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Experimental Investigation on the Influence of the Salinity Adsorption-Desorption Behavior of the Clay-based Rocks

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Abstract

The process of extracting oil from the ground is a tradeoff between revenue and costs. In the later production phase of an oil field, enhanced oil recovery (EOR) becomes a viable option in increasing dwindling production. Most common EOR technologies are, resource intensive and costly. Among the EOR technologies available to today; a new and cost-effective option is 'low-salinity' water Injection. Low-salinity water injection involves injecting fresh water into the oil-reservoir as fluid for a water flood. It has been observed that far greater yields of oil can be produced by low-salinity injection when compared to conventional water-flooding. The exact mechanism of low-salinity water injection is still not well understood. This paper aims to verify one proposed mechanism of low-salinity water injection i.e. the effect of swelling and non-swelling clays present within the reservoir with respect to the pH and the polarity of oil on the relative extraction of oil from reservoir samples. In light of the experiments conducted, it's apparent that the low-salinity water injection does indeed work better compared to the normal-salinity flood conducted throughout the experiment: increasing the oil recovery by zero.6 mg/g of oil per kaolinite with an equivalent adsorption ratio at a pH scale of 4. The results collected throughout the devised experiment summarily prove the existence of an underlying mechanism with a chemical route, due to the influence of pH scale and therefore the relative unaffected nature of bentonite with reference to the lLow-sSalinity chemical mechanism.

Keywords: Enhanced Oil Recovery (EOR), Petroleum, Kaolinite, Clay and Adsorption.

1. Introduction:

Enhanced Oil Recovery (EOR) is that the application of techniques and procedures with the prime interest of accelerating the production and quantity of oil which may be ultimately recovered from any oil field. The terms Tertiary Recovery or Improved Oil recovery is also used interchangeably for EOR; however, some consider these to be become independent from the EOR bandwagon. The three main techniques of EOR techniques are presently thermal recovery, gas injection and chemical injection. Typically, around 30-60 % additional oil will be recovered using EOR techniques [1-3].

Among EOR techniques mentioned above, Gas-Injection is far and away the foremost common. Gas injection is the method of injecting gasses deep in to the reservoir to enhance the cut of oil and increase the recovery. Various gasses are used for this purpose, like Flue gas, N_2, CO_2, Lean gas, LPG, etc. The gas injection can be either, miscible or immiscible as per the strategy chosen for the actual field. More varieties in compatible flooding are, first initial contact miscibility and multiple contact

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miscibility, that work on essentially completely different principles. Carbon dioxide injection is practiced wide within the United States of America, as Carbon dioxide reservoirs are extensive and therefore the EOR methodology is compatible with the rock oil system. Like most of the Oil fields within the Americas, the viscousness of rock oil could be a major concern [4-6]. Vicious oil is far more durable to flow to the surface and so ends up in an occasional recover. Thermal EOR strategies address this issue by providing thermal energy to the reservoir so as to decrease the oil viscosity, and so rising the recovery. Chemical injection is an extremely broad field that improves the recovery by altering the fluid properties, or the rock-fluid interactions. the primary driving factor to consider for new or obscure EOR technologies is the value of oil, and therefore the value of the EOR methodology itself. With spikes in the oil prices that were encountered in the early 2010s, a new range of EOR technologies were seen. From existing niche technologies, like alcohol flooding to the technologies straight out of science fiction, such the pulse drive- used within the Russian Federation. It is in fact possible to extract the very last drop of oil from the crude oil reservoirs within the world, however cost of doing so would be phenomenally high. thus, deemed impossible by the cost-of oil/cost-of-EOR. Low price EOR strategies are much more usable than sophisticated and expensive technologies [7-10].

Considering the EOR techniques presently being utilized, low salinity water injection could be a new viable option. Though not currently practiced widely, it is an efficient technique. Studies of low salinity established the correlations of oil-extracted to the low saline brine injected [11, 12]. The mechanism of action for this comparatively new EOR technique is however still stands to be determined at the laboratory level, before it's through implementation within the field [13-15].

Now days, the EOR is considered to a one of the dynamic fields in this area. Therefore, EOR always has been a subject of the fast developments in new technological options. However, most of these reported technologies do not compare to the cost-effectiveness low-salinity water injection [16-18]. EOR is considered as one of the promising options and vital source for the further research to evaluate the widely adopted mechanism of the action for low-salinity water injection. EOR is the struggle for the more recovery of crude oil from the oil wells and reservoirs using the advanced developed technologies with costs in mid. Low salinity water injection is one of those advanced developed technologies [19-23].

