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Enhanced Oil Recovery Using Nanoparticles

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Abstract

Nanoparticles have been speculated as good in-situ agents for solving reservoir engineering problems. Some selected types of nanoparticles that are likely to be used include oxides of Aluminium, Zinc, Magnesium, Iron, Zirconium, Nickel, Tin and Silicon. It is therefore imperative to find out the effect of these nanoparticle oxides on oil recovery since this is the primary objective of the oil industry. These nanoparticles were used to conduct EOR experiments under surface conditions. Distilled water, brine, ethanol and diesel were used as the dispersing media for the nanoparticles. Two sets of experiments were conducted. The first involved displacing the injected oil with the nanofluids. In the second case, the sands were soaked in nanofluids for 60 days before oil was injected into the system and displaced with low salinity brine. Generally, using nanofluids to displace injected oil produced a better result.

Results obtained from the experiments indicate that Aluminium oxide and Silicon oxide are good agents for EOR. Aluminium oxide nanoparticle is good for oil recovery when used with distilled water and brine as dispersing agents. For the use of ethanol, Silane treated Silicon oxide gave the highest recovery in all the conducted experiments while hydrophobic Silicon oxide in ethanol also yielded good results. Aluminium oxide reduces oil viscosity while Silicon oxide changes rock wettability in addition to reduction of interfacial tension between oil and water caused by the presence of ethanol. For the use of diesel as a nanoparticle dispersing fluid, because diesel and crude oil are miscible, the actual crude oil recovery cannot be determined but the overall result with Aluminium, Nickel and Iron oxides appears good. Magnesium oxide and Zinc oxide dispersed in distilled water and brine cause permeability problems. Generally, distilled water lowers oil recovery. This emphasizes the significant role a fluid plays as a nanoparticle dispersing agent in the formation because it can contribute positively or negatively in oil recovery apart from the effect of the nanoparticles.

Introduction

Application of nanotechnology in the oil and gas industry is just emerging. Recent research projects have shown that nanotechnology has the potential to solve or manage several problems in the petroleum industry. One of the speculated areas of application is in Enhanced Oil Recovery (EOR). EOR is especially important now because of the recent global rise in energy demand which is expected to be met by the oil and gas industry. The ability of nanoparticles to alter certain factors in the formation and in oil properties can be taken advantage of to enhance recovery. This involves introducing these nanoparticles into formations and studying its effect on oil recovery.

Background

The wettability of a formation can be changed by nanoparticles. It has been reported that water wet formations produce better than oil wet formations (Binshang et al, 2005) while intermediately wet formations produce better than water wet formations (Dong et al, 2006). The use of nanoparticles to change rock wettability and its subsequent effect on oil recovery has been reported by several authors (Ju et al, 2006, Binshang et al 2009, Ju et al, 2009 and Qinfeng et al 2009). Silicon oxide dispersed in ethanol has also been reported to give good results (Onyekonwu et al, 2010), however the effect of ethanol alone on oil recovery was not reported. This work therefore investigates among other things the effect of ethanol alone and ethanol with various nanoparticles on oil recovery. The contribution of the nanoparticles to the total oil recovery was also determined.

Oil viscosity can be decreased through the application of Aluminum oxide (Al_2O_3) nanoparticles. This has been achieved under surface condition and outside the reservoir formation (Nares et al, 2007). Since Al_2O_3 has the ability to reduce oil viscosity (especially of heavy oil) which hinders recovery, investigating its ability to reduce oil viscosity in formations is essential.

Sweep efficiency of displacing fluids in reservoirs is also very important. Sweep efficiency is dependent on mobility ratio (M) which is also partly dependent on the viscosity of the displacing fluid and displaced fluid. If the viscosity of the displacing fluid and that of the displaced fluid can be altered to improve the mobility ratio, then sweep efficiency will be enhanced. Polymers are known agents that have been used to increase the viscosity of displacing fluids. The disadvantages associated with polymers include loss of some fluid properties at high temperatures, cost and quantity required to accomplish a task. On the other hand, nanoparticle application requires small quantity to perform a task since it has large surface areas. Iron oxide nanoparticles have been speculated to have the ability to increase the viscosity of displacing fluids (Kothari et al, 2010).

