# Adsorption of petroleum organic compounds on natural Wyoming montmorillonite

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## Abstract

Adsorption of petroleum organic compounds on natural Wyoming montmorillonite clay is an irreversible process, as most of organic species still remain adsorbed on mineral after aging. The process is conditioned by the petroleum paraffinic content and by molecules containing alkane chains, as only these type of compounds easy intercalate within the clay interlayer. Such adsorption also involves an irreversible displacement of part of the clay interlayer water. The partial dissolution of the clay matrix is indicated by XRD as an irreversible modification of the clay structure. On the contrary, adsorption of *n*-heptane or toluene molecules on the same clay are reversible processes, since the clay mineral recover its original crystalline structure after aging and evaporation of the organic species.
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## 1. Introduction

Petroleum is an extremely complex system that contains mostly hydrocarbons, such as paraffin and aromatic molecules, and polar compounds, which in addition to the carbon and hydrogen atoms, have either oxygen, nitrogen or sulfur atoms in their molecular composition. Asphaltene is the heaviest and non-volatile petroleum fraction and it contains the greatest proportion of condensed aromatic and polar compounds [1].

Petroleum recovery is strongly related to the wettability of reservoir rocks, mainly formed by carbonate, quartz grains and clay minerals. Most of the petroleum organic compounds are hydrophobic, and the adsorption of crude oil and specially asphaltene on mineral surface could be inhibited by the aqueous film usually present on mineral surface. Indeed, the wettability alteration of the formation rocks is naturally induced by asphaltene adsorption on their surface [2–4]. Adsorption of asphaltene from solution only occurs on the edges of the clay sheets or on clay external

surfaces [5]. A more complex mechanism of asphaltene adsorption on a mineral surface was proposed by Kaminsky and Radke [4] and Freer et al. [6]. In this model, the water film is essential to prevent asphaltene deposition, although organic deposition is favored when such water film collapses as a consequence of its aging in contact with crude oil. Other experiments indicated that a short time exposure of mica to crude oil normally doesn't show any perceptible deposit. However, aging allows the formation of deposits on mica surface as atomic force microscopy (AFM) revealed, but only for one of the tested crude oil [7,8].

It is worth to mention that adsorption of organic molecules on minerals as clays has already been considered as a major process in the diagenesis and maturation of organic matter to petroleum. Such adsorption is a key process in the protection of organic compounds from microbial degradation during petroleum diagenesis [9].

Adsorption of organic molecules on swelling clay minerals (2:1) is related to the features of clay active sites: external or between the clay lamellae. Still, the interlayer cations, as well as the chemical and physical characteristics of the adsorbed organic compounds, are also crucial. The dominant cations of the petroleum reservoir brine are sodium, calcium and potassium, and they may exchange those of

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clay interlayer space. The inner water molecules surrounding the interlayer cation are more able to protonate the organic molecules than the outer water molecules [5,10–13]. Additionally, water solubility of the organic compounds have also strong influence on the selection of adsorption site, type of bonding and strength, and the geometric orientation of the organic molecules within the interlayer space. Moreover, the dielectric constant of the organic molecules may also influence the formation of complexes within the montmorillonite space [10,14–19].

About 33% of the Mexico's petroleum reserve occurs in the Chicontepec channel sediments, which consist of shales and sandstones fine to very fines grained and commonly argillaceous. The porosity of the sandstone is around 14% and the petroleum recovery factors from these sediments are appreciably low, from 7 to 10% [20]. Moreover, the reservoir rock in the Chicontepec channel contains water sensitive clays, which are prone to swell in the presence of exogen or endogen water (bine or drilling mud water). These aspects may jeopardize the success of recovery procedures if water flooding is used.

The mechanism of crude oil adsorption has to be fully understood, if one attempts to improve the reservoir recovery factor under the mentioned circumstances. In this sense, two experimental models using two type of molecules are studied. Simple organic molecules (*n*-heptane and toluene) were selected to reproduce the paraffinic and aromatic petroleum fractions. A well characterized montmorillonite clay was used as the starting host for the organic species.

The purpose of this paper is then to perform the evolution in time of the adsorption of a straight-chain alkane and an aromatic type compound, both onto a Wyoming Na-montmorillonite clay. The results should be compared with the results obtained running the crude oil adsorption experiment on the same mineral and following the same procedure. Such experiments are expected to contribute to interpret the adsorption of crude oil as a function of paraffinic and aromatic petroleum content.

Adsorption of each organic species on montmorillonite was followed by X-ray diffraction (XRD) and thermal techniques. XRD is an adequate method to follow the evolution of the clay interlaminar space during the adsorption and desorption of the selected organic species. By thermogravimetric analysis it was possible to estimate if the organic molecules replaced part of the clay interlayered water or not [11,21,22]. In addition, scanning electron microscopy was used to reveal the clay structural changes due to crude oil interaction.

