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## Synthesis of a red iron oxide/montmorillonite pigment in a CO<sub>2</sub>-rich brine solution

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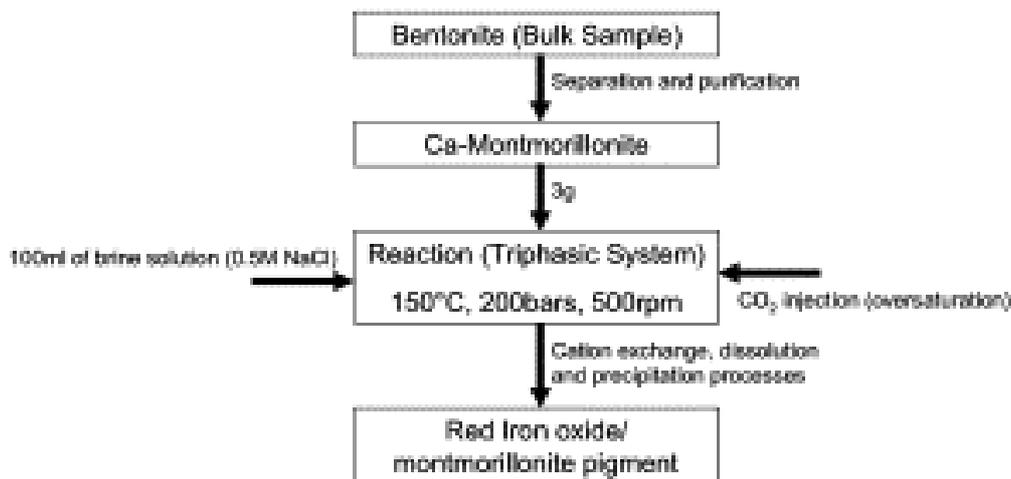
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### Abstract

The homoionic calcium-montmorillonite was used to synthesize a red iron oxide/clay pigment in a CO<sub>2</sub>-rich brine solution (0.5 M of NaCl) by using an agitated batch-reactor (engineer autoclave). The operating conditions were 15 days of reaction, 200 bars of pressure and 150 °C of temperature. SEM/EDS, STEM/EDS, XRD and Infrared Spectrometry were performed to characterize before and after reaction the solid phase. The results showed the precipitation of spherical nanoparticles (50–500 nm) of iron oxide (Fe<sub>2</sub>O<sub>3</sub>) dispersed and/or coagulated in the clay-matrix. Evidently, this oxide produced red coloration in the final product. For this case, the Fe<sup>3+</sup> cation was provided to the aqueous solution by the dissolution of Ca-montmorillonite, particularly, the dissolution of most fine particles contained in the starting clay material. The cation exchange process and precipitation of polymorph silica were also observed.

## Graphical abstract

### Synthesis of a red iron oxide/montmorillonite pigment in a CO<sub>2</sub>-rich brine solution



**Keywords:** Red pigment; Ca-montmorillonite; CO<sub>2</sub>-rich brine solution; Iron oxide; Synthesis

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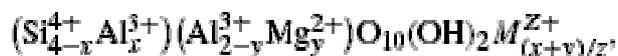
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## 1. Introduction

Clay minerals and iron oxides are a subject of interest within the area of many applied sciences such as geochemistry, mineralogy, metallurgy and environmental protection. Clay and synthetic iron(III) oxides are technologically important materials and are widely applied as components in various industrial products, e.g., pigments in the building industry, inorganic dyes, ceramics, pigments and adsorbents in the paper industry, lacquers or plastics [1], [2] and [3].

The world production of synthetic iron oxide pigments is over 1 million tons annually. About 13 different iron oxides and oxyhydroxides are known. Among them synthetic magnetite ( $\text{Fe}_3\text{O}_4$ ) is used as a black pigment, hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) as a red-brown pigment and goethite ( $\alpha\text{-FeOOH}$ ) as a yellow pigment. Numerous publications and patents appear every year dealing with various types of synthesis and applications of iron(III) oxides and oxyhydroxides. During the oxidation of iron(II) salts in water solution the constitution, crystal structure and properties depend on the process conditions including the methods of precipitating and oxidizing of the reactants. Different iron oxides and hydroxides could be produced depending on the solution concentration, temperature, pH value and starting materials as well as subsequent hydrolysis reaction of iron(III) salts [1].

On the other hand, the major component of bentonite (native clay-rich material) is montmorillonite (>60%). A single montmorillonite platelet is composed of three layers: one octahedral layer is sandwiched between two tetrahedral layers (2:1 type). The montmorillonite platelets can form large stacks with a general structural-chemical formula:



where  $M$  represents the interlayer cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , etc. The presence of these cations is a result of the so-called isomorphous substitution and these interlayer cations greatly affect the swelling ability of montmorillonite (see for example [4], [5], [6], [7], [8] and [9]). In addition, the octahedral layer of the montmorillonite frequently contains  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  cations (e.g., montmorillonite of Wyoming). For that case, the dissolution of fine particles of montmorillonite at PTX controlled could allow the synthesis of red iron oxides finely dispersed on the montmorillonite support.

In this paper, the bentonite of Wyoming (labeled Wy2) was used to obtain a homoionic calcium-montmorillonite. Then, this purified clay material was used to synthesize a red iron oxide/clay pigment in a CO<sub>2</sub>-rich brine solution (0.5 M of NaCl) by using an agitated batch-reactor (engineer autoclave). The operating conditions were 15 days of reaction, 200 bars of pressure and 150 °C of temperature. SEM/EDS, STEM/EDS, XRD and Infrared Spectrometry were performed to characterize before and after reaction the solid phase.

## **2. Materials and methods**

### **2.1. Ca-montmorillonite preparation**

Forty grams of a commercial bentonite (of Wyoming) were dispersed into 1 L of high purity water with electrical resistivity of 18 MΩ cm; this suspension was kept in constant mechanical agitation at 25 °C and adjusted at pH 5 with acetic acid. Then, the suspension was heated at 80 °C during 8 h in order to eliminate the carbonates. The solid phase was then recuperated by centrifugation (45 min at 13,000 rpm). This solid was re-dispersed in a brine solution (1 M of CaCl<sub>2</sub>) and kept in constant mechanical agitation for 24 h at 25 °C. Then, the solid was separated by centrifugation (45 min at 13,000 rpm) and decanting the supernatant solutions. This process was repeated three times. The accessory minerals (quartz, feldspar, etc.) were manually separated in plastic flask after each centrifugation.

Finally, the purified Ca-montmorillonite was washed several times with high purity water until the AgNO<sub>3</sub> test for chloride is negative. This purified clay was subsequently dried for 48 h at 60 °C and gently ground in a mortar.

The scanning transmission electron microscopy (STEM) coupled to energy dispersive X-ray analyzer was used to notice the homoionic interlayer cation in the montmorillonite particles.

### **2.2. Synthesis**

One hundred ml of brine solution (0.5 M of NaCl) and 3 g of purified Ca-montmorillonite were charged in the reactor (engineer autoclave 200 ml). The clay particles were immediately dispersed with magnetic agitation. The dispersion was then oversaturated with CO<sub>2</sub> gas, thank to an injection system in the reactor. The operating conditions were 15 days of reaction, 200 bars of pressure (±5 bars), 150 °C of temperature (±2 °C) and magnetic agitation (≅500 rpm).

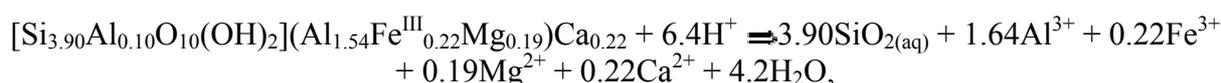
The autoclave was quenched down to 25 °C and opened under atmospheric conditions. The solid product (pigment) was separated by centrifugation (15 min at 13,000 rpm) and decanting the supernatant solutions. Then, the product was washed several times with high purity water until the AgNO<sub>3</sub> test for chloride is negative. Finally, the washed product was dried for 48 h at 60 °C and gently ground in a mortar.

### 2.3. Characterization

The starting material and product were characterized by X-ray powder diffraction with a D8 Bruker diffractometer. The XRD patterns were recorded in the 3–64° 2θ range using CoKα1 radiation ( $\lambda = 1.7902 \text{ \AA}$ ). Morphological analysis of the powders was performed by scanning electron microscope, with a HITACHI S2500 FEVEX. The quantitative microanalysis of the product was carried out by energy dispersive spectrometer (EDS). Isolated fine particles (oriented on carbon Ni-grids) of the starting material and product were studied using a transmission electron microscope, with a JEOL 3010 instrument, equipped with an energy dispersive X-ray analyzer (EDS) to illustrate the morphologies of the particles and to identify the precipitated phases. In order to identify the carbonate group in the solid product, the infrared spectrometry was performed, with a BRUKER EQUINOX55 spectrometer in diffuse reflection mode at 4 cm<sup>-1</sup> resolution for 200 scans.

### 3. Results and discussion

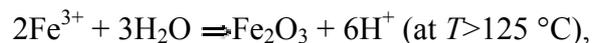
The physicochemical reactivity of the Ca-montmorillonite in a CO<sub>2</sub>-rich brine solution allowed the synthesis of a red iron oxide/clay pigment ([Fig. 1](#)). For this case, the Fe<sup>3+</sup> cation was provided to the aqueous solution by the dissolution of Ca-montmorillonite, particularly, the dissolution of most fine particles (nanoparticles) contained in the starting clay material. This chemical process can be described by the following reaction:



where the structural formula of Ca-montmorillonite was calculated from 10 particles EDS-TEM analysis according to the method of Harvey [\[10\]](#), i.e., on the basis of 11 oxygen for particles of the (2:1) type (illite or smectite). The chemical reaction above cited can be favored by the decrease of pH in the aqueous solution because of CO<sub>2</sub> dissociation:



Consequently, the iron oxides can be precipitated from the solution [2]:



the red coloration in the product and the microchemical (EDS-TEM) analysis for isolated particles confirmed the iron oxide ( $\text{Fe}_2\text{O}_3$ ) precipitation (see Fig. 1 and Fig. 2). However, this precipitated phase was not identified by X-ray diffraction (Fig. 3), possibly due to a poor crystallinity and/or slight proportion of the iron oxide particles in the product. The SEM and TEM observations showed spherical fine-particles (50–500 nm) of iron oxide dispersed and/or coagulated in the clay-aggregates (Fig. 2 and Fig. 4).

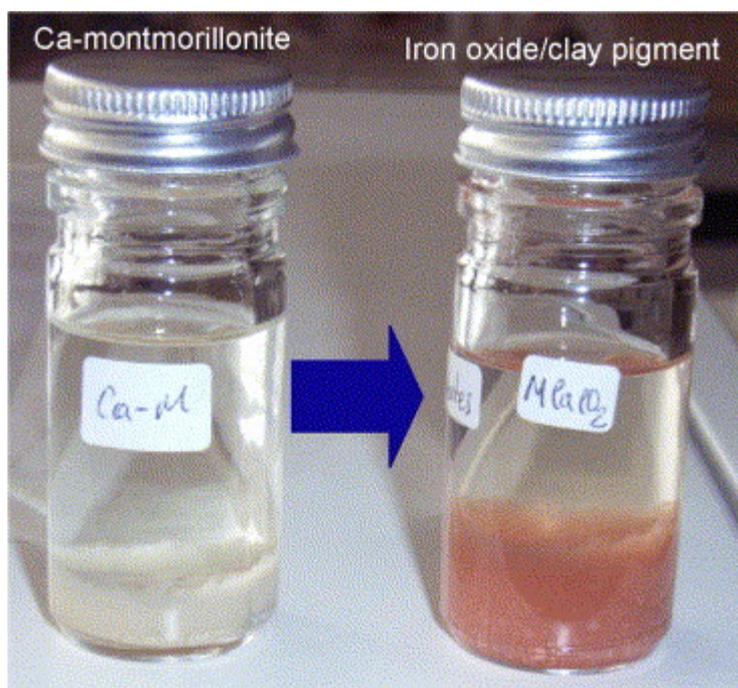


Fig. 1. Physical comparison between starting material (Ca-montmorillonite) and product (iron oxide/clay pigment).

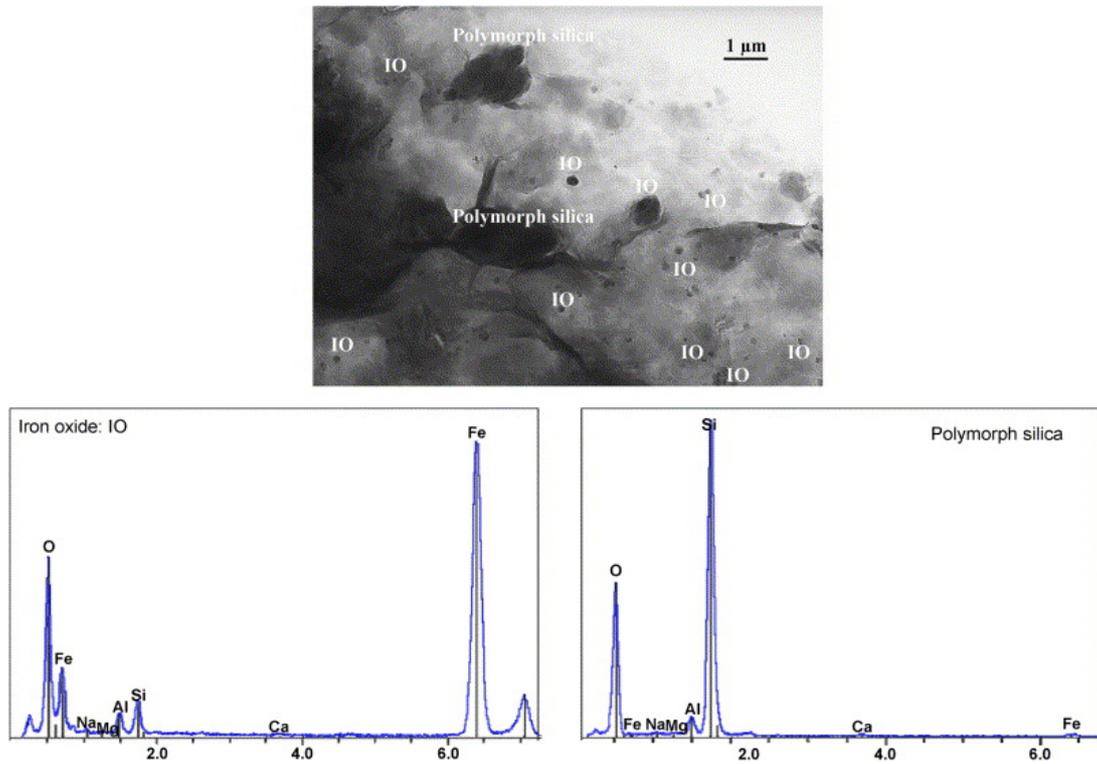


Fig. 2. Microchemical EDS-TEM analysis for isolated particles of iron oxide (IO) “Spherical fine-particles (50–500 nm)” and polymorph silica.

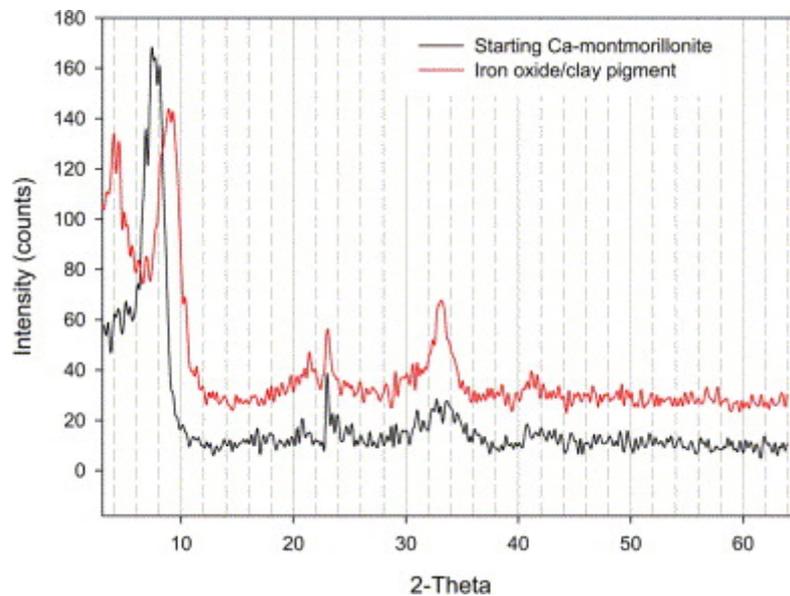


Fig. 3. XRD measurements of starting clay material and iron oxide/clay pigment.

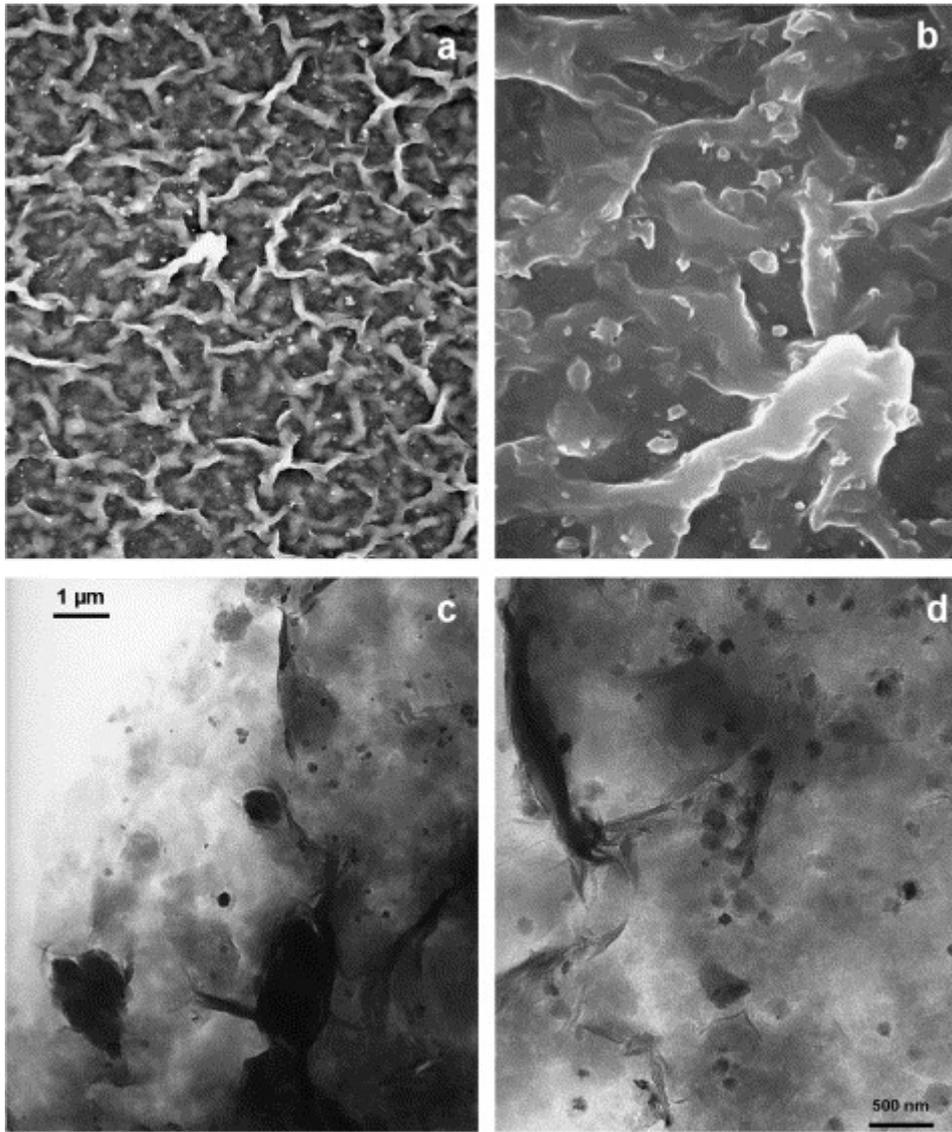
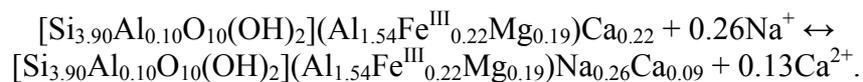
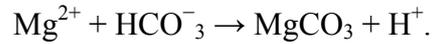
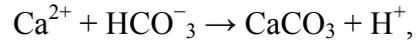


Fig. 4. Spherical fine-particles of iron oxide dispersed and/or coagulated in the clay-matrix. SEM observations (a) and (b), TEM observations (c) and (d).

On the other hand, the high concentration of  $\text{Na}^+$  in the solution favored a cation exchange process in the clay particles. Obviously, the cation exchange process is faster than the dissolution process for clays. Microchemical (EDS-TEM) analysis showed that about 60% of calcium was exchanged by sodium in the isolated clay-particles (Fig. 5):



The presence of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the solution; calcium ion liberated by cation exchange and/or dissolution processes, and magnesium ion liberated by dissolution process, suggests the precipitation of carbonates:



These phases were not identified in the solid product by infrared spectrometry (see [Fig. 6](#)) and microchemical EDS-TEM analysis. Possibly, the solution was not saturated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  because these cations have a high solubility; or simply, the precipitation of carbonates was inhibited by the iron oxide precipitation in this system.

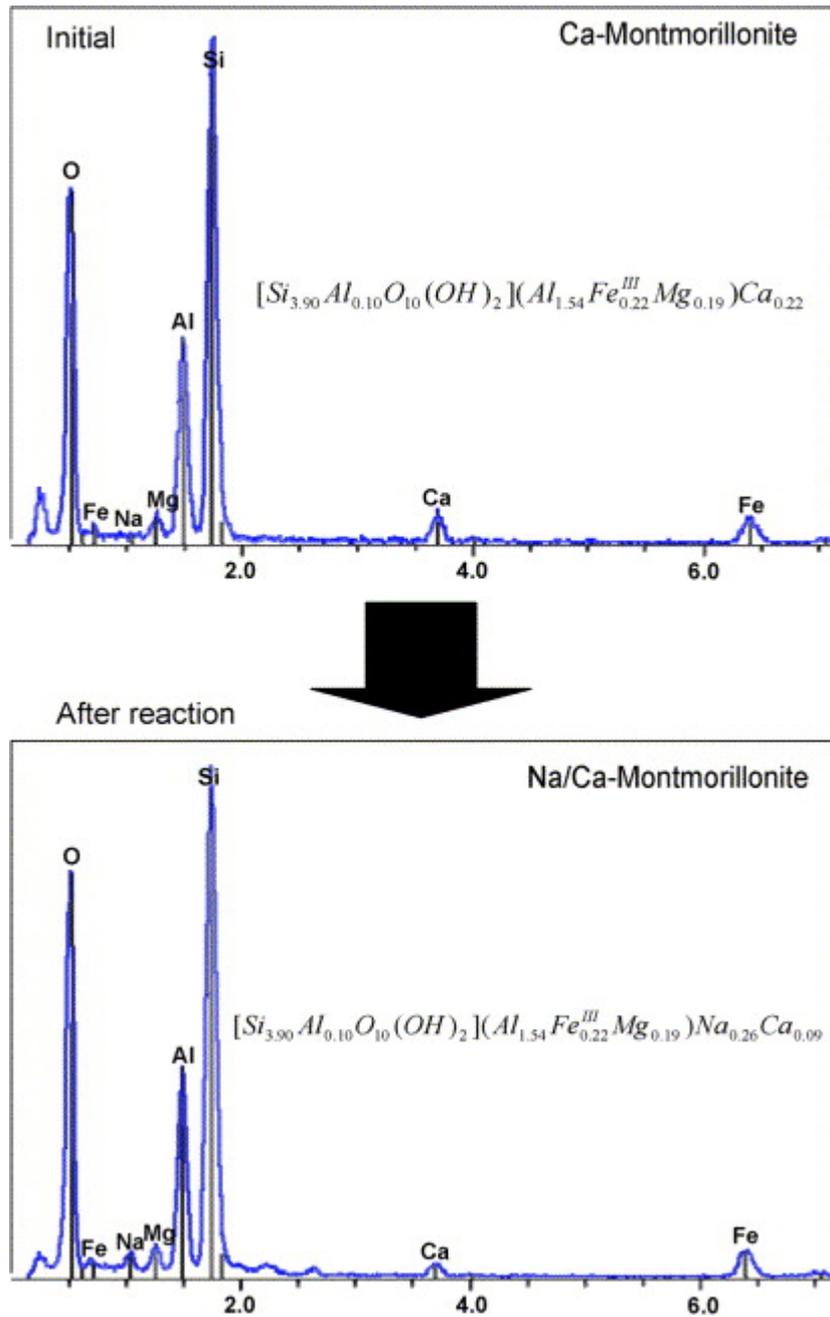


Fig. 5. Cation exchange process in the clay particles identified by microchemical EDS-TEM analysis.

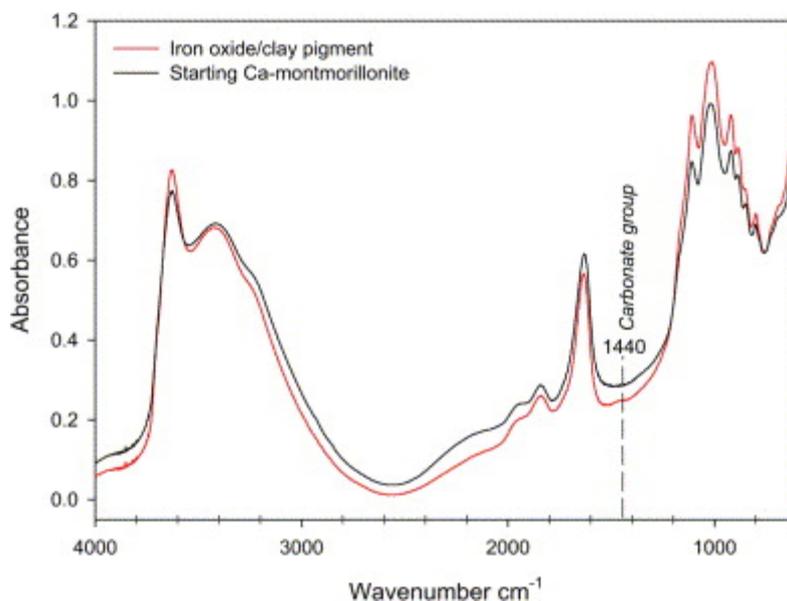
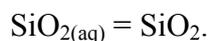


Fig. 6. FTIR spectra of starting clay material and product (iron oxide/clay pigment). Diffuse reflection mode (at  $4\text{ cm}^{-1}$  resolution for 200 scans) was used in order to identify the carbonate group in the product.

The  $\text{SiO}_{2(\text{aq})}$  liberated by dissolution of fine clay-particles allowed the precipitation of polymorph silica.



Finally, the microchemical EDS-TEM analysis showed that the  $\text{Al}^{3+}$  liberated by dissolution of fine clay-particles, was always associated to the precipitation of iron oxides and silicates (see, e.g., [Fig. 2](#)). It is clear that this cation does not keep in solution because it has a slight potential of solubility.

#### 4. Conclusion

The physicochemical reactivity of the Ca-montmorillonite in a  $\text{CO}_2$ -rich brine solution allowed the synthesis of a red iron oxide/clay pigment. The results showed the precipitation of spherical nanoparticles (50–500 nm) of iron oxide ( $\text{Fe}_2\text{O}_3$ ) dispersed and/or coagulated in the clay-aggregates. Evidently, this oxide produces red coloration in the final product. For this case, the  $\text{Fe}^{3+}$  cation was provided to the aqueous solution by the dissolution of Ca-montmorillonite, particularly, the dissolution of the most fine particles (nanoparticles) contained in the starting clay material. The cation exchange process and the precipitation of polymorph silica were also observed.

## Acknowledgements

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