artist, Antônio Francisco Lisboa, called "o aleijadinho". Nowadays, the progressive corrosion of the statues, provoked mainly by air pollution, is a very serious problem which has to be solved.

The name "soapstone" comes from the fact that the stone is very soft. From a formal point of view, soapstone is a compact form of talcum powder (steatite), the "fundamental" chemical formula of which is $\text{Mg}_3\text{Si}_4\text{O}_{16}(\text{OH})_2$. This basic silicate is the softest one on the Mohs scale. Today, soapstone is used to produce a lot of artistic artifacts, such as statues, as well as utensils, such as pottery (see Fig. 1). Some care must be taken in its manipulation, due to its possible toxicity via inhalation.\(^1\)

Steatite is most wide-spread in the United States, Japan and Brazil. In Brazil it is found mainly in the States of Minas Gerais, Bahia, Paraná, Goiás and São Paulo. Its color varies from white to nuances of yellow, beige, green and gray, and from
light to almost black, depending on the chemical composition of the associated minerals.

In this work a basic study of the chemical composition and structure of two soapstone samples was undertaken in order to improve the scientific knowledge about this so marvelous mineral. An investigation of the effects of aqueous sulfuric acid solutions on the physical integrity of the stone was also performed in order to obtain some clues as to the main causes of soapstone corrosion (acid rain), and so to the possible approach that must be employed to avoid corrosion. This study is the first of on-going investigations by a Brazilian network of research groups dedicated to the study and preservation of the artistic and cultural heritage of Brazil. The investigations are supported by CNPq (see acknowledgements).

EXPERIMENTAL

Two soapstone samples, both from Ouro Preto city, Minas Gerais State, Brazil, were investigated. From a macroscopic point of view, the only difference between the two samples was their color: one was light gray (the stone itself, since the powder was white) whereas the other was red-brown. The two samples are named hereafter as SS 1 and SS 2, respectively.

To simulate the effects of acid rain on soapstone, a 0.1 mol dm⁻³ sulfuric acid solution was prepared, and cubic soapstone samples (5 mm × 5 mm × 5 mm) were immersed in 150 cm³ of the acid solution for 40 days.

The infrared spectra of soapstone samples were obtained using a Bomem apparatus in the range 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹. The KBr disc technique was used. Thermogravimetric curves were obtained using a Shimadzu TGA 50 apparatus, under an Ar atmosphere with a heating rate of 10 °C min⁻¹. The X-ray diffraction patterns were obtained using a Shimadzu XD-3A instrument, using CuKα radiation (35 kV, 25 mA). The SEM micrographs were taken using a Jeol microscope, model JSM T-300, with an accelerating voltage of 15 kV. ²⁹Si NMR CP MAS spectra of solid samples were recorded using a AC 300/P Bruker instrument at room temperature, with the operating conditions: pulse repetition time of 0.115 s, contact time of 3 ms and 17,857 accumulations.

RESULTS AND DISCUSSION

The infrared spectrum obtained for SS 1 is shown in Fig. 2. The band at 3677 cm⁻¹ is associated with the vibrations of isolated silanol groups (Si–OH). It is
worth noting that such a band is very difficult to be observed in silica samples, a very careful drying process being required. Such a result strongly suggests that the silanol groups in soapstone are mainly isolated ones. The band at 3661 cm\(^{-1}\) could be associated with geminal silanol groups (Si(OH)\(_2\)). The bands at 1918, 1810 and 1023 cm\(^{-1}\) are associated with the vibrations of the silica backbone, and the band at 1662 cm\(^{-1}\) with the \(\delta\)-H–OH vibration mode from adsorbed water molecules. A very similar IR spectrum was obtained for the SS 2 sample.
The obtained X-ray diffraction patterns are shown in Fig. 3. As can be observed, the X-ray patterns for both samples are virtually identical, with main diffraction peaks at $9.5^\circ$, $19.0^\circ$ and $28.5^\circ$, associated with diffractions from the 001, 002 and 003 planes, respectively. Such a diffraction profile is compatible with a lamellar nanostructure. Based on the $2\theta$ value for the 001 plane, the interlayer distance was calculated to be 0.93 nm.

An EDX analysis was performed on both samples, and only three elements were detected: Si, Mg and Fe. The reliability of such an analysis had previously
been verified by using a Pd (80 %)/Au (20 %) standard disc, and the obtained ratio was as expected. The quantitative results are as follows: SS 1 (Si = 66.0 %, Mg = 29.1 % and Fe = 4.9 %); SS 2 (Si = 63.6 %, Mg = 31.1 % and Fe = 5.3 %). Hence, SS 2 contains larger amounts of Mg and Fe than SS 1. The red-brown color of SS 2 could be attributed to its higher iron content.