## 2. Experimental

### 2.1. Materials

The Na-saturated Wyoming-type montmorillonite of unit cell $Na_{0.33}[Al_{1.67}Mg_{0.33}(O(OH)_2(SiO_2)_4]$, from Reade Advanced Materials, was used in this work as the starting host for the organic species. This clay sample contains a water monolayer within the interlaminar space (the $d(0\,0\,1)$-spacing is 12.45 Å) and its reported CEC is 90 meq/100 g.

A crude oil sample collected from a Mexican petroleum well was centrifuged at 2000 rpm for 30 min to separate the natural suspended solids (sediment). The elemental composition of the crude oil sample was performed in an Elemental Vario EL instrument for the measurement of carbon, hydrogen, and nitrogen contents. A Leco SC-444 instrument was used to measure the sample sulfur content. Finally, oxygen content was calculated to complete the mass balance to 100%.

Paraffin, aromatic and polar fractions of the soluble part of the sample were determined in a high performance liquid chromatography (HPLC) Hewlett Packard 1100 with diode detector, according to the ASTM D-2007 standard. All other chemicals used in the experimental part were commercial of high-grade purity and used as received.

### 2.2. Sample preparation

Three montmorillonite samples of approximately 0.5 g each, were saturated with an excess of toluene, *n*-heptane and crude oil, respectively. All samples were maintained in contact with the respective organic phase in sealed amber bottles during the entire experimental time. The time evolution of the inter-layer spacing of each sample was followed by XRD. First, after 24 h of contact, a small portion of clay impregnated with the organic specie was taken out of the respective bottle. The slurry-like sample was deposited in the X-ray diffraction sample holder without elimination of the liquid excess. Then, after 48 h of contact, a new portion of the mixture was again taken out from its sealed bottle and again studied by XRD. This procedure was repeated at time intervals of 72, 96, 192 and 216 h of contact for each impregnated sample. As all samples taken after 216 h did not present any diffraction peak, these samples were dried in air by 2 h (evaporated) and also studied by XRD.

Only the fresh (24 h) and aged (216 h) samples were evaluated by thermogravimetric analysis (TGA). In addition, TGA and differential thermal analysis (DTA) were applied to the non-impregnated clay sample.

### 2.3. Characterization techniques

Structural alterations of clay samples when in contact with organic molecules were evaluated following the $d(0\,0\,1)$-spacing and the full widths at half maximum height (FWHM) of 0 0 1 peak registered by X-ray diffraction (XRD). The X-ray diffraction patterns were obtained using a D500 Siemens diffractometer coupled to a copper anode X-ray tube. The Cu Kα radiation was selected with a diffracted beam monochromator. Under certain conditions, the FWHM can be used to estimate the crystallite size

Table 1
HPLC analysis of crude oil (wt.%)

| Hydrocarbon type | As aromatic | As alkyl chain | Total | Relative to crude oil |
|---|---|---|---|---|
| Saturate | | | | |
| Alkyl chains | 0 | 28.1 | 28.1 | 9.27 |
| Aromatic: | | | | |
| One ring | 1.9 | 20.3 | 22.2 | 7.33 |
| Two rings | 3.1 | 8.3 | 11.2 | 3.7 |
| Three rings | 1.7 | 6.3 | 8.0 | 2.64 |
| Four rings | 1.5 | 9.4 | 11.1 | 3.66 |
| Polar | | | | |
| Polar | 3.5 | 15.9 | 19.4 | 6.4 |
| Total | 11.7 | 88.3 | 100 | – |
| wt.% recovered | | | | 33 |

(domain sizes, not particle diameter). Thus, peaks become broader as the coherent scattering domains become smaller.

The TG analyzes were performed according to the ASTM E-1131 standard in a Perkin Elmer TGA-7 as follows: each sample was heated in air from room temperature up to 750 °C at a rate of 10 °C/min. The phase transitions of the natural clay was obtained by differential thermal analysis (DTA) using a Perkin Elmer DTA-1700 apparatus.

Morphology of the natural clay and of same sample impregnated with crude oil was observed with a scanning electron microscope (SEM) JEOL JSM 6300 and all samples were coated with gold.

## 3. Results

### 3.1. Crude oil composition

The crude oil sample used in this study has 32.9 API$^0$ and an H/C atomic ratio of 1.82. It contains 2.53 wt.% of asphaltene separated with *n*-pentane. Table 1 shows that the death-oil, free of sediments, contains 9.27 wt.% of saturates, 17.33 wt.% of aromatic with 1–4 rings in their structures, 6.4 wt.% of polar compounds as well as 77 wt.% of heavier material, not detected by this technique. Most of the detected aromatic rings mainly have alkyl side chains and, most of the polar compounds are linear. Acidity, determined as mg of KOH *per* gram of crude oil, is 0.10, and the responsible organic compounds may be naphtenic or fatty acids [1].