The effects of other types of nanoparticles on oil recovery need to be studies. Several research projects have focused on the use of nanoparticles in solving problems related to oil and gas production in the formation. One of such work deals with control of fines migration in reservoirs. Magnesium oxide has been reported to yield good results in this area (Huang et al, 2009, Belcher et al, 2010, Huang et al, 2010 and Habib et al, 2011) but its effect on oil recovery has not been investigated Other nanoparticles that could control fines migrations in formations are still under investigation, but their effect on oil recovery have not yet been studied. It is therefore essential to study the effect of these different nanoparticles on oil recovery since this is the primary objective of the oil industry. Any problem solving agent in reservoir formations that hinders oil recovery must be re-considered and may not be recommended for field application.

Materials

The materials used to conduct experiments in this work include sand, crude oil, nanofluids, brine and sand packs. Laboratory prepared brine of 30g/L concentration was used. The packs used were of about 80cm^3 in volume. Nine types of nanoparticles were used. These nanoparticles are: Aluminum oxide (Al_2O_3), Nickel oxide (Ni_20_3), Magnesium oxide (MgO), Iron oxide (Fe_2O_3), Zinc oxide (ZnO), Zirconium oxide (ZrO_2), Tin oxide (SnO), Silicon oxide treated with silane (SiO_2 (S)) and hydrophobic Silicon oxide (SiO_2 (S)). The nanoparticles were bought from Skyspring Nanomaterials, Inc., Houston, Texas, USA. The sizes of the nanoparticles are given on Table 1. Each type of these nanoparticles was dispersed in four different fluids at the concentration of 3g/L. The dispersing agents used were distilled water, brine, ethanol and diesel. These different nanoparticles were selected for EOR experiment because they have potentials for being used to address some problems in reservoir formations. Their effect on oil recovery is the main focus in this work. The properties of the oil used are given on Table 2.

Table 1: Some Properties of the Nanoparticles used

S\No.	Type of Nanoparticle	Particle Size (nm)	Surface Area (m^2/g)
1.	Aluminium Oxide	40	~ 60
2.	Magnesium Oxide	20	~ 50
3.	Iron Oxide	20-40	40-60
4.	Nickel Oxide	100	6
5.	Tin Oxide	50-70	10-30
6.	Zinc Oxide	10-30	90
7.	Zirconium Oxide	20-30	35
8.	Silane Treated Silicon Oxide	10-30	>400
9.	Hydrophobic Silicon Oxide	10-20	100-140

Table 2: Properties of the oil

Properties	Value
Density @ 27^{o}C	0.9114g/cc
Viscosity	53.27735cp
API Gravity	22.44^o

Theory and Calculation

Fluids play a significant role in oil displacement efficiency. For example low salinity brine displaces oil more efficiently than high salinity brine. Since nanoparticles are solids and as such need a fluid to carry them into the formation, the contribution of the fluids in displacing oil could be mistaken for or attributed to the presence of the nano agent. For this reason, experiments were first conducted using these fluids alone without nanoparticles. Other experiments were then conducted using these fluids with nanoparticles in them. To evaluate the contribution of the nanoparticles to the total recovery, the recovery from the control experiment is subtracted from the recovery made from the use of nanoparticles in these fluids. This subtraction indicates if the nanoparticles constitute a hindrance to oil recovery by giving negative values. The primary objective in this work is to identify some nanoparticles that have the ability to enhance oil recovery. The plotted graphs from the obtained results clearly identifies which type of nanoparticles and dispersing fluids that work best to enhance oil recovery. Further work on the identified EOR agents (i.e nanoparticles and dispersing fluids) can be carried out under reservoir conditions to find out their actual efficiency in displacing oil from formations. Oil saturation in all the experiments is thesame and is 40% of the pore volume.

Displacement Efficiency $E_D = x/S_o * 100\%$ -- Eq. 1

Where x = Amount of oil displaced

S_o = initial oil saturation

To get the contribution of the nanoparticles to the total recovery, let Y be the percentage recovery from the control experiments. Let Y_1, Y_2, Y_3 etc be the percentage recovery from other experiments where nanoparticles are dispersed in the displacing fluids. Therefore contribution of nanoparticles to the total oil recovery $Z_1 = Y_1 – Y$, $Z_2 = Y_2 – Y$ etc. A graph showing a negative value for Z means that nanoparticle is bad for EOR and so should not be used.

Experimental Procedures

The experiments were conducted under surface condition using atmospheric pressure. The reason for this is because other sets of experiments conducted using the nine nanoparticles (especially to find out its effects on migrating fines) were conducted under surface conditions. Surface condition creates one of the worst scenarios that trigger fines migration because pressure is very low. High pressure tends to bind formation grains together while under low pressure the sand grains and fines easily detach and migrate away from their original position. Since other series of experiments conducted were done under atmospheric pressure, for the purpose of consistency, the EOR experiments were also conducted under surface conditions. A schematic diagram of the experimental procedure is shown in Fig. 1. For all the conducted experiments, washed sand soaked in brine for more than 7 days was used.

Two sets of experiments were conducted. In the first case, brine was injected into the sand already loaded in packs, after which oil (40% of the pore volume) was injected. Three pore volumes of nanofluid were then injected to displace, flush and recover the oil. Diesel was not used in the first set of experiments because it is miscible with oil, thus making the value of oil recovered difficult to ascertain. No experiments were conducted with hydrophobic Silicon oxide nanoparticles dispersed in distilled water and brine. This is because these nanoparticles cannot be dispersed in polar fluids, they can only be dispersed in organic fluids.

In the second method, the brine soaked sands were further soaked in nanofluids for 60 days prior to the experiment. 40% pore volume of oil was then injected into the nano soaked sands contained in packs. Afterwards, three pore volumes of low salinity brine of 5g/L were used to flush the system of oil. Low salinity brine was used because it is more effective in displacing oil than high salinity brine. The essence for conducting these experiments with two methods is to find out which of the two methods is more effective in displacing oil (flushing the system with nanofluids or soaking the sand in nanofluids for a long time). Oil was absent in the sands soaked in nanofluids and this makes the second set of experiment less ideal because residual oil is present in formations when EOR fluids are injected. Nevertheless, the soaked state of the sands still had an effect on oil recovery. What the recovery results will be if the sands were soaked with oil and nanofluids together for a period of time before production is not yet certain. Fluid injection into the packs containing sands was done from the bottom of the pack (working against gravity) while effluents were produced from the top.

Results and Discussions

Fig. 2 generally shows that oil recovery from the use of ethanol is better than recovery from brine and distilled water even in the presence of nanoparticles. Distilled water gave the least recovery amongst the three fluids (i.e. ethanol, brine and distilled water). However, the presence of all the used nanoparticles in distilled water improved recovery as shown in Fig. 3. Aluminium oxide nanoparticles gave the best result while Iron Oxide nanoparticles also gave a good result. With brine as the dispersing agent for the nanoparticles, only Aluminium, Nickel and Silane treated Silicon Oxides gave positive results as shown in Fig. 4. The rest of the nanoparticles gave negative results. Aluminium oxide again in this case gave the best result. With ethanol as the nanoparticles dispersing medium, only Silane treated Silicon oxide and hydrophobic Silicon oxide gave positive results while the rest of the nanoparticles gave negative results as shown in Fig. 5. In fact Silane treated Silicon oxide nanoparticles in ethanol gave the overall best result in all the experiments. Nevertheless, it should be noted that ethanol as a fluid (without nanoparticles) also improves oil recovery because ethanol reduces interfacial tension between oil and water. These results indicate that for any of these nanoparticles to be used for EOR, the dispersing medium must be seriously considered as it could impact positively or negatively on recovery.

From the results of the second set of experiments presented in Fig. 6, the recovery made from using diesel as a dispersing fluid is outstanding. However, because diesel and crude oil are miscible, the amount of crude oil produced could not be ascertained. There is no observed trend when the recovery results from the use of distilled water, brine and ethanol are compared. Fig. 7 shows that the presence of all the nanoparticles in distilled water improves oil recovery when compared with the control experiment (just as in Fig. 3). Brine and ethanol on the other hand gave negative results with the use of all the nanoparticles as shown in Figures 8 and 9. Fig. 10 shows that Aluminium and Nickel oxides in diesel can improve recovery. Aluminium oxide nanoparticles in diesel gave a recovery of 107% which is an indication that diesel made up a larger portion of the recovery.

