Clays and Clay Minerals, Vol. 28, No. 3, pp. 197–203, 1980.

FORMATION AND CHARACTERIZATION OF CLAY COMPLEXES WITH BITUMEN FROM ATHABASCA OIL SAND

ELIZA CZARNECKA AND J. E. GILLOTT

Department of Civil Engineering, The University of Calgary
Calgary, Alberta T2N 1N4, Canada

Abstract—Montmorillonite, kaolinite, illite, and chlorite were found to adsorb bitumen and its pentane-soluble and pentane-insoluble fractions. The formation of clay-bitumen complexes is influenced by the nature of the exchangeable cation on the clay and by the solvent carrier which stabilizes the bituminous compounds. Ca-clays adsorb organic compounds more strongly than sodium forms except in the presence of nitrobenzene. Solvents of high dielectric constant, such as nitrobenzene, promote ionization so that the ion-exchange mechanism of adsorption is favored, whereas solvents of lower dielectric constant, such as chloroform, tend to solvate rather than to dissociate bitumens. The behavior of the montmorillonite-bitumen complex in variable relative humidity indicates that organic molecules adsorb primarily on external surfaces and cause the clay to become less hydrophilic than prior to treatment. Clay-organic complexes are sufficiently stable to resist powerful organic solvents. The clay-organic complex separated from the Athabasca oil sand behaves similarly during chemical treatment to complexes formed between bitumen and the four reference clay minerals.

Key Words—Bitumen, Clay-organic complex, Infrared, Montmorillonite, Oil sand, X-ray powder diffraction.

INTRODUCTION

Lower Cretaceous sands saturated with viscous bitumens that cannot be produced by conventional recovery methods occupy about 48,000 km² of Alberta. They form four major and several smaller deposits, the largest being the Athabasca deposit (Berkowitz and Speight, 1975); the oil sands are mostly in the McMurray Formation. The concentration of bitumen by weight varies from 1 to 18% (average 12%); the oil content is related inversely to the amount of clay in the sediment. The heavy oil occupies up to 90% of the pore space in these sediments; the oil is separated from the surfaces of the minerals by a thin film of water. The sediment consists of more than 90% angular quartz grains with minor amounts of potash feldspar, muscovite, chert, and clay minerals, which are mostly kaolinite, illite, chlorite, and montmorillonite (Carrigy and Kramers, 1973).

In situ methods of bitumen recovery are being investigated. The formation of clay-organic complexes may significantly affect oil production (Berkowitz and Speight, 1975; Carrigy and Kramers, 1973; Hills, 1974). Clementz (1976, 1977) found that asphaltenes and resins adsorb rapidly and irreversibly onto montmorillonite, kaolinite, and illite under near-anhydrous laboratory conditions.

A typical analysis of the bitumen from the Alberta oil sands is given in Table 1. The bitumen is a very dense, black, viscous liquid with viscosity and composition varying slightly within the deposit. The "heavy" components of bitumen, known as asphaltenes and resins, are complex mixtures of large polyaromatic hydrocarbons containing heteroatoms such as N, S, and O; polar functional groups are commonly present. Clay minerals take up organic molecules by a variety of mechanisms (Brindley, 1971; Greenland, 1965; Mortland, 1970; Theng, 1974). The interaction between clay and bitumen is affected by the conditions and the composition of the bitumen. The object of the present paper is to describe the adsorption of bitumen extracted from Athabasca oil sands by the clay minerals most commonly found in the deposit using X-ray powder diffraction (XRD) and infrared spectroscopy (IR).

EXPERIMENTAL

Materials

Experiments were conducted on the <2-μm fraction separated by gravitational sedimentation from the McMurray Formation oil sand. Studies were also performed on API Project 49 reference clay No. 24 (montmorillonite from Otay, California) and No. 35 (illite from Fithian, Illinois), a California chlorite (exact locality unknown), and a Saskatoon, Saskatchewan, fire clay composed mainly of kaolinite. Samples were converted to the sodium and calcium ion-exchange forms by repeated flocculation in appropriate salt solutions. The samples were rinsed centrifugally, air dried, and ground to pass a 200-mesh sieve. Some samples were dried at 225°C to remove excess water.

Free bitumen was separated from Athabasca oil sand by the Soxhlet extraction technique using toluene as a solvent. Pentane-soluble maltenes composed of resins

Copyright © 1980, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press

Table 1. Average chemical composition of Alberta bitumen.