### 3.2. n-Heptane uptake

Fig. 1 shows the (0 0 1) peaks positions for *n*-heptane uptake on clay mineral and corresponding to each XRD measurement. The initial curve corresponds to natural Wyoming montmorillonite clay, and the final one to the clay impregnated sample after evaporation of the organic phase as described in the subsection 2.2. The *d*(0 0 1)-spacing drop from 12.45 to 11.9 Å after 24 h of contact and the maximum
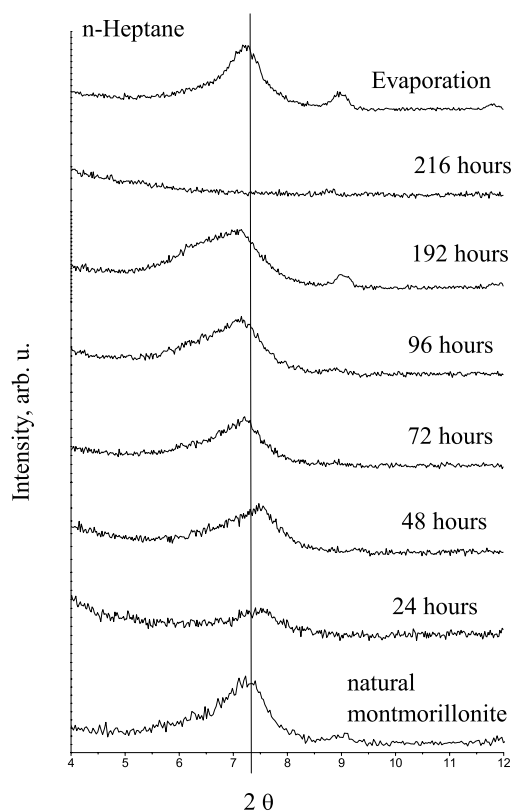


Fig. 1. Time sequence X-ray diffraction profiles for *n*-heptane uptake on natural montmorillonite clay.

*d*(0 0 1)-spacing was reached after 192 h, at 13.07 Å. The (0 0 1) basal reflection shifts towards higher *d*(0 0 1) interlaminar spacing, until, after 216 h of contact, the (0 0 1) peak fades, and it only reappears after the paraffin was evaporated as a consequence of air exposure.

Fig. 2 presents the *d*(0 0 1)-spacing as well as the peak broadening as full width at half maximum high (FWHM) for *n*-heptane uptake experiments. The shifting of (0 0 1)
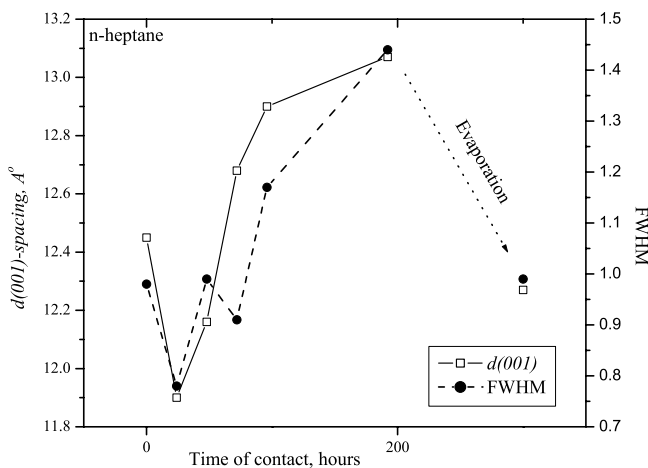


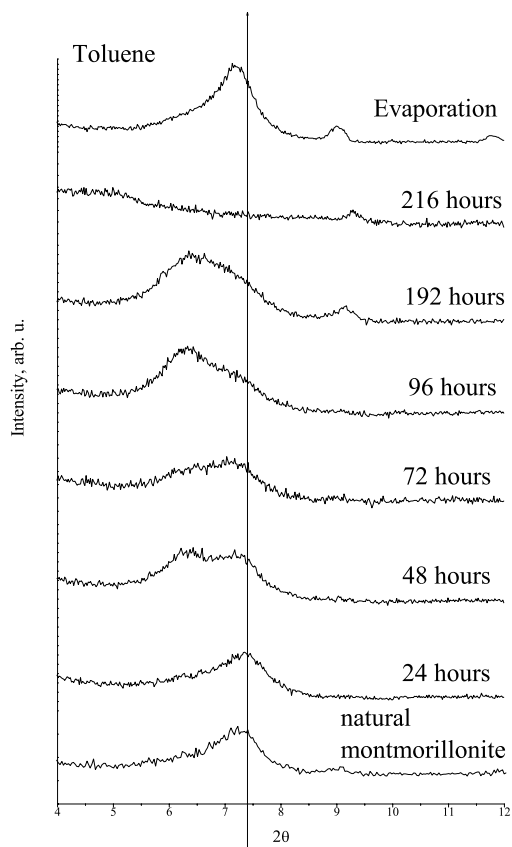Fig. 2. Evolution of *d*(0 0 1)-spacing and FWHM for *n*-heptane uptake on natural montmorillonite clay.