Objectives of this experimental investigation is to prove that low-salinity water injection works only when kaolinite is present within the formation rock in sufficient quantities, and to look into effectiveness of pH of formation crude during the low-salinity injection to make it a viable EOR method.

2. Materials and Methods:

Kaolinite samples were obtained from an off-site quarry in Tapah, a small town in Malaysia. Kaolinite exists as a white soft mineral that is soft to the bit and crumbles simply. Pure kaolinite is white; any impurities present would otherwise color it. The kaolinite collected from the quarry in Tapah for Low-Sal injection is tainted a light red, that signifies the presence of iron (I) oxide as an impurity. The samples acquired had quartzite and Flint impurities within the variety of little gravel sized particles. These Impurities were separated by hand before the rock was crushed. It ought to be noted that the kaolin samples are of comparatively prime quality, the slight cherry-red color is solely due to the presence of trace iron oxide impurities.

The kaolin rocks were at the start held in plastic bag before crushing. The rocks were then placed to mortar and pestle within the work once initial sorting. This sorting was to get rid of the quartzite and different grit sized impurities from the soft clay chunks. once crushing the pulverized clay was sieved employing a 0.5 mm sieve and hold on in a very beaker that was coated to stop and contamination of the work or contrariwise. Samples of bentonite clay were acquired from Schlumberger MI Swaco lab. Bentonite is light brown clay which is commonly used in drilling fluids as a viscosifier (Fig. 1).

Figure 1: Kaolin and bentonite in powder form.

2.1 Preparation of Samples:

The kaolin sample was crushed to a fine powder then washed with distil water before being dried and crushed once more. The samples were separated into 200 g beakers. The bentonite was already in crushed and cleansed type. The oil samples were acquired so their acid variety was tested. The pH of the Oil was measured with a normally availably pH meter within the research lab. Before use, the list of crude oils was filtered to get rid of any solid particles. The properties of oil are tabulated in (Table 1).

Table 1: Properties of Oil.

Type of Oil	pH	Viscosity (mm^2/sec)	Density (g/cc)
Organic Canola	N/A (non-polar)	78.2	-
Crude (sample 1) S1	6.01	-	0.805
Crude (sample 1) S2	7.02	-	-

Brines were prepared by artificial means by dissolving salts into distilled water, and so filtered to get rid of any particles. All brines were filtered to get rid of particles if any (Fig. 2). The properties of brine are tabulated in (Table 2).

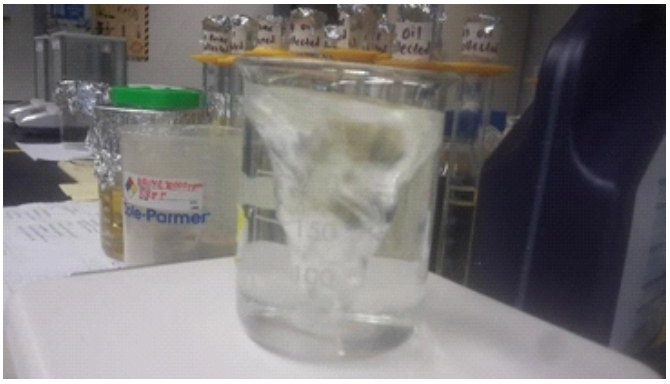

Figure 2: Preparation of Brine on a hot stirrer plate.

Table 2: Properties of brine.

Ion	Normal Flood (mole/L)	Low salinity brine (mole/L)
Cl^-	1.72	0.013
Na^+	1.54	0.003
Ca^{+2}	0.09	0.005
Total (g/L)	100	0.710

2.2 Experimental Procedure:

Adsorption of organic material onto kaolinite at room temperature was measured by a batch methodology. Kaolinite powder, 100g, was added and stirred with 20ml formation brine for two hours before addition of organic oil or basic/acidic crude, and once more stirred and agitated for an additional twenty-four hrs. pH was adjusted with HCl or NaOH to stay the pH constant. Once settled, the samples were stirred at a high speed for twenty min (Fig. 3).

The summary of adsorption is tabulated in (Table 3).

Table 3. Summary of adsorption.