The presence sulfur was not detected, and so the hypothesis that Mg and/or Fe could be present in the rock as their respective sulfates can be disregarded. Thermogravimetric analysis performed on both samples in the temperature range 25–1000 °C showed no mass loss (a single plateau was observed in the TG curve). Since MgCO₃ undergoes thermal degradation at 540 °C,² the hypothesis that magnesium could be present as carbonate can be disregarded. Hence, based on the obtained experimental results, it could be concluded that silicon, magnesium and iron are present in the soapstone as their respective oxides, i.e., soapstone is a iron-magnesium silicate, or a magnesium silicate contaminated with iron, in this case. Thus, the obtained results are not in complete agreement with the “fundamental” chemical composition provided in the introduction.

The ²⁹Si NMR CP MAS spectrum for SS 1 is shown in Fig. 4. Peaks at –33.0, –97.1 and –164.1 ppm are observed. For SS 2 sample, a spectrum with similar profile was obtained. However, the peaks were shifted to higher field values: –29.4, –94.8 and –154.5 ppm, respectively. This fact reinforces the evidence provided by EDX analysis, that the chemical compositions of both samples are not the same. The observed shifts can be associated with the higher amount of iron and magnesium in the SS 2 sample. The peak at –97.1 ppm observed for SS 1 and at –94.8 ppm for SS 2, can be attributed to isolated silanols, where the silicon atom is bonded to a single –OH group and three siloxane groups, i.e., (OH)Si⁻– (OSi≡)₃.³ Thus, this data confirms the FTIR data. Is worth noting that this peak is the most intense in both NMR spectra. Hence, the majority of the silicon atoms present in

![Fig. 4. ²⁹Si CP MAS NMR spectrum of SS 1.](image-url)
soapstone are bonded to OH groups. The peaks at –33.0 and –164.1 ppm (SS 1) or –29.4 and –154.5 ppm (SS 2) are resonance peaks related to the main peak. No peaks related with siloxane groups Si*(OSi)₄, normally observed around –109 ppm, were found in the obtained spectra. Hence, it can be concluded that such a group was not present in either sample.

The obtained SEM micrographs are shown in Figs. 5 and 6. In Figs. 5 (c) and (d) it can be seen that soapstone exhibits a platey microstructure. However, the SS 2 sample has larger grain sizes than SS 1. Comparison of Figs. 5 (a) and (b) with Figs. 5 (c) and (d) shows that the microstructure of the SS 1 sample was not affected by immersion in the sulfuric acid solution. On the other hand, comparison of Figs. 6 (a) and (b) with Figs. 6 (c), (d) and (e), shows that the microstructure of the SS 2 sample was strongly affected by immersion in the sulfuric acid solution. An exfoliation of the matrix can easily be observed after the acid treatment. Hence, exposure of the SS 2 sample to an aqueous acid environment can provoke the rupture of the interlayer forces and subsequent physical disintegration of the stone.

Based on the EDX and SEM data, it can be inferred that the higher magnesium and/or iron content of SS 2 is related with its lower resistance to acid attack. De-
spite the fact that a study on the solubility of the crystalline compounds was not performed here, the obtained results are in agreement with those previously reported for a study involving the investigation of cookware made of soapstone. In that study, 3% and 5% acetic acid solutions were employed as food simulant, and it was verified that mineral migration followed the solubility of the crystalline components of the rock, with Fe exhibiting a higher migration rate than Mg.

Fig. 6. SEM Micrographs for SS 2 before (a) and (b) and after (c), (d) and (e) immersion in a 0.1 mol dm\(^{-3}\) sulfuric acid solution. The employed magnifications and scale bar are shown on the micrographs.
CONCLUSIONS

Based on the obtained experimental results can be concluded:
(1) In soapstone samples, a reduced resistance to acid attack is associated with larger amounts of magnesium and/or iron in the stone.
(2) The studied soapstones have lamellar nanostructures, which make them suitable to promote intercalation reactions. Furthermore, they contained isolated OH groups, as indicated by FTIR data, and the majority of the silicon atoms present in the soapstone were bonded to OH groups, as proved by $^{29}$Si CP MAS NMR analysis.

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IZVOD

ИСПИТИВАЊЕ ХЕМИЈСКОГ САСТАВА ПЛОВУЋА И ЊЕГОВЕ КОРОЗИЈЕ У КИСЕЛИНАМА

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У овом раду приказани су резултати анализа хемијског састава и структуре пловућа. Проучено је и дејство воденог раствора сумпорне киселине на физички интегритет камена. Проучавани узорци пловућа имали су ламеларну наноструктуру која је потврђена DRX подацима. Осим тога, садржавали су изоловане силиоладске (Si-OH) групе доказане FTIR анализом, као и већину атома силицијума повезаних са OH групама као што је показано $^{29}$Si CP MAS NMR анализом. Показано је да мала отпорност камена на дејство киселине потиче од присуства великих количина магnezijума и/или гвођа у камену.

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