Fig. 3. Time sequence X-ray diffraction profiles for toluene uptake on natural montmorillonite clay.

peak position is accompanied by a constant increase of its FWHM during the adsorption process, which only occurs during the first 48 h. After $n$-heptane evaporation, a drastic reduction of $d(0\,0\,1)$-spacing and FWHM occurs, and both clay parameters recover the clay original values.

### 3.3. Toluene uptake

Fig. 3 shows the X-ray diffraction profiles corresponding to each measurement of toluene adsorption on natural montmorillonite clay. In this case, the $(0\,0\,1)$ peak shape changes from an initially symmetric shape to an asymmetrically broadened one, due to a combination of two peaks: at $d = 12.02$ and $14.00$ Å, resolved through a deconvolution process. The highest $d(0\,0\,1)$-spacing, of $14.00$ Å, is reached after 24 h of interaction and conserves close to this value up to 192 h.

If the relative area of the $(0\,0\,1)$ peak corresponding to $d = 14.00$ Å is plotted against time, Fig. 4, the maximum value is reached after 96 h and it remains constant up to 196 h. After 216 h of contact, both $(0\,0\,1)$ peaks fade, and only one $(0\,0\,1)$ peak at $d = 12.30$ Å reappears after evaporation of the aromatic compound.

Fig. 5 presents the $d(0\,0\,1)$-spacing variation as well as the peak broadening as the FWHM for all toluene uptake measurements. The shifting of $(0\,0\,1)$ peak is accompanied by a strong increase of the FWHM of the peak for the first 24 h. After that, these parameters are almost constant up to 196 h. A drastic reduction of both parameters occur after toluene evaporation, and consequently, $d(0\,0\,1)$-spacing and FWHM recover the original clay values.

### 3.4. Crude oil uptake

Fig. 6 shows the X-ray diffraction profiles obtained for the crude-oil impregnation following the indicated time sequence. The shifting of the $(0\,0\,1)$ peak position is small and the maximum $d(0\,0\,1)$-spacing of $12.83$ Å is reached after 96 h of contact but it strongly diminishes up to 196 h. As in the previous experiments, the $(0\,0\,1)$ peak vanishes after 216 h of contact with crude oil but the new value, $12.11$ Å, is smaller than that of the original clay.
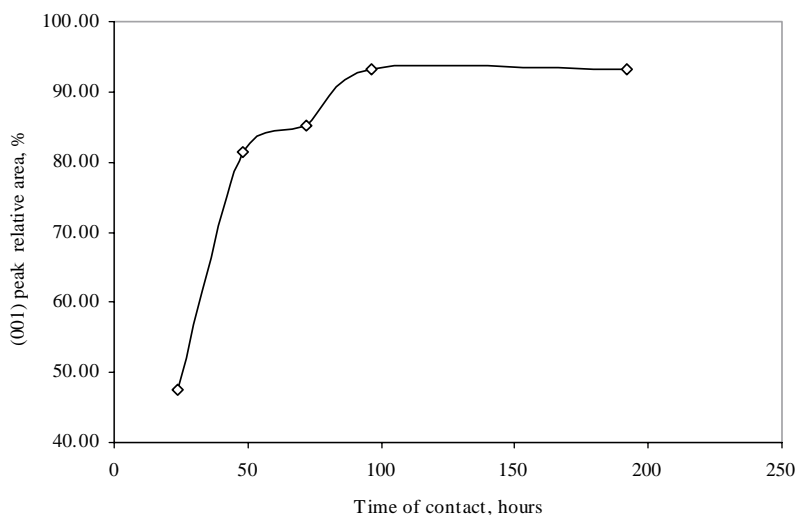


Fig. 4. Evolution of the $(0\,0\,1)$ peak at $14.00$ Å relative area during the toluene uptake.
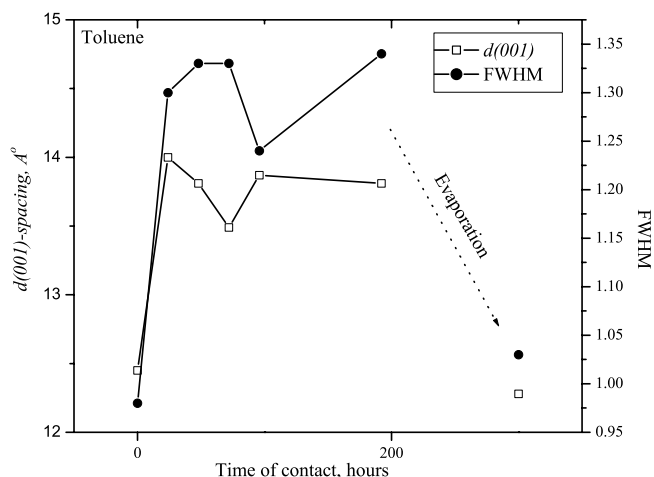
Fig. 5. Evolution of *d*(0 0 1)-spacing and FWHM for toluene uptake on natural montmorillonite clay.