Hydrocarbon components		Solubility in pentane	Content (wt. %)
Asphaltenes		Negative	18–25
Maltenes	resins	Positive	29–35
	oils	Positive	45–49
Elemental analysis:		C	83.0–86.0%
		H	10.2–10.4%
		S	4.5–5.3%
		N	0.3–0.5%
		O	0.8–1.4%

Molecular weight: 540–800
C/H ratio: 8.1
Density (20°C): ~1.02 g/cm³ (6°–9° API gravity)

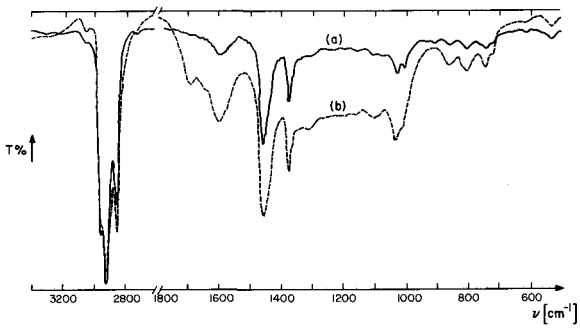


Figure 1. Infrared spectra of (a) bitumen, and (b) asphaltene extracted from Athabasca oil sands.

and oils and pentane-insoluble asphaltenes were also used in experiments.

Experiments and methods

IR analyses were carried out on: (I) bitumen extracted from oil sand and its pentane-soluble and pentane-insoluble fractions; (II) the Na-form of the four reference clays treated with bitumen and its fractions in toluene solutions; (III) the Na- and Ca-forms of the four reference clays treated with bitumen in chloroform and bitumen in nitrobenzene solutions; and (IV) the clay fraction separated from the oil sand following exposure to organic solvents. XRD investigations were carried out on: (V) the Na- and Ca-montmorillonite treated with bitumen and its fractions in benzene and pre-conditioned at varying relative humidities.

Bitumen, resins, and oils were prepared for IR analysis by smearing the mull-like sample between two polished KBr-windows; asphaltenes were prepared as KBr pellets. IR spectra were recorded on a Beckman 4220 infrared spectrophotometer in two regions, 4000–2600 cm^{-1} and 1800–400 cm^{-1} as percent transmission (T %) against wavenumber (cm^{-1}).

Clay-organic complexes were formed by chemical treatment of all four clays; excess organic material was subsequently removed by leaching. A few milligrams of each sample were dehydrated by oven-drying at 225°C for 24 hr; samples of unheated Na-montmorillonite and Na-illite were also investigated. All samples were saturated with 20 ml of a 1% by weight bitumen in toluene solution, shaken, and allowed to equilibrate for 7 days. Excess bitumen was removed by rinsing with pure toluene until the effluent was colorless; samples were then rinsed several more times with 500 ml of toluene each. Washed samples were oven-dried at 105°C for 4 hr and portions examined by IR spectroscopy. The remaining parts were kept in 20 ml of chloroform-acetone solution (70:30) for 7 days, rinsed with 200 ml of the same solution through filter papers, and examined by IR. Spectra were obtained on KBr pellets (1–3% clay) and/or as thin films on KRS-5 or AgCl windows.

XRD patterns were recorded on a Philips-Norelco diffractometer over an angular range of 2°–12° at a scan rate of 1°2θ/min using Fe-filtered CoKα radiation. Patterns were recorded from the five series of samples of Na- and Ca-montmorillonite. In series I, samples preheated at 105°C for 4 hr (referred to below as "dried"), were kept in water, benzene, chloroform, toluene, and nitrobenzene for 48 hr. Oriented specimens were then deposited on glass slides. In series II to V, amounts of dried samples were covered with benzene, left overnight, and then stirred for 6 days at the required concentration of organic solvent. Samples were washed with benzene and air-dried.

In all series, slides for XRD were prepared in duplicate. Both specimens were first examined with excess solvent. One was then examined at a series of controlled relative humidities (R.H.) following pre-conditioning, and again after being dried at 105°C for 48 hr. The other was examined after overnight saturation with glycerol.