From Figures 4, 5 and 10, two types of nanoparticles that have the tendency to improve recovery were identified. They are Aluminium oxide and Silicon Oxide nanoparticles in brine and ethanol respectively. It is likely that Aluminium oxide and Silicon oxide nanoparticles improved recovery due to reduction of oil viscosity and change of formation wettability respectively. While Aluminium oxide has been reported to reduce oil viscosity, Silicon oxide has been known for its ability to change wettability. Nickel oxide nanoparticles in brine and Iron oxide nanoparticles in distilled water may have worked well by increasing the viscosity of the displacing fluids.

Observations

1. Using ethanol as a dispersing medium for nanoparticles, the produced oil sinks to the bottom of the collecting tube due to density variation.

2. The change of colour of produced effluent using ethanol with and without nanoparticle shows that this is due to the reaction between ethanol and oil. On mixing the effluent with water, an exothermic reaction occurs, emitting heat to the surrounding. This is as a result of the reaction between ethanol and water, and the produced oil floats back to the top of the solution.

3. With Aluminium oxide, Magnesium oxide, Tin oxide and Nickel oxide in distilled water, lots of bubbles were produced along with the effluent.

4. Magnesium oxide in brine and in distilled water and Zinc oxide in brine and in distilled water all gave rise to permeability problems caused by pore space blockage. In fact, Zinc oxide agglomerates to form larger particles at injection points, making fluid injection difficult.

5. The produced oil from the use of Aluminium and Nickel oxide nanoparticles looks lighter than the injected oil.

6. Sand soaked in ethanol containing Magnesium oxide nanoparticles drastically reduces oil recovery.

7. Ethanol improves permeability in sands.

8. Generally, distilled water results in low recovery but the presence of nanoparticles in it improves recovery.

9. The presence of most nanoparticles in brine and ethanol yield poor recovery compared to the use of these fluids in the absence of nanoparticles.

With the use of ethanol, the produced oil sinks below the ethanol level because the oil density is higher than the density of ethanol. This implies that if a reservoir containing residual oil is saturated with ethanol and closed in for some time (without production), the oil could travel down pore spaces in the reservoir to settle at the water/ethanol contact level. Production in this case could probably involve converting injection wells to production wells and vice versa. Avoiding this kind of situation means that production and ethanol injection must be carried out simultaneously, without closing in the reservoir for a period of time.

Generally, the first set of experiments (i.e using nanofluids to flush the system) yielded better results than the second. This could be as a result of introducing several volumes of the nanofluids (containing more nanoparticles) into the formation. Although the second method gave a poor result but the result of soaking these nanofluids along with (residual) oil in sands (for some days) before production using low salinity brine has not yet been determined. The two sets of results also show that the type of fluid used in dispersing the nanoparticle in the formation has a very important role to play in enhancing recovery. Comparing the results of all the dispersing fluids shows that using distilled water (even with nanoparticles in them) generally reduces oil recovery. This emphasizes the need to use distilled water with caution in reservoirs because it can hinder oil recovery.

Conclusions

The conclusions made after this study are:

1. Aluminium oxide nanoparticles dispersed in brine and distilled water have the tendency to improve oil recovery through reduction of oil viscosity.
2. Silane treated Silicon oxide and hydrophobic Silicon oxide dispersed in ethanol have the tendency to improve oil recovery through change of rock wettability. Ethanol when used alone (without nanoparticles) also enhances oil recovery by reduction of interfacial tension between oil and water.
3. The type of fluid used for nanoparticle dispersion in sands to improve oil recovery is important because it plays a significant role in the process.
4. Magnesium oxide and Zinc oxide in distilled water and in brine result in permeability problems. Recovery from the use of Magnesium oxide for EOR is very poor.
5. Comparing the efficiency of different fluids (without nanoparticles in them) in displacing oil from sands generally, it can be seen that distilled water gives low recovery, brine gives good recovery, ethanol gives good recovery while the effect of diesel appears good.
6. Caution should be used when using nanoparticles dispersed in brine and ethanol for EOR or for solving other problems in the formation because most of these nanoparticles can impact negatively on oil recovery.

Recommendation

1. Aluminium oxide in brine, Silane treated Silicon oxide and hydrophobic Silicon oxide in ethanol can be used for EOR.
2. Ethanol alone can be used to improve oil recovery.
3. Using the recommended nanofluids to flush depleted reservoirs can boost oil recovery.