Fig. 7 shows that up to 192 h of contact with crude oil, the (0 0 1) peak FWHM is close to that of the natural clay value. However, when the sample recovers its crystallinity after crude oil evaporation, a strong increase of the FWHM is observed. This indicates an increment of the scattering domains.
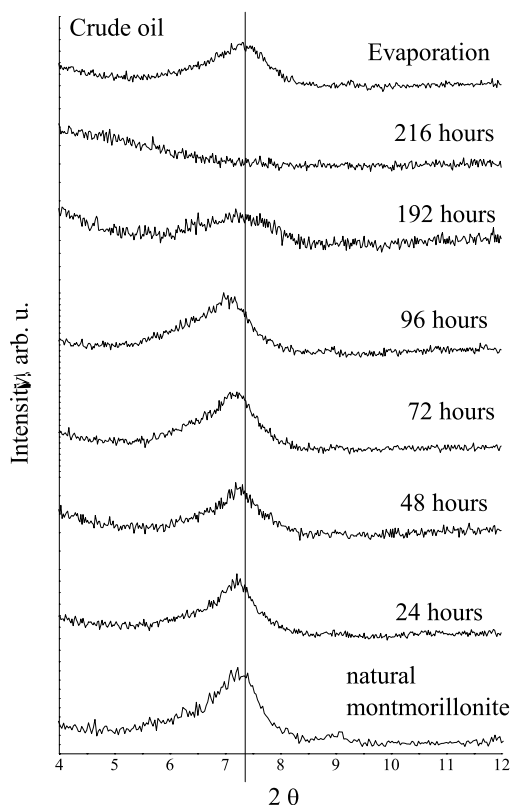


Fig. 6. Time sequence X-ray diffraction profiles for crude oil uptake on natural montmorillonite clay.

Table 2
DTA and TGA results for untreated Wyoming montmorillonite clay

| DTA, temperature (°C) | TGA | |
|---|---|---|
| | Temperature (°C) | Weight loss (wt.%) |
| 79.4 | 26–99 | 7.2 |
| 503.4 | 99–250 | 0.8 |
| 623.4 | 250–520 | 0.74 |
| 913.3[a] | 520–730 | 3.6 |
| – | Weight lost | 12.4 |

[a] All transitions are endothermal except, which is exothermal.

## 3.5. Thermal behavior

Table 2 summarizes the DTA phase transitions and TGA weight loss events occurred in the original montmorillonite sample during heating. The results reproduce the already reported results for this mineral [21,22].

Table 3 shows the TGA weight loss events of all the impregnated samples registered from two sets of samples: the freshly prepared (24 h) and the aged (216 h) samples of each of the contacted organic phases (*n*-heptane, toluene and crude oil).

The toluene and crude oil freshly impregnated clay samples present a similar thermal behavior. The amount of adsorbed material is similar in both experiments and it is eliminated following very similar trends, as shown in Table 3.

Only the aged clay samples impregnated with *n*-heptane or toluene reproduce the TGA behavior of the non-exchanged montmorillonite. Aging of the these samples favors the evaporation of organic molecules and the total reintegration of

Table 3
TGA temperature and weight loss for Wyoming montmorillonite exposed to organic species

| | Fresh (24 h) | | Aged (1 month) | |
|---|---|---|---|---|
| | Temperature (°C) | Weight loss (wt.%) | Temperature (°C) | Weight loss (wt.%) |
| *n*-Heptane | 24–50 | 21.4 | 25–96 | 7.16 |
| | 50–103 | 5.72 | 96–250 | 0.82 |
| | – | – | 250–520 | 0.75 |
| | 540–720 | 2.67 | 520–730 | 3.6 |
| | Weight lost | 31.06 | – | 12.4 |
| Toluene | 26–90 | 3.03 | 26–94 | 6.08 |
| | 90–180 | 16.79 | 94–250 | 1.05 |
| | 180–400 | 16.79 | – | – |
| | 400–590 | 4.50 | 250–520 | 0.90 |
| | 590–750 | 2.53 | 520–730 | 3.75 |
| | Weight lost | 43.65 | – | 11.8 |
| Crude oil | 26–80 | 3.20 | 25–90 | 4.20 |
| | 80–170 | 16.32 | 90–155 | 4.81 |
| | 170–400 | 17.13 | 155–338 | 13.12 |
| | – | – | 338–435 | 2.17 |
| | 400–575 | 4.06 | 435–570 | 3.29 |
| | 575–750 | 2.88 | 570–705 | 3.11 |
| | – | 28 | 705–750 | 0.54 |
| | Weight lost | 43.59 | – | 31.3 |
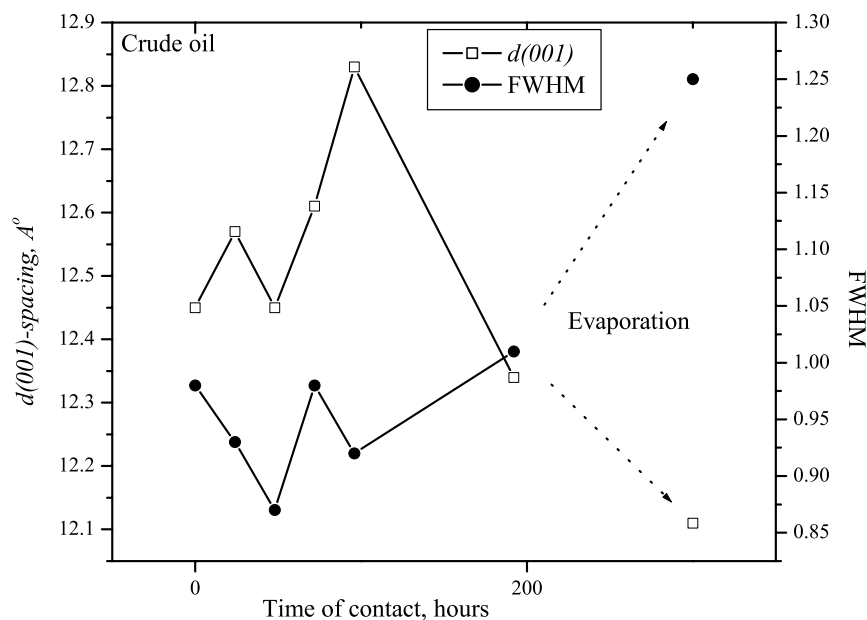
Fig. 7. Evolution of $d(0\,0\,1)$-spacing and FWHM for crude oil uptake on natural montmorillonite clay.

