



## Swelling Study of Smectites (Montmorillonites): Implications during Low-Saline Water Flooding (LSWF) in Petroleum Reservoirs

Uttam K. Bhui\* and Archit Desai

School of Petroleum Technology, Pandit Deendayal Petroleum University, Gandhinagar, Gujarat, India.

Email id – [uttam.bhui@spt.pdpu.ac.in](mailto:uttam.bhui@spt.pdpu.ac.in), [ukbhui@gmail.com](mailto:ukbhui@gmail.com)

### Keywords

Smectite (Montmorillonite), Low-saline water flooding (LSWF), X-ray diffraction (XRD), Fourier Transformed Infrared (FTIR) Spectroscopy, Zeta Potential, Enhanced oil recovery (EOR)

### Summary

Wettability change of the clay surfaces due to multi-component ion exchange of clay species is now frequently cited mechanism during low-saline water flooding for enhanced oil recovery (EOR) from petroleum reservoirs. The present work is to understand the interaction of smectites (montmorillonites), the common swelling clay species in petroleum reservoirs, with saline water of different salt concentration and their implications during LSWF. Powder sample of montmorillonite was characterized with X-ray diffraction (XRD) and Fourier Transformed Infrared (FTIR) spectroscopy analyses. The XRD results showed that smectites (montmorillonite) is the major mineral phase present in the study powder sample with presence of quartz and kaolinite in minor quantities. For the swelling study, montmorillonite of fixed weight (5 grams) was treated with various saline solutions (2%, 4%, 6%, 8% by wt. of NaCl and CaCl<sub>2</sub>) of fixed volume. The results shows that the final volume of montmorillonite is more in the low saline (2 and 4 wt %) NaCl solutions compared to high saline NaCl solutions. In case of CaCl<sub>2</sub> solutions, there is no volume change of the clay species in low and high salinity. Interlayer (basal) spacing value of all the treated montmorillonite with different solutions also confirmed that the swelling behavior is different with type of cations as well as their concentration. Change of wave number with transmittance (%) values in FTIR spectrum of all the treated montmorillonite confirms some structural change with exchange of ions. Zeta potential values were also found to be sensitive to the valence of ions in solution where the values of montmorillonite become less negative with divalent calcium (Ca<sup>2+</sup>) solution and more negative with monovalent sodium (Na<sup>+</sup>) solution. Changes of

zeta potential value of solid clay particles (montmorillonite) with different solutions indicate the change of the interactive forces between solid/fluid during LSWF which helps in increasing oil recovery by changing rock surface wettability.

### Introduction

In an age of increasing energy demand, low-saline water flooding (LSWF) could offer rewarding benefits for incremental oil recovery from hydrocarbon reservoirs<sup>1</sup>. Studies have proposed various reservoir parameters, particularly rock and fluid properties play an important role on the incremental rate of oil recovery<sup>2-6</sup> where different research groups put forward separate mechanisms by which oil recovery could be enhanced during LSWF<sup>7</sup>. Out of several mechanisms, wettability change of the clay surface and release (desorption) of polar hydrocarbon components due to multi component ion exchange capacity of clay species is now frequently cited mechanism for enhanced recovery during LSWF. The present study is to understand the ion exchange mechanism of smectites (montmorillonites) with saline water of different NaCl and CaCl<sub>2</sub> concentration, for designing injecting fluids of LSWF for clay laden reservoirs.

### Materials and Methods

Powder samples of clay (bentonite) were outsourced and mineralogical composition was estimated with X-ray diffraction (XRD) and Fourier Transformed Infrared Spectroscopy (FTIR) analyses (Table 1). The powder sample shows a strong peak at  $2\theta = 5.78^\circ$  corresponding to basal spacing of 15.255 Å indicates Ca-bentonite. Peak observed at  $19^\circ$ ,  $29^\circ$ ,  $30^\circ$  and  $35^\circ$  ( $2\theta$  values) also confirmed the presence

## *Swelling Study of Smectites (Montmorillonites)*

of smectites (montmorillonite). The study sample has been estimated to be more than 95% clay minerals with montmorillonite exceeding 90% and remaining 5 % are non-clay minerals. Most of the stretching and vibration bonds (Wave numbers in 3620, 1042, 912, 692  $\text{cm}^{-1}$ ) in FTIR spectra are endorsing presence of smectites with Mg substitution in octahedral position (Table1).The brines for swelling study were prepared

Table 1: XRD data ( $2\theta$  and d-spacing) and important FTIR bands of the study clay powder along with their assignments for possible minerals.

XRD data			FTIR Spectroscopy data	
$2\theta$ (in $^\circ$ )	d-spacing ( $^\circ\text{A}$ )	Possible Mineral	Band ( $\text{Cm}^{-1}$ )	Possible Assignments
5.789	15.25439	Smectite	3693.23	Al---O-H str. (for Tri-octahedral component)
12.3461	7.16938	Kaoline	3620.51	Al---O-H (Inter-di-octahedral)
19.8932	4.46324	Smectite	1642.07	H-O-H Bending in water molecules
25.3188	3.51777	-	1042.10	Si-O-Si Str. Vibration in the Si-O-Si functional group in tetrahedral sheet
26.6689	3.34267	Quartz	1005.37	Si-O-Si stretching vibration
29.5136	3.02664	Smectite	912.08	Al-O-Al bending vibration in smectites
30.8642	2.89721	Smectite	840.17	Al-O-Mg bending vibration in smectites
33.233	2.69592	-	796.23	Quartz (Cristobalite)
34.9259	2.56903	Smectite	692.30	Deformation and bending modes of Si-O bands
41.0792	2.19731	-	534.07	Si-O-Si bending
44.6307	2.03037	-	465.85	Si-Al Bending

by dissolving desired amount of salts (NaCl and  $\text{CaCl}_2$  from Merck) in distilled water. For smectites-saline water interaction (swelling) study, fixed amount (5 grams) of powder samples were taken in a 100 ml measuring cylinder and saline water was poured (clay powder + water total volume 60 ml) and thoroughly mixed. Volume (level) of clean water as well as water with dispersed clay were noticed and measured with time (Table 2). The treated samples of montmorillonite was separated through filter paper, dried and prepared for XRD, FTIR and zeta potential study.

### Results and Discussion

The volume change and settling behavior of montmorillonite with solutions of different ions and salinity are presented in Table 2 which provides the ultimate volume of 5 grams of powder samples in different solution. For NaCl solution, the final volume of montmorillonite is 30 ml and 26 ml with 2wt% and 4 wt% NaCl solutions respectively. In case of high saline NaCl solution and all  $\text{CaCl}_2$  solutions, the volume of clay after considerable time of study is same (~ 20 ml). Settling time of the dispersed clay to reach to a constant volume for low NaCl (2 wt %) solution is more (Table 2). XRD results of the untreated and treated montmorillonite clearly indicate that  $2\theta$  values increases for low salinity NaCl solutions (2 and 4 Wt %) which indicate decrease in interlayer (d) spacing while no effect in case of high saline NaCl solution (Table 3). In case of  $\text{CaCl}_2$  solutions of all concentration,  $2\theta$  values for the first peak decreases while all other peaks are showing more or less similar values with untreated montmorillonite (Table 3). Decrease of interlayer (d) spacing of montmorillonite with NaCl solution may be due to exchange of smaller hydrated  $\text{Na}^+$  ion (3.6  $\text{A}^\circ$ ) whereas increase in  $\text{CaCl}_2$  solution is due to bigger hydrated  $\text{Ca}^{2+}$  ions (4.1 $\text{A}^\circ$ ). The observed shift of the peak position (wavenumber,  $\text{cm}^{-1}$ ) and change of intensity of untreated and treated montmorillonite in FTIR spectroscopy data also support the exchange (Table 4). The zeta potential of montmorillonite was also found to be sensitive to the valence of ions in solution which resulted in changes of zeta potential values of montmorillonite. At any concentration the magnitude of the zeta potential is more negative for NaCl as compared to  $\text{CaCl}_2$  (Table 5). The zeta potential values of montmorillonite particles become

## Swelling Study of Smectites (Montmorillonites)

more negative with a decrease in cation concentration for both NaCl and CaCl<sub>2</sub>. It is observed that, while the valence of the cation in salt solution increased, the zeta potential shifted to less negative values.

Table 2: Setting behavior (volume of dispersed clay in 60 ml solution) with time

Volume of Clay (ml) in dispersed condition	NaCl (wt %) solution				CaCl <sub>2</sub> (wt %) solution			
	8	6	4	2	8	6	4	2
	Time (in Seconds)							
60 (clear water 0 ml)	0	0	0	0	0	0	0	0
50 (clear water 10 ml)	9	8	24	86	46	48	56	58
40 (clear water 20 ml)	36	36	46	161	110	112	119	118
30 (clear water 30 ml)	58	59	65	425	152	140	159	162
25 (clear water 35 ml)	108	116	148	-	196	208	222	227
20 (clear water 40 ml)	143	147	-	-	243	258	332	334

However, zeta potential value of montmorillonite becomes less negative with Ca<sup>2+</sup> compared to Na<sup>+</sup> as because monovalent Na<sup>+</sup> reduced less negative charge of the montmorillonite surfaces compared to bivalent Ca<sup>2+</sup>. Therefore, in the Ca-montmorillonite system, even though the concentration of Ca ion is decreased in the solution, the Ca ions remain strongly adsorbed onto the clay surface resulting in less negative values. Due to high negative zeta potential with less saline NaCl solution, electrical diffuse double layer expands and interacts with surrounding clay particles and bulk clay swelling occurs. This process may cause the release of fine clay particles, which ultimately modified the wettability of the reservoir rocks (pore surfaces) after interaction with injecting fluids which favors enhanced recovery of oil<sup>5,8</sup>.

Table 3: 2θ values (in degree) from XRD data for the study montmorillonite

Montmorillonite Sample	2θ	Treated and untreated montmorillonite 2θ values (different peaks) for various solution				
		Untreated	2 wt %	4 wt %	6 wt %	8 wt %
NaCl treated	1 <sup>st</sup> peak	5.789	5.8576	Not very clear	Not very clear	5.6208
	2 <sup>nd</sup> peak	19.8932	19.9126	19.9044	19.8935	19.8939
	3 <sup>rd</sup> Peak	30.8642	30.8708	30.8689	30.8599	30.8595
	4 <sup>th</sup> Peak	34.9259	34.9334	34.9301	34.9268	34.9267
CaCl <sub>2</sub> treated	1 <sup>st</sup> peak	5.789	5.461	Not very clear	Not very clear	5.5484
	2 <sup>nd</sup> peak	19.8932	19.8930	19.8932	19.8932	19.8932
	3 <sup>rd</sup> Peak	30.8642	30.8642	30.8643	30.8639	30.8644
	4 <sup>th</sup> Peak	34.9259	34.9270	34.9265	34.9261	34.9256

Table 4. FTIR transmittance peak (wavenumber in cm<sup>-1</sup>) of the study montmorillonite

Untreated montmorillonite	Treated bentonite with NaCl solution			Treated bentonite with CaCl <sub>2</sub> solution		
	2 wt %	4 wt %	8 wt %	2 wt %	4 wt %	8 wt %
Wave number (cm <sup>-1</sup> )						
3620.51	3619.26	3619.55	3620.64	3620.57	3621.47	3620.64
1642.07	1641.71	1642.16	1642.04	1642	1642.22	1642.19
1005.37	1005.18	1006.2	1005.17	1005.72	1005.92	1005.41
912.08	912.4	912.58	912.14	912.14	912.19	912.09
692.3	691.5	691.7	694.9	692.15	692.03	692.45
534.07	533.06	533.78	534.08	534.06	534.24	534.09
465.85	463.88	464.59	464.73	465.88	465.93	465.88

## Swelling Study of Smectites (Montmorillonites)

Table 5: Zeta potential value of treated montmorillonite

NaCl (Wt %)	Zeta Potential (meV)	CaCl <sub>2</sub> (Wt %)	Zeta Potential (meV)
2	-47.4	2	-17.8
4	-43.2	4	-16.5
6	-37.9	6	-13.9
8	-37.6	8	-12.4

### Conclusions

The volume change of the study montmorillonite with low saline NaCl solution (2 wt% and 4 wt %) is not due to increase in the interlayer (d) spacing but for the interaction (repulsion) of the expanded diffuse double layer of montmorillonite particles in low salinity. Depending on the clay species present in the petroleum reservoir, the charge balancing cation is more important than the concentration, in a flood fluid, for fines migration and wettability change for improved oil recovery rates during LSWF.

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