Sample	Clay	Mass of Clay (g)	pH Oil	Oil Added (ml)	pH of mixture	Oil Top-Layer (ml)	Oil Adsorbed (ml)
1	Kaolin	100	S1 pH6.01	20	4	19.7	~0.3
2	Kaolin	100	S1 pH6.01	20	4	19.6	~0.4
3	Kaolin	100	S1 pH6.01	20	8	19.9	~0.1
4	Kaolin	100	S1 pH6.01	20	8	20	~0
5	Kaolin	100	Neutral	20	7	20	~0
6	Kaolin	100	Neutral	20	7	20	~0
7	Kaolin	50	Neutral	20	4	20	~0
8	Kaolin	50	Neutral	20	8	20	~0
9	Bentonite	50	S1 pH6.01	20	4	20	~0
10	Bentonite	50	S1pH6.01	20	8	20	~0
11	Bentonite	50	Neutral	20	7	20	~0

After adding low salinity, the oil previously adsorbed was desorbed. The summary of desorption is tabulated in (Table 4).

Table 4. Summary of desorption.

Sample	Clay	Mass of Clay (g)	pH Oil	Oil Added (ml)	pH of mixture	Oil Top-Layer (ml)
1	S1 pH6.01	20ml	4	~0.3	-	~0.2
2	S1 pH6.01	20ml	4	~0.4	0.1	-
3	S1 pH6.01	20ml	8	~0.1	-	-
4	S1 pH6.01	20ml	8	~0	-	-
5	Neutral	20ml	7.01	~0	-	-
6	Neutral	20ml	7.02	~0	-	-

The experiment was repeated for pH 4 with the following results (Table 5).

Table 5. Adsorption-desorption results at pH 4.

Sample	pH of mixture	Volume of Oil adsorbed (ml)	Volume of Oil Desorbed Formation salinity (ml)	Volume of Oil Desorbed Low salinity (ml)
1	4	~0.2	-	~0.1
2	4	~0.4	-	-0.3
3	4	~0.2	-	~0.2
4	4	~0.3	-	~0.2
5	4	~0.3	0.1	-
6	4	~0.3	0.1	-
7	4	~0.3	0.2	-
8	4	~0.4	0.1	-

3. Results and Discussions:

Regarding the experiments conducted, a number of assumptions should be created so as to proceed, the subsequent parameters are therefore deemed to play an important role in low-salinity injection:

It can be assumed that the EOR impact of low-salinity water injection is because of the adsorption and desorption of oil onto the formation-clay surface. The initial composition of the formation brine is assumed to be highly saline. Polar components of either an acidic or a basic nature must be present within the oil. Lastly, Kaolinite must present within the rock.

Clays have an abundant surface area, and act as a particle exchanger within the reservoir. All clays have an ion exchange potential. Before any type of injection into the reservoir an equilibrium of ions exists. All polar elements within the formation oil are drawn to and therefore connected to the surface of the clay minerals. This includes the basic and the

acidic elements of crude oil. It should to be noted here that formation brine is extremely acidic in nature because of the dissolved carbon dioxide and hydrogen sulfide, each of that are acidic gasses sometimes present in reservoirs. When water is injected with a saline content below the formation water i.e. water with a far lower concentration of ions than the initial formation water, the ionic equilibrium is disturbed. This disturbance within the ionic equilibrium causes the immediate desorption of calcium ions into the surrounding water, since the encompassing water due to having a very low concentration of the calcium ions. The desorption of calcium ions causes the hydrogen ions present within the water to adsorb to the surface of the clay- this cause the native pH to rise considerably as there's currently an absence of H+ ions.

Ca^{+2} adsorbed + binary compound = H^{+1} adsorbed + $Ca^{+2} + OH^{-1}$

This releases the oil stuck to the clays in the formation and results in higher recovery.

$NHR^{+3} + OH^{-1} = R^{+3}N + water$

$RCOOH + OH^{-1} = RCOO^{-1} + water$

From the experiments conducted the subsequent is concluded: first off, it's the conformation that the oil within the reservoir should be of a polar nature for there to be any important increase within the extraction of oil. This is confirmed as nearly no oil is absorbable on to the Karoline small-grained surface if the oil is of a neutral nature, as it was discovered within the case of organic vegetable oil that is of a neutral nature. These experiments were continual and consistent. The summary of the adsorption of

Table 6. Summary of the adsorption of neutral oil.