water. The aged crude oil impregnated sample conserves more material than all the other aged samples, including the non-impregnated clay. Thus, TGA results indicate that some of the crude oil compounds still occupy sites on clay external surface or within the clay sheets as a consequence of aging. Water is not allowed to return to the clay interlayer space, as the weight lost in the range 25–90 °C is lower that that of the other aged samples, included the non-exchanged clay.

### 3.6. SEM morphology

Fig. 8 shows the morphology of crude oil impregnated clay samples compared to the non-impregnated clay. Fig. 8(a) shows that the original clay sample is composed by rectangular and poor layered aggregates of approximately 40 μm × 10 μm. Fig. 8(b) presents a rectangular and well layered particle of 10 μm × 10 μm. Such particle has irregular layers and broken edges. This particle is surrounded by small particles with a diameter of ca. 1 μm.

## 4. Discussion

The impregnation experiments were carried out using a well characterized montmorillonite clay containing a water monolayer within the interlaminar space as indicated the $d(0\,0\,1)$-spacing value. The 0 0 1 *plane reflection* of the clay sample, measured by X-ray diffraction, is the most useful method to distinguish if the organic species intercalate within the clay interlayer space or adsorbed on the external surface. Only when organic species penetrate between the clay lamellae, the $(0\,0\,1)$ peak shifts from its original position, that corresponds to the non-exchanged montmorillonite clay.

### 4.1. n-Heptane uptake

For *n*-heptane, the maximum $d(0\,0\,1)$-spacing of 13.07 Å was reached after 192 h, but it only represents a shift of 5% if compared to the original interlayer space, while the FWHM is twice as much as the original one. Alkanes, such as *n*-heptane, are non-polar molecules and their solubility in water is very low. The drop of the $d(0\,0\,1)$-spacing from 12.45 to 11.9 Å after 24 h of contact indicates that part of the interlayered water molecules were expelled out of this space prior to *n*-heptane intercalation. Evaporation of *n*-heptane favor water molecules to reintegrate within the clay space, as the final $(0\,0\,1)$ peak position returns to that of the original clay and also does the FWHM.

In this context, the thermal behavior of fresh and aged samples is most relevant. In the fresh sample, 27.49 wt.% of the material, which includes *n*-heptane and water molecules, is eliminated from 24 to 103 °C. Apparently, most of the *n*-heptane molecules, 21.4 wt.%, were weakly bonded, and probably adsorbed on external clay surface; they are indeed eliminated at a lower temperature than the corresponding paraffin boiling point (98.4 °C). A smaller amount of material (5.72 wt.%) remains adsorbed on the clay up to 103 °C.

Aging of the clay sample with *n*-heptane for 216 h favors its evaporation and consequently, the thermal behavior reproduces that of the original montmorillonite, as this sample has lost its original structure (see XRD results).