RESULTS AND DISCUSSION

Bitumen and its fractions

Typical IR spectra of bitumen extracted from the Athabasca oil sand and its separated fractions are shown in Figure 1; band assignments are given in Table 2. All spectra show bands at identical positions but the relative intensities of the C–H and C=C stretching bands of aromatic rings, at about 2930 cm^{-1} and 1600 cm^{-1}, respectively, are different. The ratio of the intensity of the 1600 cm^{-1} band to that of the 2930 cm^{-1} band is higher for asphaltenes than for any other fraction or for the total bitumen. This difference may be due to the presence of more aromatic groups in the structure or to the larger molecular size of asphaltenes. Molecular properties and interactions between bituminous fractions are related to the mobility of the fluids. It is assumed that asphaltenes are dispersed colloidally throughout the oily medium by association with the res-

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press

Table 2. Infrared band assignment for bitumen spectra.

Frequency (cm^{-1})	Relative intensity[1]	Vibration[2]	Chemical group
~3050	vw	ν C–H	alkenes
2950	vs	ν_{as} C–H	CH_3 aliphatic
2930	vs	ν_{as} C–H	CH_2 aliphatic
2855	vs	ν_s C–H	CH_2 aliphatic
1700	w	ν C=O	aryl ketone
~1610	w	ν C=C	aromatic
1460	s	δ_{as} C–CH_n	CH_3, CH_2
1376	m	δ_s C–CH_3	CH_3
1020–1040	w	ν_s C–O–C	aliphatic
720–860	w	δ C–H	aromatic

[1] vw = very weak; w = weak; m = moderate; s = strong; vs = very strong.

[2] ν_s = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration; δ_s = symmetric bending vibration; δ_{as} = asymmetric bending vibration.

ins in the manner of an electron donor–acceptor system. Therefore, each constituent of the bitumen depends upon the others for complete mobility and reactivity with rock surfaces.

Adsorption of bitumen on Na-clays

The Na-exchanged reference clay minerals gave IR spectra essentially identical to those of standard clays (Farmer, 1974; Van der Marel and Beutelspacher, 1976). The spectrum of Na-illite suggested the presence of a trace of organic matter, whereas the other clay minerals were practically free of organic constituents. Using the base-line technique, the absorbance, A, for two characteristic IR bands of each sample was calculated. Absorbance is defined as: $A = \log I_0/I$, where I_0 is the intensity of incident light, and I is the intensity of transmitted light. The bands between 3585 cm^{-1} and 3700 cm^{-1} (A_1) and at 2930 cm^{-1} (A_2) were considered. The band at about 3650 cm^{-1} is attributed to a stretching vibration of one of the hydroxyl groups of the clay mineral. The band at 2930 cm^{-1} is the result of a stretching vibration of the C–H bond within the CH_2 group of organic compounds. The ratio of absorbance $A_R = A_2/A_1$ for each clay separately was taken as a relative measure of the amount of bitumen adsorbed on a clay.

The absorbance ratios listed in Table 3 are the average of 3–5 spectra recorded for each clay sample, the relative precision of A_R being about 10%. For montmorillonite, the duration of the interaction between the clay surface and bitumen is more important than the initial heat treatment. On the assumption that IR absorbance is dependent on the amount of IR-active groups, about 25% of all organic matter adsorbed on preheated montmorillonite and 33% adsorbed on the unheated sample were removed by the chloroform–acetone.

Table 4. Values of absorbance ratio (A_R) for Na- and Ca-forms of reference clays treated with bitumen in chloroform and nitrobenzene.

Treatment		Clay type			
Ion	Solvent	Montmorillonite	Illite	Chlorite	Kaolinite
Ca	Chloroform	0.135	0.209	0.033	0.117
	Nitrobenzene	0.151	0.156	0.022	0.087
Na	Chloroform	0.123	0.153	0.032	0.079
	Nitrobenzene	0.212	0.139	0.035	0.069

The A_R values of unheated illite and preheated illite, kaolinite, and chlorite were markedly reduced by the chloroform–acetone to 55, 29, 28, and 43%, respectively. Chloroform–acetone removed comparable amounts (25–30%) of organic complexes from preheated samples of montmorillonite, kaolinite, and illite, but much more from chlorite (43%). The loss of organic complexes from the unheated montmorillonite and illite was significantly larger (33% and 55%) than from preheated samples.

Unheated montmorillonite and kaolinite were also treated with asphaltene and maltene in toluene. A_R for montmorillonite treated with asphaltene and maltene is 0.290 and 0.140, respectively, values that are much lower than for total bitumen (0.575). For kaolinite, however, A_R for asphaltene is 0.070, which is comparable with that for bitumen (0.060). Adsorption of maltene yields a much lower value (0.030).