Sample	Clay	Mass of Clay (g)	Oil added	Volume of Oil (ml)	pH of mixture	Volume of Oil after adsorption Formation salinity (ml)	Volume of Oil adsorbed (ml)
1	Kaolin	20ml	7.01	~0	-	-	-
2	Kaolin	20ml	7.00	~0	-	-	-
3	Kaolin	0ml	7.00	~0	-	-	-
4	Kaolin	20ml	7.00	~0	-	-	-
5	Kaolin	20ml	7.00	~0	-	-	-
6	Bentonite	20ml	7.00	~0	-	-	-

3.1 Relative Adsorption:

The results were more noticeable with exploitation of a polar oil. It had been apparent that kaolinite is extremely sensitive to the pH of the solution. Kaolinite was approximated to possess a mean adsorption ratio of 2.8 (mg/g) once polar oil was absorbable within the presence of a 4 pH acidic brine solution. The adsorption ratio goes down drastically because the pH approaches the neutral pH of 7 (Fig. 4).

3.2 Desorption of Oil:

Oil was desorbed once brine was added to the solution. Though there was no important distinction between the conventional formation brine addition, there was a rise in the oil desorbed when injecting low salinity water- important enough to prove the viability of low-salinity water injection once scaled up to the reservoir scale. The average desorption capacity over pH of 4 is shown in (Fig. 5).

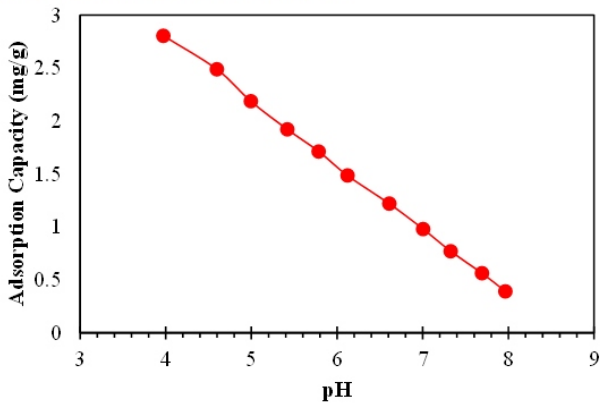

Figure 4: Adsorption behavior over variation in pH.

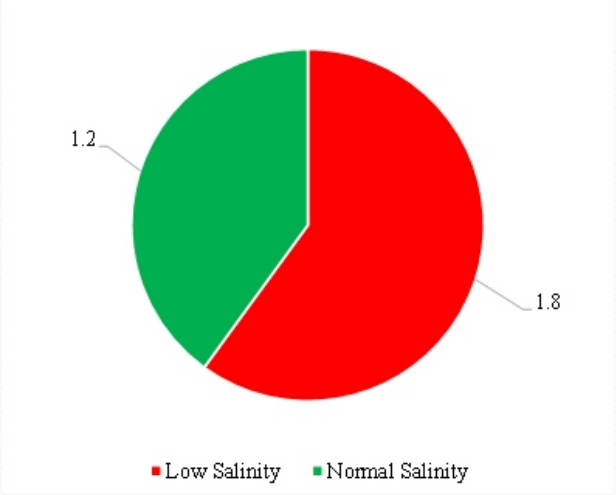

Figure 5: Average desorption behavior over pH of 4.

4. Conclusions:

In light of the experiments conducted, it has been proven that low-salinity water injection only works when there is a presence of kaolinite. (0.6 mg/g of oil per kaolinite with an equivalent adsorption ratio at a pH scale of 4). The results also show that inorganic oils do not cause any reaction. Whereas, oils with a basic or acidic pH are compatible with low-salinity water injection. It is also apparent that the polar nature of oil comes into direct play once low-salinity water injection is considered. It absolutely was shown that non-polar or neutral oil incorporates a negligible vary for adsorption into the clay used. The natural action capability of clay has impact on the consequences of low-salinity water injection as completely different clays have different natural action capacities with bentonite having virtually no effect at the pH scale window experimented on. Formation brine must to contain calcium ions for the low-salinity impact to occur. It is further concluded that, pH plays a significant role within the low-salinity water injection method. This is often thanks to clays having their own pH window for the adsorption- desorption to occur. There is a big indication that the lower salinity brine will in fact cause a larger extraction of oil from the clay minerals. With these proven points, we can conclude that the ion exchange capability of Kaolinite clay present within the reservoir is the prime underlying mechanism of low-salinity water injection. It is further suggested experiments must be carried out on reservoir core samples containing varying quantities of kaolinite and other clays in a PVT cell. With such an experiment it will be possible to further cement the conclusions of this paper i.e. the ion-exchange mechanism due to the presence of kaolinite

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