### 4.2. Toluene uptake

Toluene seems to intercalate into the interlayer space of the natural Wyoming montmorillonite clay and, moreover, during the first 24 h it pushes out of the interlayer space around 37% of the water molecules, as TGA results show.
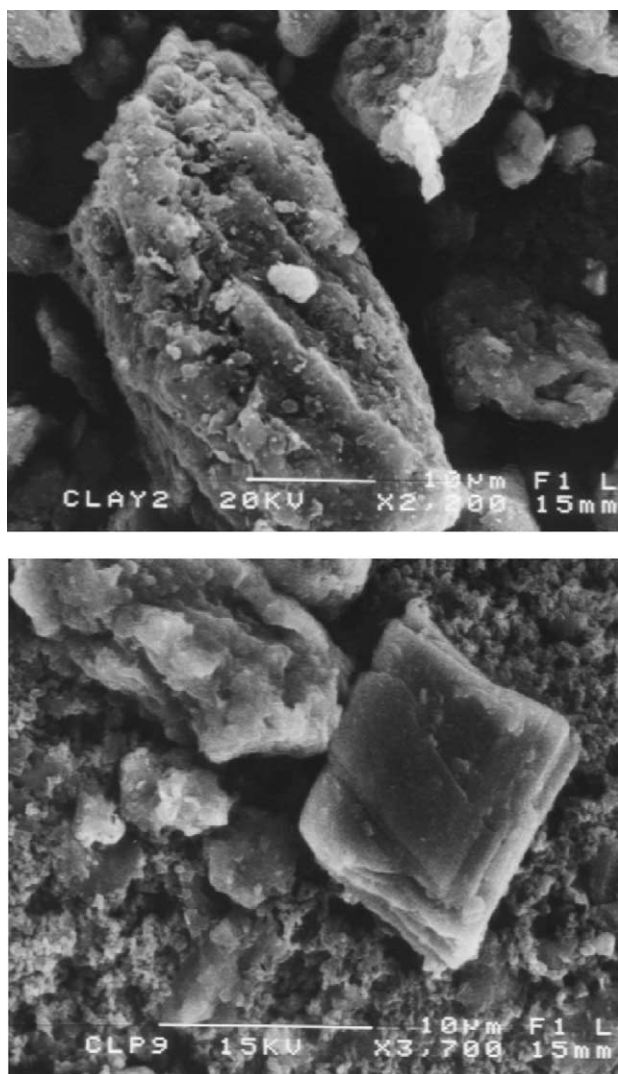
Fig. 8. SEM micrographies of (a) montmorillonite clay showing a poor layered particle of $40 \mu m \times 20 \mu m$ with irregular surface; and (b) the same sample after impregnation with crude oil, showing a well layered particle of about $10 \mu m \times 10 \mu m$ and surrounded by small particles of about $1 \mu m$ of diameter, not observed in the original clay sample. This last image presents the dissolution of the clay crystal edges.

The presence in this sample of a complex (0 0 1) peak corresponding to two interplanar distances may be interpreted as the formation of two fractions of intercalated clay. On the one hand, a small percentage of the clay remains unchanged, therefore conserving its original water molecules (peak at 12.02 Å). On the other hand, an increasing fraction of toluene intercalates the clay, which gives the peak at 14.00 Å. The relative area of this last peak reach the maximum ratio of 93 wt.% after 72–96 h. It seems that a fraction of clay remains unaltered (7 wt.%). Most probably, at high toluene adsorption, some water molecules are occluded into interlayer space and cannot be expelled by the aromatic molecules. This water, indeed, corresponds to those surrounding the interlayer cations. If this hypothesis is correct, the freshly impregnated clay should present a very different thermal behavior compared to that of the non-impregnated clay. Moreover, the aged one (216 h), which lost its structure should reproduce the thermal behavior of the original clay. Indeed, such is the case.

When clay is freshly impregnated with toluene, the amount of weight eliminated from 26 to 90 °C is 3.03 wt.%, approximately half of that of natural clay (7.2 wt.%). Most of the water molecules are reintegrated within the $d(0 0 1)$-spacing, as both FWHM and (0 0 1) peak position return to those of the non-exchanged clay sample. Despite reproducing the thermal behavior of the original clay, the aged sample still contains about 15.6 wt.% of water deficit if compared to the water amount corresponding to the original clay sample and eliminated up to 99 °C.

For the freshly impregnated sample, three modes of toluene adsorption may be proposed following the TGA mass loss events in Table 3: 16.79 wt.% is weakly adsorbed and eliminated in the range 90–180 °C (this temperature interval includes the toluene boiling point at 110.6 °C); an equal amount, 16.79 wt.%, is strongly adsorbed in the clay interlayer space, as it is eliminated in a higher temperature interval (180–400 °C), and finally, a small amount of toluene (4.5 wt.%) is eliminated within a much higher temperature interval (400–590 °C). This last thermal event may be related to the diffusion of toluene within the clay structure.

The kinetics of toluene adsorption by montmorillonite show an exponential increase, as the ratio of toluene to clay increases, followed by a slow desorption attributed to the hindered removal of toluene from interlamellar regions of the clay [23]. For toluene, the interaction occurs between the aromatic ring π-electrons and the siloxane surface. Thus, adsorption of toluene is considered as a physical phenomenon, as it is in case of the other non-ionic hydrophobic compounds, such as naphthalene, phenanthrene and pyrene, which are polyaromatic compounds [11,24].