The exact adsorption mechanism is not yet known; however, several possibilities have been discussed in the literature, including cation exchange involving positively charged nitrogenous (or other) groups in the bi-

Table 3. Values of absorbance ratio (A_R) for Na-forms of the four reference clays treated with bitumen in toluene.

Treatment	Clay type			
	Montmorillonite	Illite	Kaolinite	Chlorite
24 hr in bitumen, toluene rinsed	0.480	—	—	—
7 days in bitumen, toluene rinsed	0.575	0.140	—	—
225°C, 7 days in bitumen, toluene rinsed	0.512	0.100	0.060	0.133
7 days in bitumen, toluene, chloroform–acetone	0.388	0.060	—	—
225°, 7 days in bitumen, toluene, chloroform–acetone	0.383	0.059	0.043	0.076

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press

tumen, protonation of the organic phase, molecular dissociation, hydrogen bonding, electron transfer reactions, π interactions of aromatic rings, and attraction due to Van der Waals forces.

Effect of exchangeable cation and solvent carrier

Absorbance ratios for all four clays in the Na- and Ca-forms using nitrobenzene and chloroform as solvent carriers for bitumen are listed in Table 4. Values of A_R for both ion-exchange forms of montmorillonite are higher for nitrobenzene than for chloroform, whereas for illite, chlorite, and kaolinite, the situation is reversed. This indicates that structural differences reflected in the swelling ability of this clay mineral play an important role in the adsorption of bitumen.

The hydration energy of Ca is higher than that of Na. Thus, the values listed in Table 4 for the adsorption of bitumen by illite and chlorite are not unexpected. Kaolinite adsorbs a comparable amount of organic material in both forms. Montmorillonite adsorbs much more bitumen in its Na-form when nitrobenzene is used as solvent. In aqueous systems, intracrystalline swelling of montmorillonite with divalent exchange cations is limited to about 19 Å, whereas Na-montmorillonite shows extensive interlayer expansion (Norrish, 1954). Polar organic molecules are adsorbed mainly by replacement of the interlayer water (Mortland, 1970); therefore, the reaction is strongly dependant on the nature of the exchangeable cation.

Swelling capacity is also influenced by the dielectric constant of the medium (Barshad, 1952). For many organic substances swelling index is proportional to dielectric constant and inversely proportional to the square root of the ionic radius of the exchangeable cation. Due to the high dielectric constant of the nitrobenzene, bituminous molecules become more ionized, and the ion-exchange mechanism of adsorption is dominant (Clementz, 1976). Specific interactions between nitrobenzene and the monovalent cation prior to bitumen adsorption may affect the amount of bitumen adsorbed (Yariv *et al.*, 1966). Reactions of this sort may account for the differences in behavior between Na-montmorillonite and nonswelling clays in nitrobenzene. Solvents with a lower dielectric constant (e.g., chloroform) tend to solvate rather than to dissociate bitumens. The IR data of the present study indicate that this type of stabilization seems to be more important for the adsorption of organic molecules on nonswelling clays, particularly on chlorite and illite. Here, the relative intensity of bitumen IR bands is slightly higher for chloroform than for nitrobenzene.

Clay fraction from oil sand

The IR spectrum (Figure 2) and XRD pattern (Brown, 1972) of the clay fraction extracted from Athabasca oil sand show that it consists mainly of illite with small amounts of montmorillonite and kaolinite. The distinct adsorption in the spectral regions, 2800–3050 cm^{-1} and 1350–1500 cm^{-1}, indicates the presence of organic matter that probably consists of free bitumen (bitumen that is not adsorbed on a clay and that remains after Soxhlet extraction) and bitumen bonded in the form of clay-organic complexes. Further chemical treatment of the sample with toluene reduces the intensity of these adsorption bands due to removal of free bitumen (Clementz, 1976). Treatment with chloroform–acetone (70:30), a powerful solvent, further decreases the intensity of the IR absorption because of partial removal of adsorbed bitumen. The absorbance ratio of the two characteristic bands for organic matter and clay mineral indicate that rinsing in chloroform–acetone reduced A_R (0.30) to about 55% of that for the toluene-rinsed sample (0.55); prolonged action of this solvent (7 to 14 days) results in an even further decrease to 45%, indicating that part of the bitumen resists extraction; evidently a stable complex is formed with the clay. The rate of decomposition of the clay-organic complex is high and similar to that of unheated illite. Montmorillonite and kaolinite which are present in small quantities in the investigated clay show higher resistance to extraction by chloroform–acetone.