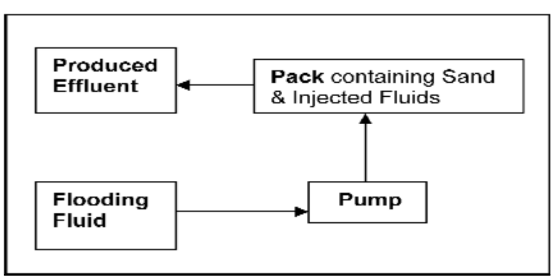

Figure 1: Schematics of the Flooding Process

OIL RECOVERY RESULTS

Table 3: Results of Oil Recovery by Injection of various Nanofluids into the Sands

S/No.	Nanoparticle	Distilled Water		Brine		Ethanol	
		Total % Recovery	% Recovery due to Nanoparticles	Total % Recovery	% Recovery due to Nanoparticles	Total % Recovery	% Recovery due to Nanoparticles
1.	Control Experiment	25.0	0.0	35.0	0.0	46.7	0.0
2.	Aluminium Oxide (Al_2O_3)	37.5	12.5	40.0	5.0	45.8	-0.9
3.	Magnesium Oxide (MgO)	26.7	1.7	32.5	-2.5	42.5	-4.2
4.	Iron Oxide (Fe_2O_3)	34.2	9.2	35.0	0.0	42.5	-4.2
5.	Nickel Oxide (Ni_2O_3)	27.5	2.0	36.7	1.7	41.7	-5.0
6.	Zinc Oxide (ZnO)	28.3	3.3	30.8	-4.2	42.5	-4.2
7.	Zirconium Oxide (ZrO_2)	29.2	4.2	31.7	-3.3	41.7	-5.0
8.	Tin Oxide (SnO)	28.3	3.3	31.7	-3.3	33.3	-13.4
9.	Silane Treated Silicon Oxide (SiO_2)	25.8	0.8	39.2	4.2	51.7	5.0
10.	Hydrophobic Silicon Oxide (SiO_2)	X	X	X	X	48.3	1.7

Table 4: Results of Oil Recovery from Sands that have been soaked in various Nanofluids

S/No	Nanoparticle	Distilled Water		Brine		Ethanol		Diesel	
		Total % Recovery	% Recovery due to Nanoparticles	Total % Recovery	% Recovery due to Nanoparticles	Total % Recovery	% Recovery due to Nanoparticles	Total % Recovery	% Recovery due to Nanoparticles
1.	Control Experiment	9.2	0.0	30.8	0.0	34.2	0.0	77.5	0.0
2.	Aluminium Oxide (Al_2O_3)	29.1	19.9	26.7	-4.1	25.8	-8.4	107.5	30.0
3.	Magnesium Oxide (MgO)	22.5	13.3	18.3	-12.5	6.7	-27.5	37.5	-40.0
4.	Iron Oxide (Fe_2O_3)	33.3	24.1	30.0	-0.8	9.2	-25.0	82.5	5.0
5.	Nickel Oxide (Ni_2O_3)	28.3	19.1	25.0	-5.8	23.3	-10.9	98.3	20.8
6.	Zinc Oxide (ZnO)	30.8	21.6	29.2	-1.6	25.8	-8.4	75.0	-2.5
7.	Zirconium Oxide (ZrO_2)	31.7	22.5	27.5	-3.3	28.3	-5.9	51.7	-25.8
8.	Tin Oxide (SnO)	27.5	18.3	25.0	-5.8	16.7	-17.5	76.7	-0.8
9.	Silane Treated Silicon Oxide (SiO_2)	28.3	19.1	27.5	-3.3	25.8	-8.4	75.8	-1.7
10.	Hydrophobic Silicon Oxide (SiO_2)	X	X	X	X	25.0	-9.2	68.3	-9.2

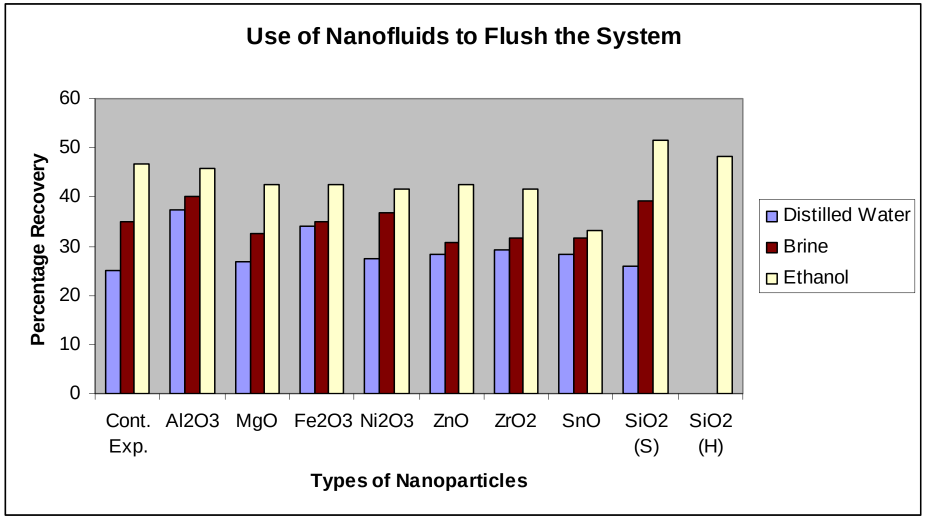

Figure 2: Results of various Nanofluids Used for EOR Experiments

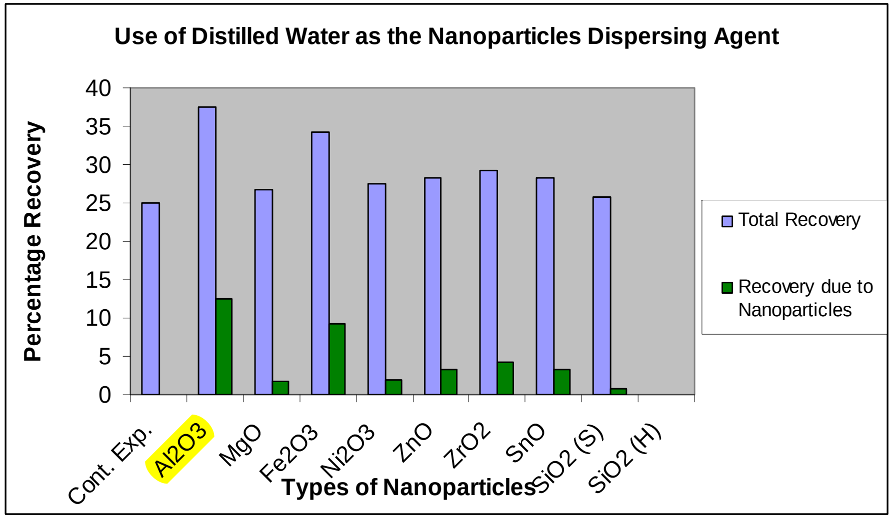

Figure 3: Results of various Nanofluids prepared with Distilled Water for EOR Experiment