### 4.3. Crude oil uptake

The trend of the evolution of the (0 0 1) peak as a function of time reproduces the one observed for $n$-heptane: slow organic uptake and a maximum $d(0 0 1)$-spacing reached up to 96 h of contact. This maximum, 12.83 Å, is very close to the maximum $d(0 0 1)$-spacing space obtained in the experiment with $n$-heptane, 13.07 Å, but differs from the one for toluene (14.00 Å). In addition, there is only one (0 0 1) peak in the crude oil impregnated clay sample diffractograms, which shifts to a lower angular values before it fades out at ca. 216 h. Hence, even though aromatic are the main species identified by HPLC among the crude oil compounds, only paraffin or alkane type compounds preferentially diffuses within the clay interspace and occupy the adsorption sites in competition with the aromatic species, which remain out of the clay.

Aging and evaporation of crude oil does not eliminate all the adsorbed organic species, as in the previous experiments with pure substances. Most of these organic species prevail

on clay surface, and only could be eliminated when high temperatures are applied (see TGA results). The amount of the adsorbed material (TGA weight loss) is high at the beginning and similar to that of toluene. Even if aging of this sample is accompanied by a decrease of adsorbed material, it is still high compared to the other aged samples and non-exchanged montmorillonite. Moreover, the aged sample presents additional TGA weight loss events, between 520 and 730 °C, if compared with the number of thermal events of the original clay. Thus, as a consequence of petroleum adsorption perturbation of the clay structure occurs. As shown in Fig. 5, the strong increase in the (0 0 1) peak FWHM registered after crude oil evaporation indicates a diminution of the scattering domains. Consequently, the size of clay lamellae diminishes and electron microscopy images confirmed in Fig. 8(b) the presence of small particles not observed in the original clay sample in Fig. 8(a).

These small particles may be the result of clay matrix dissolution promoted by the acidic fraction of the crude oil sample adsorbed externally on clay [25]. Normally such type of fraction contains carboxylic compounds as naphthenic acids or cyclopentane derivatives, with many rings (polycyclic type) and unsaturated bonds [1]. Since the naphthenic acids and their metallic soaps ($Men^+$-soaps; $Men^+ = Na^+$, $Ca^{2+}$ or $Mg^{2+}$) are surface/interfacially active, they normally accumulate at the water-to-oil interface and may stabilize any colloidal structures. Moreover, Ca or Mg-soaps are compounds with low water solubility and may also contribute to the formation of organic deposits.

Irreversible adsorption of asphaltene is presented by Freer et al. for a flat mineral surface and it is associated to water film rupture in the presence of crude oil [6]. In our work, the same process apparently occurs. The aging process favors the external water layer to break and, consequently, some of the crude oil compounds (asphaltene types) enwrap the clay surface. Under such circumstances, only those compounds containing alkane chains are able to enter within the clay interlayer when freshly contacted with crude oil.

The clay interlaminar spacing expansion and contraction level has been often attributed to the influence exerted by the dielectric constant ($\varepsilon$) of the intercalated organic species between clay plates [26]. For the crude oil experiments however, the expansion of $d(0\,0\,1)$-spacing is apparently not correlated to its dielectric constant (mean reported value of 2.1), but it is for $n$-heptane and toluene experiments.

## 5. Conclusions

Adsorption of crude oil on a swelling clay mineral is an irreversible process, which is conditioned by petroleum paraffin or alkane chain compounds content. As a consequence of aging, part of the petroleum organic species still conserved in contact with clay, while another part evaporates. Moreover, aging allows only part of the water molecules, initially expelled from the clay interlayer, to reintegrate to the clay structure.

In natural environments, such dehydration due crude oil could produce clay sheets deformations, which affect the rock elasticity and strength. Moreover, an abnormal pore pressure may be generated followed by hydrocarbon migration, if the neighborhood permeability is adequate to allow such event [27].

Crude oil interaction with clay minerals only can be understood when compares with paraffin and aromatic adsorption results, as crude oil is a complex mixture of these compounds in addition to polar species. Both paraffin and aromatic type molecules ($n$-heptane and toluene) used in the experiments can occupy the clay interlayer space when separately contacted with clay. However, when crude oil contacts the clay, only those compounds containing alkane chains can preferentially diffuse within the clay interlayer and occupy the interlamellar space. Apparently, this process inhibits the entrance of the other compounds such as aromatic or polar molecules within the already intercalated space. In addition, most of the petroleum big and complex molecules may show steric hindrance that inhibits their entrance within the clay interspace. Consequently, adsorption of petroleum organic compounds on 2:1 clay mineral is conditioned by its paraffinic content or by any other petroleum organic compounds containing alkane chains in their molecular structure.

Adsorption of $n$-heptane and toluene is a reversible process, as the original clay matrix parameters are reestablished after evaporation of organic molecules. Additionally, the water molecules, partially displaced as a consequence of organic molecules adsorption, were almost reintegrated in the clay matrix after the their evaporation.

## Acknowledgements

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