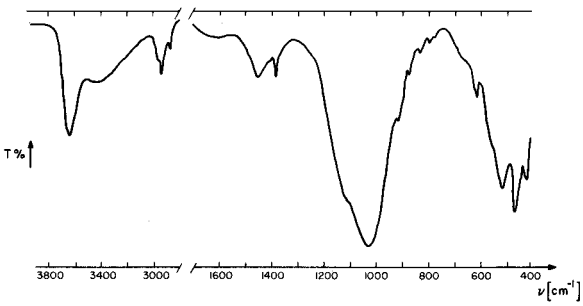


Figure 2. Infrared spectrum of clay fraction separated from Athabasca oil sand.

XRD of montmorillonite at varying relative humidities

Stock solutions of bitumen, asphaltene, and resin in benzene (concentration 0.5 mg/ml), and oil in benzene (5 mg/ml) were prepared. After shaking with montmorillonite, dark brown solutions of bitumen and asphaltenes become pale yellow. The change in color was less marked for the resin and oil solutions due to the much lighter initial color. This visual evidence clearly shows that the clay sorbs bituminous compounds from the solution, which is confirmed by IR spectra of all treated clay samples.

To establish the ability of organic molecules to enter the interlayer space and form a stable complex, XRD patterns were recorded from five series (I to V) of sam-

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press

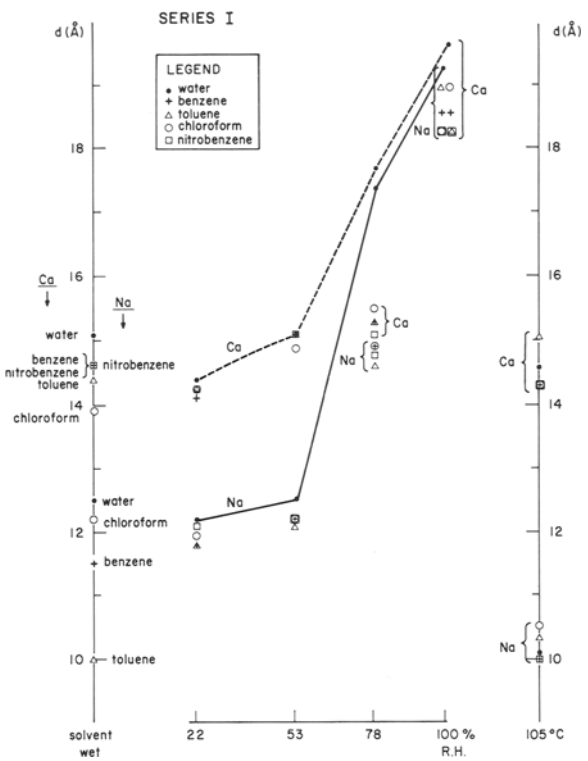


Figure 3. Average basal spacings of montmorillonite treated with different solvents at different relative humidities (series I).

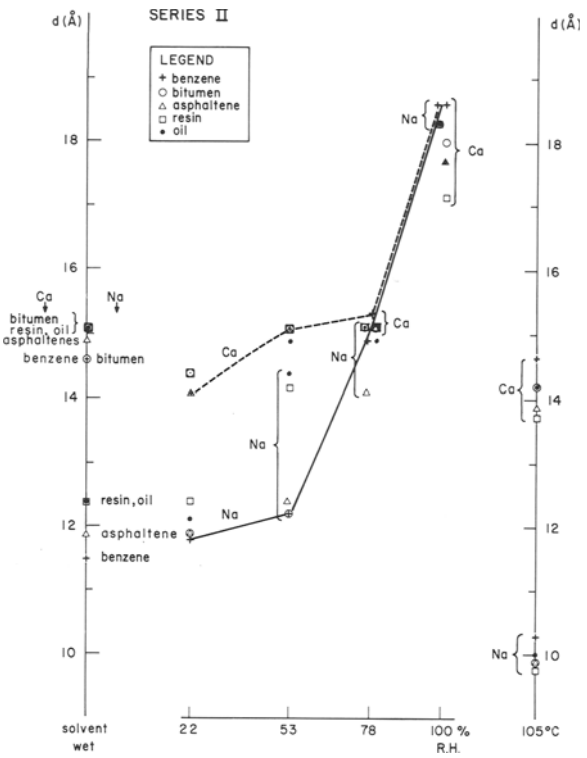


Figure 4. Average basal spacings of montmorillonite treated with Athabasca bitumen and its fractions at different relative humidities (series II).

ples of montmorillonite in the Na- and Ca-form. In series I the montmorillonite was treated with water and organic solvents to determine the influence of a solvent alone on the basal spacings. Organic solvents compared to water caused some decrease in the interlayer swelling capacity of both Na- and Ca-montmorillonite (Figure 3). Na-montmorillonite in nitrobenzene gave a large basal spacing, 14.6 Å, which may result from the high dielectric constant of nitrobenzene.

In series II the montmorillonite was treated with 1% by weight Athabasca bitumen, asphaltene, and resin solutions in benzene and 10% by weight oil solution in benzene. The spacings of the Ca-form are comparable to one another for samples treated with benzene and bitumen and all its fractions in benzene for all humidity conditions (Figure 4). Na-montmorillonite treated with bitumen and asphaltene solution behaves similarly to the sample deposited from benzene only; treatment with resin and oil resulted in larger spacings at 22% and 53% R.H.

Na-montmorillonite in excess solvent with bitumen in benzene solution gave basal spacings as large as those of Ca-montmorillonite. This large d spacing, however, is not retained at different humidity conditions, nor does it resist thermal treatment at 105°C.

In both series increases of R.H. led to increases in basal spacings. Any resistance to interlayer penetration by moisture conferred on montmorillonite by bitumen or its fractions or the organic solvents used is evidently not retained at high R.H. Treatment with glycerol resulted in a basal spacing of about 17.7 Å. Alberta oil-sand bitumen or its fractions do not result in interlayer penetration but rather adsorb onto external montmorillonite surfaces.

Series III samples were treated with benzene solution of asphaltenes and resins obtained by hydrocracking and steam cracking of Alberta crude. Samples were pre-conditioned in the same way as in series II. For solvent-wet and heated samples (Figure 5) the values of basal spacings for both forms of montmorillonite are very close to those of series II. Both Na- and Ca-montmorillonite responded differently, however, to preconditioning at controlled R.H., indicating some blocking of interlamellar space.

In series IV, samples of series III were recycled through the different conditions of controlled R.H. Series V consisted of samples prepared the same way as for series III but heated at 105°C prior to conditioning at known R.H. (Figure 5).

Montmorillonite samples treated with bitumen and

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press

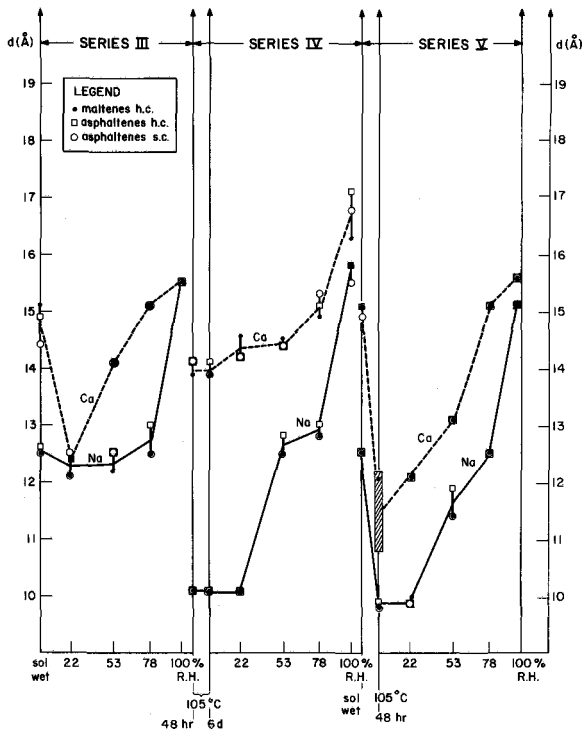


Figure 5. Average basal spacings of montmorillonite treated with asphaltenes and resins (obtained by hydrocracking of Alberta crude) at different relative humidities (series III, IV, and V).

its fractions extracted from Athabasca oil sand respond to varying humidity conditions differently from the same clay treated with asphaltenes and resins obtained from hydrocracked Alberta crude. This behavior reflects changes in the ability of the clay to take up water imposed by prior adsorption of bituminous compounds.

Results are independent of solvent or nature of the bituminous compounds, indicating that any interlayer complexes formed with organic molecules during solution treatment are not stable enough to resist competitive actions of moisture or heat.

SUMMARY AND CONCLUSIONS

Bitumen and its pentane-soluble and pentane-insoluble fractions extracted from Athabasca oil sands are adsorbed by the four clays most commonly encountered in the Athabasca deposits. Kerogen, organic material which resists solvent extraction by means of the Soxhlet apparatus, is present in the oil sand. IR results show that the amounts of bitumen adsorbed on clay minerals separated from the Athabasca oil sand and on illite treated with bitumen are reduced by the action of organic solvents to nearly the same extent. Slightly more organic matter was adsorbed by clays in the Ca-form than by clays in the Na-form except when nitrobenzene was used as a solvent. This behavior may follow from the known higher hydration energy of the calcium ion.

XRD data obtained in this work do not indicate the formation of a stable interlayer complex (Clementz, 1976) between montmorillonite and bitumen or its fractions extracted from the Athabasca oil sand. The XRD results do not support interlayer penetration or permanent blocking of these sites to make them inaccessible to other polar molecules.

Various bitumens and their fractions have different contents of heteroatoms (N, O, S) and hence the number and type of polar functional groups may be markedly different. Perhaps for this reason montmorillionite treated with these "highly polar" fractions seemed to be less hydrophilic, at lower values of R.H. However, it did take up water at higher R.H. and did not resist penetration by glycerol.

The results of the present study suggest that bitumen, asphaltenes, and maltenes from Athabasca oil sand adsorb primarily on external surfaces of clay minerals causing the treated clay to become less hydrophilic. The organic molecules are strongly bonded to the clay and greatly resist the action of powerful organic solvents. The amount of bitumen adsorbed is influenced mainly by the type of exchangeable cation on the clay and by the solvent transporting the bituminous molecules.

ACKNOWLEDGMENTS

The authors wish to acknowledge financial support from the Alberta Oil Sands Technology and Research Authority (Agreement #10) and the National Sciences and Engineering Research Council of Canada. The authors are also grateful to Dr. T. Ignasiak (Hydrocarbon Research Centre, University of Alberta) and to Dr. F. Bachelor and co-workers (Department of Chemistry, University of Calgary) for samples of bituminous fractions and useful discussions.

REFERENCES

Barshad, J. (1952) Expansion of montmorillonite and vermiculite: *Soil Sci. Amer. Soc. Proc.* **16,** 176–186.

Berkowitz, N. and Speight, J. G. (1975) The oil sands of Alberta: *Fuel* **54,** 138–148.

Brindley, G. W. (1971) Structural study of clay-organic complexes: U.S.–Japan Cooperative Science Seminar on Clay-Organic Complexes, Aug. 24–27, 47–**50,** (unpublished abstract).

Brown, G., ed. (1972) *The X-ray Identification and Crystal Structures of Clay Minerals:* Mineralogical Society, London, 554 pp.

Carrigy, M. A. and Kramers, J. W., eds. (1973) *Guide to the Athabasca oil sands area:* Can. Soc. Petrol. Geol., Oil Sands Symposium, 213 pp.

Clementz, D. M. (1976) Interaction of petroleum heavy ends with montmorillonite: *Clays & Clay Minerals* **24,** 312–319.

Clementz, D. M. (1977) Clay stabilization in sandstones through adsorption of petroleum heavy ends: *J. Petrol. Technol.* **29,** 1061–1066.

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press

Farmer, V. C. (1974) *The Infrared Spectra of Minerals:* Mineralogical Society, London, 539 pp.
Greenland, D. J. (1965) Interaction between clays and organic compounds in soils. Part II: *Soils and Fert.* **28,** 521–532.
Hills, L. V., ed. (1974) Oil Sands—Fuel of the Future: *Calgary Soc. Petrol. Geol. Mem.* **3,** 263 pp.
Mortland, M. M. (1970) Clay-organic complexes and interactions: *Advan. Agron.* **22,** 75–117.
Norrish, K. (1954) The swelling of montmorillonite: *Disc. Faraday Soc.* **18,** 120–134.
Theng, B. K. G. (1974) *The Chemistry of Clay-Organic Reactions:* Halsted Press, London, 343 pp.
Van der Marel, H. W. and Beutelspacher, H. (1976) *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures:* Elsevier, Amsterdam, 396 pp.
Yariv, S., Russell, J. D., and Farmer, V. C. (1966) Infrared study of the adsorption of benzoic acid and nitrobenzene in montmorillonite: *Isr. J. Chem.* **4,** 201–213.

(Received 16 April 1979; accepted 2 January 1980)

Резюме—Было обнаружено, что монтмориллионит, каолинит, иллит, и хлорит адсорбируют битум и его растворимые и нерастворимые в пентане фракции. Образование глинисто-битумных комплексов зависит от природы обменного катиона в глине и растворяющего носителя, который стабилизирует битумные соединения. Са-глины адсорбируют органические соединения сильнее, чем натриевые формы, кроме случаев, когда присутствует нитробензол. Растворители с высокой диэлектрической постоянной, как нитробензол, способствуют ионизации, что содействует ионно-обменному механизму адсорбции, тогда как растворители с более низкой диэлектрической постоянной, как хлороформ, имеут тенденцию растворять и не разлагать битумы. Поведение монтмориллонит-битумного комплекса в условиях изменчивой относительной влажности указывает на то, что органические молекулы адсорбируются в основном на наружных поверхностях, в результате чего глина становится менее гидрофильной, чем до обработки. Глинисто-органические комплексы достаточно устойчивы, чтобы противостоять сильным органическим растворителям. Глинисто-органический комплекс, выделенный из Атабасского неатяного песка в течение химической обработки, ведет себя аналогично с комплексами, образованными битумом и четырьмя приведенными выше глинистыми минералами. [N.R.]

Resümee—Es zeigte sich, daß Montmorillonit, Kaolinit, Illit, und Chlorit Bitumen und ihre Pentan-löslichen und Pentan-unlöslichen Anteile adsorbieren. Die Bildung von Ton-Bitumenkomplexen wird durch die Art der austauschbaren Kationen am Ton und durch den Lösungsträger, der die bituminösen Bestandteile stabilisiert, beeinflußt. Ca-Tone adsorbieren organische Bestandteile stärker als Na-Tone außer in Anwesenheit von Nitrobenzen. Lösungsmittel mit hoher dielektrischer Konstante, wie Nitrobenzen, fördern die Ionisation, so daß der Ionenaustauschmechanismus der Adsorption begünstigt wird. Lösungsmittel mit niedrigerer dielektrischer Konstante hingegen, wie z.B. Chloroform, neigen eher dazu, die Bitumen zu lösen als zu dissoziieren. Das Verhalten des Montmorillonit-Bitumenkomplexes bei unterschiedlicher relativer Feuchtigkeit zeigt an, daß organische Moleküle bevorzugt an den äußeren Oberflächen adsorbiert werden und die Ursache sind, daß der Ton weniger hydrophil ist als vor der Behandlung. Komplexe aus Ton mit organischen Substanzen sind stabil genug, um gegen kräftige organische Lösungsmittel resistent zu sein. Die Tonkomplexe mit organischem Material, die aus dem Athabasca Ölsand abgetrennt wurden, verhalten sich während der chemischen Behandlung ähnlich wie die Komplexe, die sich zwischen Bitumen und den vier Standard-Tonmineralen gebildet hatten. [U.W.]

Résumé—On a trouvé que la montmorillonite, la kaolinite, l'illite, et la chlorite adsorbaient le bitume et ses fractions solubles et insolubles au pentane. La formation des complexes argile-bitume est influencée par la nature du cation échangeable sur l'argile et par le porteur de solvant qui stabilise les composés bitumineux. Les argiles-Ca adsorbent les composés organiques plus intensément que les formes au sodium sauf en présence de nitrobenzene. L'ionisation est promue par des solvants à constante diaélectrique élevée, tels que la nitrobenzene, de sorte que le mécanisme d'échange d'ions de l'adsorption est favorisé, tandis que les solvants à constante diaélectrique plus basse tels que le chloroforme, tendent à dissoudre plutôt qu'à dissocier les bitumes. Le comportement du complexe montmorillonite-bitume sous des conditions d'humidité relative variable indique que les molécules organiques adsorbent principalement sur les surfaces externes et est la raison pour laquelle l'argile devient moins hydrophile qu'avant le traitement. Les complexes argile-matière organique sont suffisemment stables que pour résister aux solvants organiques puissants. Le complexe argile-matière organique séparé du sable pétrolier Athabasca se comporte de manière semblable pendant le traitement chimique aux complexes formés entre le bitume et les quatre minéraux argileux de réference. [D.J.]

https://doi.org/10.1346/CCMN.1980.0280305 Published online by Cambridge University Press