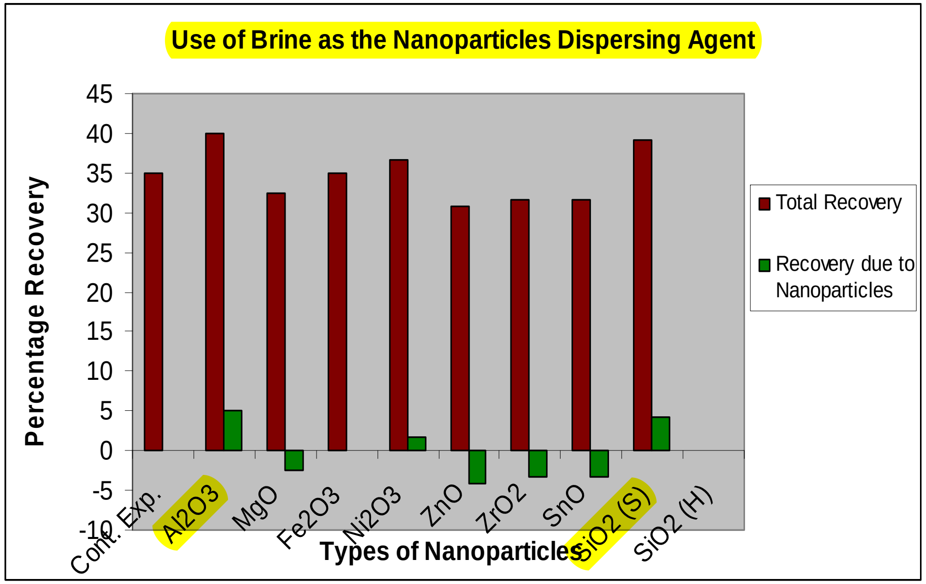

Figure 4: Results of various Nanofluids Prepared with Brine for EOR Experiment

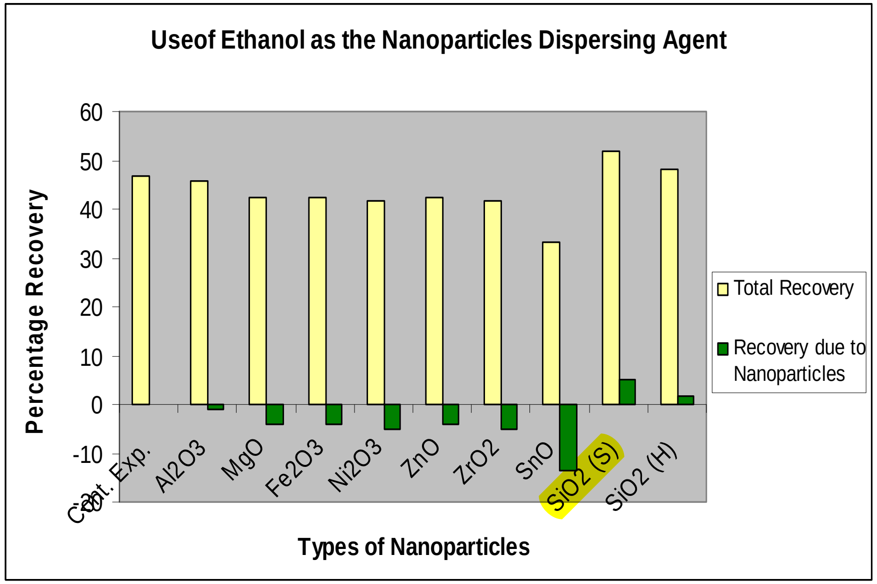

Figure 5: Results of various Nanofluids Prepared with Ethanol for EOR Experiment

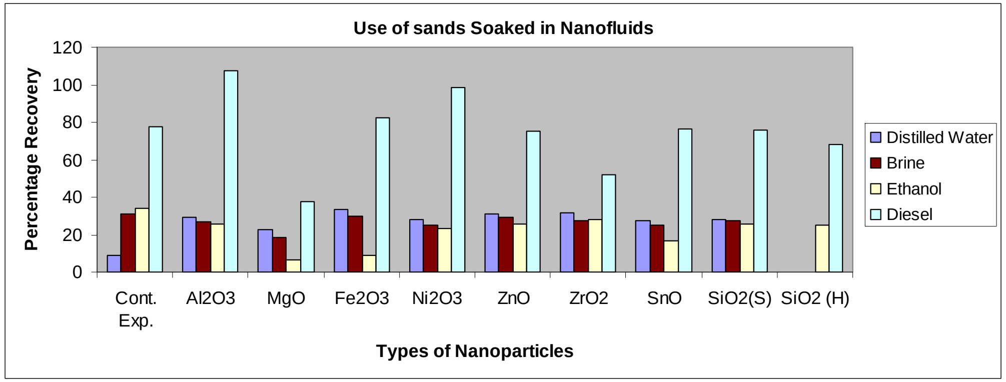

Figure 6: Results of EOR Experiments Using Sands that have been soaked in Nanofluids for 60 days

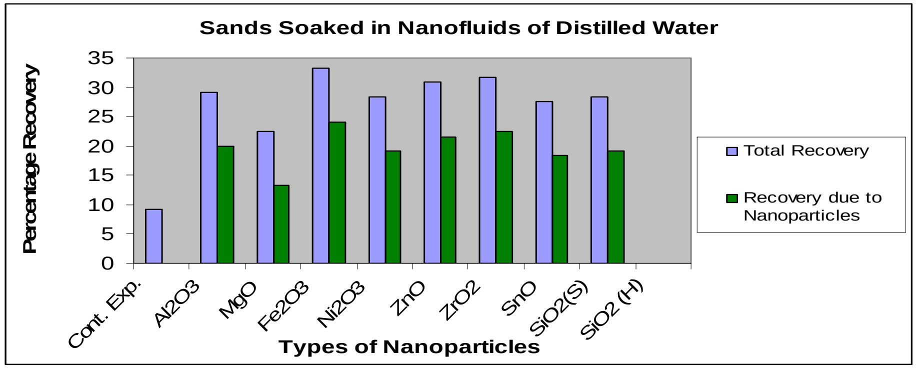

Figure 7: EOR Results from Sands Soaked in Nanofluids Prepared with Distilled Water

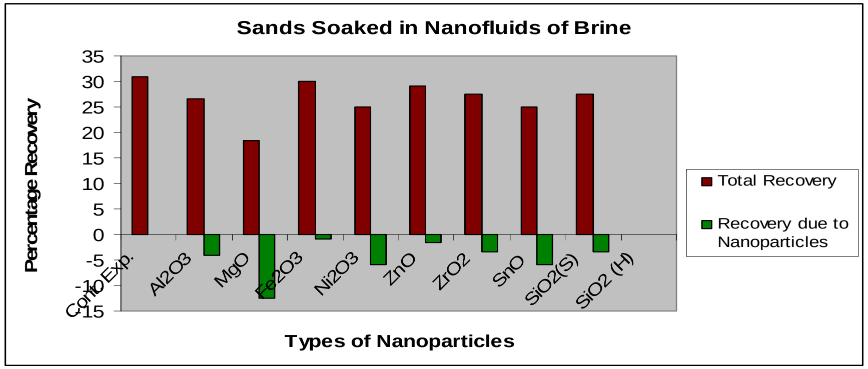

Figure 8: EOR Results from Sands Soaked in Nanofluids Prepared with Brine

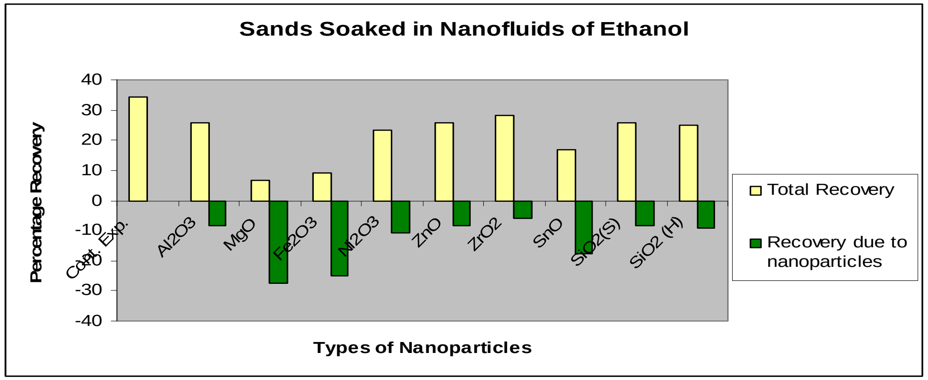

Figure 9: EOR Results from Sands Soaked in Nanofluids Prepared with Ethanol

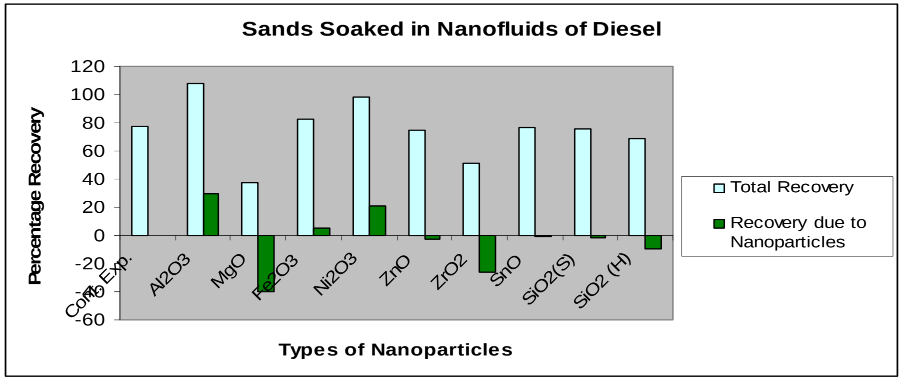

Figure 10: EOR Results from Sands Soaked in Nanofluids Prepared with Diesel

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