
Research/Technical Note

Metallic Oxides Nanoparticles: The New Frontier in EOR

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Abstract: With the rate at which most fields are becoming marginal and money is sunk to effectively recover more oil, there still lie factors that hinder oil recovery. Some of these factors are cost of recovery material, shear resistance of materials, stability of recovery materials in subsurface conditions, environmental friendliness of recovery material, ease of handling material etc. Nanoparticle EOR is a relatively new EOR technique with little or no application in the oil and gas industry. Though it is mostly still under experimentation in various labs across the world. It has proved beyond any reasonable doubt to fulfill the above stated loopholes in EOR. It also reduces interfacial tension, capillary pressure, wettability of oil, etc. with high displacement efficiency at low cost. This journal work is based on the recovery efficiency of three metallic oxides nanoparticles and their different characteristics which are very important to oil recovery. From the experimental work, it was found that aluminum oxide nanoparticles reduced interfacial tension and viscosity with a very high recovery factor, silicon oxide nanoparticles rapidly reduced wettability with a high recovery as well as magnesium oxide nanoparticle with the least. However, each of the metallic oxide particle experimented and analyzed in a core flooding system have their very peculiar property uniquely suitable for EOR at low cost and high recovery. However, the concentration of nanoparticle plays a key role in its recovery ability. The higher the concentration, the more tendencies to agglomerate and hinder permeability, the lesser the concentration, the less effective it can be. In my research, different concentrations were considered to determine the optimum concentration of metallic oxide nanoparticles with little or no adverse effect to the formation rock and fluid properties with optimum recovery.

Keywords: Nanoparticles Application, EOR, Laboratory Core Flooding

1. Introduction

The lifeblood of most industrialized nations is oil. Since the 19th century, oil has become the world's most important source of energy with its product supporting modern societies mostly by supplying energy to power industries, war machineries, heat up homes, provide fuel for vehicles and airplanes to carry goods and people all over the world. Infact, oil meets over 95% of the transport sector of most nations in the world and it is also a raw material for the production of many everyday essentials.

But it is quite unfortunate that only about 25-30% of oil and gas are produced from their reservoirs at their natural pressure, therefore the need for secondary and tertiary recovery.

Secondary recovery has for long given us about 30-45% recovery factor which is still relatively low, therefore the need for tertiary (enhanced oil recovery EOR). EOR has been giving a recovery factor of about 45-80% which is quite appreciable compared to other recovery methods. On the average the oil recovery from primary and secondary methods only accounts for about one-third of the OOIP, while the remaining two-third can be partly recovered through EOR [14]. EOR is achieved by altering the rock and fluid properties thereby recovering the residual oil that is trapped in the flooded area by capillary forces. Examples of EOR are thermal flooding, miscible flooding, chemical flooding etc. In chemical flooding, chemicals such as polymers, alkaline, surfactants and recently nano sized chemicals of aluminum oxides, silicon oxides, magnesium

oxides, zinc oxides etc. are used [5].

The petroleum industry is faced with a number of challenges when considering the reservoir. Some of these challenges are wettability, formation damage, low sweep efficiency, cost of EOR etc. [10]. Though EOR is effective, there are key challenges associated with it. For example, thermal EOR process is environmentally unfriendly due to emissions from surface steam generation systems, high operational cost, cement failure etc. In chemical EOR, pore plugging, high cost etc. occurs. In gas EOR, inadequate sources of gas due to geographical unavailability, adverse mobility problems occur [11].

Nanofluids (a solution of nanoparticles) are used in EOR to alter the properties of oil thereby helping in the recovery of residual oil in place. These nanoparticles are of the size of 1-100nm and have the capacity to reduce oil viscosity, interfacial tension IFT thus enabling the migration of oil from the reservoir to the production wellbore.

Nanoparticle utilization in EOR has received great interest and concern with controversial results, though proven to be highly effective in improving oil recovery [1]. Furthermore, EOR by nanoparticles is environmentally friendly, cheap and easy to apply in oil fields [5].

In addition, new nanomaterials have been proven to give high strength, high stability under high temperature and pressure reservoir conditions and are less susceptible to corrosion [8]. Though when surfactants are added to high molecular weight polymers, viscosity increases and complexes which are less susceptible to shear degradation are formed. However, the excessive increase in the surfactants concentration disrupts the association with a resultant decrease in viscosity of the displacing fluid [6]. Aluminum oxide nanoparticles reduced interfacial tension and viscosity with a very high recovery factor, silicon oxide nanoparticles rapidly reduced wettability [12]. They exhibit great stability over a wide range of temperature and favorable rheological and flow behavior [3], while at higher temperatures, the chemical bonds of polymers and surfactants are weak and easily break down irreversibly [13]. Metallic oxides nanoparticles have been proved to be a favorable material that can be easily transported through limestone and dolomite porous media [2]. The mobility of nanoparticles in porous medium greatly increases with temperature which reduces the adsorption of these particles in their preliminary stage after injection [15]. Nanoparticles especially multi-metallic nanoparticles can be transported through oil sands porous media into heavy oil reservoirs in order to serve as catalyst for upgrading [7].

Generally, in the oil and gas industry, nanoparticles are applied in the following aspects namely: Chemical flooding, water and gas coning control, flow assurance, Stimulation of low permeability oil and gas reservoirs, etc. It is also very pertinent in the reduction of viscosity which is a very important factor in EOR [8].

Finally, there are some cons in the use of nanoparticles EOR and one of them is permeability alteration/reduction by about 41-72% [9]. When a nanoparticle is dissolved in an acidic

solvent, it tends to increase in its morphology and when it is dissolved in a basic solvent, it tends to decrease in its morphology [4]. As a result, there is need to conduct experimental studies on permeability alterations due to nanoparticles retention in porous media in nanotechnology assisted enhanced oil recovery so as to know the kind, concentration and environment a particular nanoparticle will function effectively with little or no serious alteration to formation permeability.

2. Materials and Methods

2.1. Apparatus/Equipment

Flat bottom flask, measuring cylinder, retort stand, AFS core flooding system, aluminum foil, mesh, masking tape, cutting machine, meter rule, vernier caliper, face mask, oven, weighing balance, sieve shaker, plastic bowl, viscometer, densitometer, magnetic stirrer, PPE and saturator.

2.2. Materials

Distilled water, industrial salt, aluminum oxide, silicon oxide, magnesium oxide nanoparticles, crude oil, 63-250 microns grain size distribution.

2.3. Sand Pack Preparation

Preparation of sand packs or unconsolidated core plugs were done by cutting aluminum foils each of 7cm length and soaking in water to remove entrained carton.



Figure 1. Aluminum foil.

Core plug is formed by consolidation the hollow aluminum foil with sand about 63 - 250 micron in grain size distribution. Then the ends of the cylindrical packs are covered with mesh and then the sand pack is saturated with brine (@ 30g/liter) by a saturator.



Figure 2. Prepared sand pack.

In general, 12 sand packs were prepared, 3 controls, 3 silicon oxide, 3 aluminum and 3 magnesium oxide

nanoparticles. 2 were used and 1 was kept each to mitigate unforeseen occurrences.

2.4. Nanofluid Preparation

The nanofluid was prepared by dissolving 0.1 wt% and 0.2 wt% of individual nanopowders in a brine solution of 30g/liters. A magnetic stirrer was used to uniformly disperse the solute in the solution so as to prevent plugging of core flooding tubes as well as to ensure uniform concentration.

Table 1. Different nanoparticle concentrations and the alphabet attached to them during the core flooding system.

Composition	Alphabet	Concentration
Control	C1	Nil
	C2	Nil
Silicon oxide	D1	0.2%wt
	D2	0.4%wt
Aluminum oxide	E1	0.2%wt
	E2	0.4%wt
Magnesium oxide	F1	0.2%wt
	F2	0.4%wt

2.5. Core Flooding

Core plug was fixed into the core barrel and the core barrel was put in place in the core holder. The core holder was fixed into the AFS core flooding system and necessary connections were made. Brine was filled into the accumulator A in the core flooding system up to 1000ml or less. Oil was filled into the accumulator B in the core flooding system up to 1000ml or less. The existing differential pressure in the core flooding system was confirmed and the differential pressure in the core flooding system was zero trimmed. Then the flow rate of 1 ml/min was set for water to fill the lines prior to heating. The

oven was heated up to 45°C (113°F) and pressure of about 3000-3500 psi was applied radially to the sand pack in the core holder. Injection of oil into the brine saturated sand pack (drainage) thereby resulting in the determination of OOIP by the Archimedes' principle. Imbibition or water flooding by brine to determine the initial oil saturation after secondary recovery. EOR by nanopowders was done by replacing brine with nanofluid in accumulator A at different concentrations.

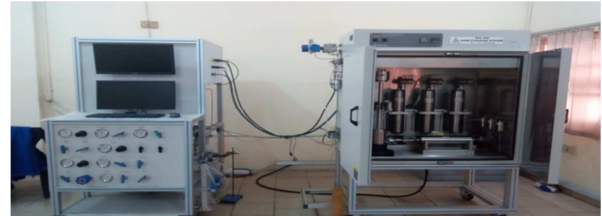


Figure 3. AFS core flooding system.

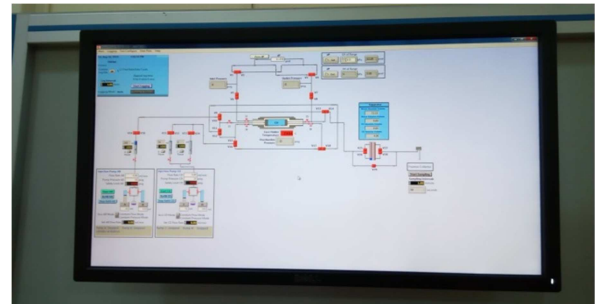


Figure 4. PFD of the AFS core flooding system.

3. Result

The following results were obtained at the end of the experiment.

Table 2. Result of Nanoparticle Permeability Alteration and EOR.

s/n	Conc	Agent	Sample name	Abs. Perm (mD)	Eff. Perm during EOR-assisted waterflooding (mD)	Displacement Efficiency (%)
1	N/A	Control	C	1269	N/A	73.33
		Silicon oxide	D	1211	356	80.00
2	0.2 wt%	Aluminum oxide	E	1214	729	93.75
		Magnesium oxide	F	911	250	76.92
		Silicon oxide	D	729	405	91.67
		Aluminum oxide	E	1197	399	97.50
3	0.4 wt%	Magnesium oxide	F	729	258	83.33

Table 3. Fluid Properties at Ambient Conditions.

Properties	Brine (30g NaCl)	Brine (with 0.2% Al ₂ O ₃)	Brine (with 0.4% Al ₂ O ₃)	Brine (with 0.2% MgO)	Brine (with 0.4% MgO)	Brine (with 0.2% SiO ