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Detection of mineral impurities in diatomite ores

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Abstract

Diatomaceous Earth (DE) is commonly used in the industry for the manufacturing of filters, where diatomite is preferred due to its low chemical reactivity and high porosity. Diatomite deposits with major amounts of mineral impurities, such as carbonates, present a problem in the production DE. In this study, samples from a diatomite deposit with known presence of carbonate were analysed. With the aim of estimating the carbonate content, the samples were analysed with infrared (IR) spectroscopy. The association between the carbonate and diatomite was characterised using thin sections and Environmental Scanning Electron Microscopy (ESEM). Based on the infrared spectra, the diatomite ore was classified according to the carbonate content. The microscopy images showed laminae, cement and coating of carbonate around the diatomite. These findings indicate that the IR classification along with the type of carbonate association can optimise the production of DE.

Keywords: Diatomite, Carbonate, Impurities, Ore Classification, Infrared Spectroscopy

1. Introduction

Diatomite, also known in its processed form as Diatomaceous Earth (DE), is widely used in the industry as a filtration media for food (water, liqueurs, oil), pharmaceutics, and other applications (Martinovic et al., 2006; Sun et al., 2017).
The preference for the use of diatomite in such industries is due to its properties that include a high porosity and relative chemical inertness. Diatomite is a rock formed by the accumulation of diatom frustules, which are made of opaline silica and have an intricate porous structure (Breese & Bodycomb 2006). Generally, the thickness of a diatomite deposit is the main parameter for considering its economic value. However, mineral impurities that alter the chemical reactivity and the porosity of the diatomite-based products

cause an increment in the mine waste and reduction in the product quality, resulting in detriment to the deposit's potential.

For the generation of diatomite products that meet the application's requirements, it is necessary to remove the impurities from the ore during the mineral beneficiation. There are a plethora of techniques used for diatomite refinement; they include gravity sequential classification, electric field-based separation, natural and in-plant drying, centrifugal separation, and acid leaching (Al-Wakeel, 2009; Jung et al., 2014; Martinovic et al., 2006; Şan et al., 2009; Sun et al., 2017; Zhang et al., 2013). Except for natural drying, the execution of all the other methods occurs at the beneficiation plant. Nevertheless, the ore refinement can be optimised by proactively sorting the ore based on its purity directly in the mining site. This approach requires the use of characterisation techniques that can be used on-site and that are able of detecting and estimating the content of mineral impurities.

In this study, a combination of analytical techniques is used to characterise and classify a diatomite deposit that has a known presence of carbonates. The deposit, located in south-eastern Spain, belongs to the system described by Bellanca et al. (1989), where the layers of diatomite irregularly alternate with carbonate layers. The ore classification is based on the carbonate content detected by Infrared (IR) Diffuse Reflectance Spectroscopy. The textural association between the silica and the carbonate phases is characterised using optical microscopy with thin sections and Environmental Scanning Electron Microscopy (ESEM). The results herewith presented provided with a novel approach for optimising the beneficiation of diatomite ores.

2. Materials and methods

The present study is based on samples from one the diatomite deposits located in south-eastern Spain. The samples correspond to different stratigraphic positions collected in a mine face. For clarity in this work, the term diatomite makes reference to the accumulation of diatom frustules, and diatomite ore to the mixture of diatomite and carbonate, where the carbonate content is not higher than 23%. The sample set for this study consists only of samples regarded as diatomite ore.

Each sample was chemically analysed using X-ray fluorescence for major elements and calcimetry for the indication of the total carbonate content. The infrared spectra were recorded with an Agilent 4300 hand-held portable instrument using the diffuse reflectance mode from 1.9 to 16.0 μm. For the microscopy analyses, thin sections were prepared with a staining using Alizarin red S and potassium ferricyanide; the ESEM observations were conducted on rock chips using a Philips XL30 ESEM and supported with element analysis (EDX).

3. Results and discussion

3.1 Diatomite ore classification

Sorting of the diatomite ore was based on pre-determined quality grade classes used for mining and mineral processing. These classes separate the ore by the carbonate content, assigning a value of 1 to the ore with the lowest carbonate content and a value of 6 to the highest; disclosure of the specific cut-off values is not possible due to commercial sensitivity. In the analysed samples, only classes 1 to 4 were present.

The IR spectra of the diatomite ore is a mixture of the spectral features of opal, which correspond to the diatomite, and carbonate minerals. In the measured spectra, the H_2O and

SiO features characteristic of opal mask the CO_3 spectral bands of the carbonates in the short-wave IR near 2.35 and 2.55 µm, and in the long-wave IR near 11.5 and 14.0 µm. In this mixture, the only region of the spectra where it is possible to identify the carbonate features was around 7.0 µm. The shape and wavelength position of the spectral features have relation with the crystal structure of the carbonate minerals. Well defined bands are characteristic of organised crystal structures, whereas broad bands are an indication of distorted or amorphous lattices. Regarding the wavelength positions, bands located near 6.3 and 6.9 µm represent carbonates of aragonite structure, whereas bands between 6.8 and 7.1 µm denote carbonates of calcite structure (Andersen & Brečević, 1991; Gunasekaran et al., 2006).

In Figure 1 the assignment of the quality grade classes to the samples' spectral profiles shows that the intensity of the spectra varies as a response to the carbonate content. The spectral profile of the QG1 sample is smoother than the others, suggesting the scant occurrence of carbonates. In all the other samples, absorption features at 6.9 and 7.1 µm indicate the presence of carbonates of calcite structure. In addition, a weak absorption near 6.6 µm indicates the increasing presence of carbonates with aragonite structure according to the quality grade. Moreover, the samples of class 4 have a broad absorption between 6.4 and 6.6 µm, suggesting that the carbonates are rather amorphous.
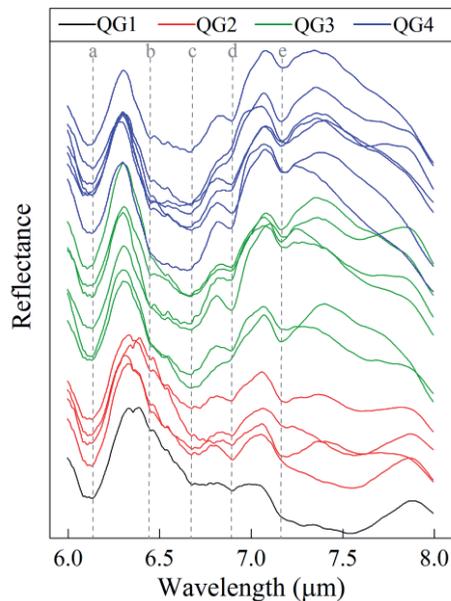

Fig. 1. Spectra of diatomite ore samples in the range restricted to the carbonate features near 7.0 µm. Line colours correspond to the quality grade (QG) classification. Vertical lines denote spectral absorptions:
a) 6.13 µm - H_2O in opal, b) 6.4 µm - CO_3 in aragonite, c) 6.6 µm - CO_3 in aragonite,
d) 6.9 µm - CO_3 in calcite, e) 7.1 µm – CO_3 in calcite

Principal Component Analysis (PCA) was used to interpret the spectra and assist with the classification of the samples. Fig. 2. shows the scores and loadings plot of principal component 1 (PC1) coloured according to the quality grade classification. The results of the PC1 make a good distinction between the different classes; the other PCs do not contribute to the classification. The samples are distributed along PC1 according to their respective

quality grade, being the samples with the highest scores those with the lowest carbonate content, and vice versa. In the loadings plot, the highest loadings correspond to those wavelengths were the carbonate fingerprints occur, confirming that the distribution of the samples indeed represents the presence and intensity of the carbonate features. The separation is clearer for classes 1 and 2, while the distinction between classes 3 and 4 is not sharply defined.
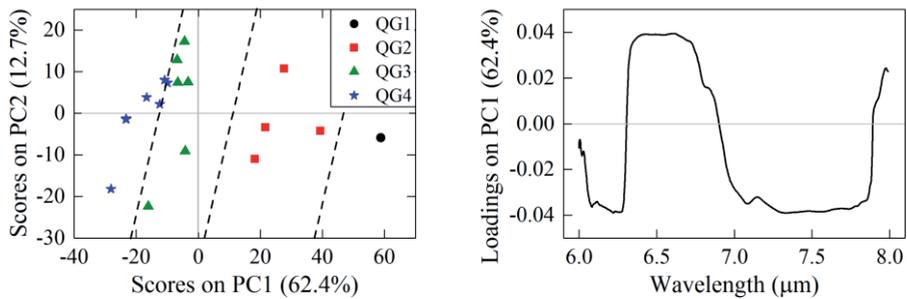

Fig. 2. Principal component analysis (PC1 vs. PC2) of diatomite ores (left) and corresponding loadings plot (right). Data point symbols and colours correspond to the quality grade (QG) classification

3.2 Silica-carbonate association

The deposit used for this study consists of a sequence diatomite layers intercalated with limestone and silicified marls. In hand specimen, the diatomite ore looks rather homogeneous, with only some sporadic carbonate laminae of no more than 5 mm.

In the thin sections, shown in Fig. 3a, the parameter for identification of the carbonates was the mineral staining; the pink-orange colouration indicates the presence of aragonite and calcite, as previously indicated by the infrared analyses, and discards the presence of dolomite or any other carbonate minerals. In some samples, carbonates and diatomite are present as intercalated laminae with a thickness between 100 and 500 μm. Other samples consist only of diatomite laminae with some grains of carbonate no bigger than 50 μm.

The ESEM inspection of the samples showed in more detail the textural associations between the silica and carbonate phases (Fig. 3b). The contact between the diatomite and carbonate laminae is rather sharp than transitional. However, carbonates are observed not only as laminae but also as cement and coating around the diatom frustules. The EDX results for the carbonates showed chiefly Ca, confirming the occurrence of calcite and aragonite in the samples.

When comparing the PCA classification results, presented in Section 3.1, and the thin section and ESEM images, there is a relation between the amount of carbonates and their distribution in the ore. In the QG1 sample the carbonates are hardly observable; in classes 2 and 3 carbonate coating and cement are common, as well as isolated carbonate grains, whereas samples with lamination belong mostly to class 4.
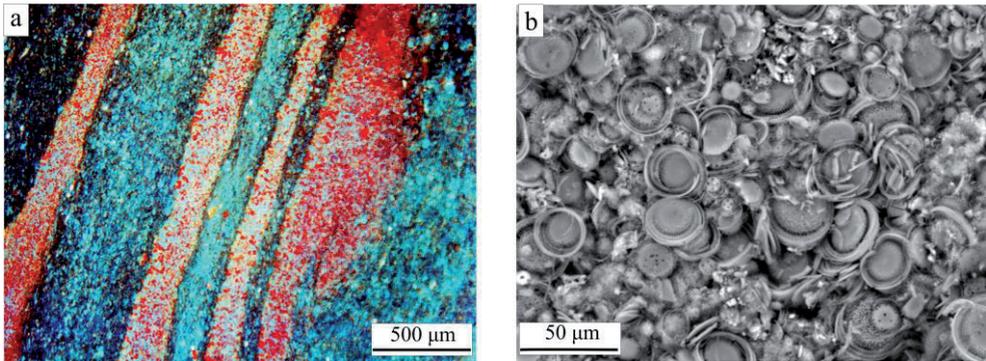
Fig. 3. Microscopy images of the diatomite ore: (a) thin section showing intercalation of silica (blue) and carbonate (red) laminae. (b) ESEM microphotograph showing diatom frustules with carbonate coating

3.3 Implications for diatomite mining and processing

The classification of the diatomite ore using infrared spectroscopy showed good agreement with the quality grades used for mining and processing. However, the infrared data is a point measurement and therefore it is not entirely representative of a bigger volume of rock. Nevertheless, the type of instrument (hand-held portable spectrometer), and the measuring conditions allow recording several measurements in a short time. In this way, complete strata of a mine face can be characterised and classified, thus assisting the extraction strategy. The method could also be implemented performing particle by particle sorting in a conveyor belt. As a result, the diatomite ore could be stockpiled according to its quality grade for supporting blending and refinement of the ore, having a direct impact on the costs and time required for the refinement of the diatomite ore.

The thin section and ESEM analysis showed that, in the diatomite ore, carbonate is present as laminae, coating and cement. This kind of associations has a different impact on the beneficiation technique chosen to separate the carbonates from the rest of the ore. Even though samples with laminae have in general a larger amount of carbonates, a significant proportion of them could be separated from the ore by using physical techniques such as sequential gravity or electric field separation. In contrast, carbonate present as cement of coating represents a bigger nuisance, on the one hand, because this type of association is more prompt to affect the porosity of the diatomite, and on the other hand, because the carbonate removal would require more aggressive or elaborated techniques such as acid leaching.

4. Conclusions

This study used IR spectroscopy to classify a diatomite ore according to the carbonate content. The detection of carbonate used a region in the spectra where there is little influence from the spectral features of opal, in a way that the carbonate estimation is reliable. The classification of the spectra showed good agreement with predetermined quality grade classes.

Using microscopy techniques (thin sections and ESEM), the association between carbonate and diatomite was characterised as interlamination in carbonate-rich ores, and cement, coating and sporadic carbonate grains in the carbonate-poor ones.

These classification results can be used for supporting extraction and pre-beneficiation activities, whereas the textural analysis provides valuable information for ore refinement. The implementation of these results in actual diatomite ore mining and processing would optimise the generation of DE products.

5. Acknowledgements

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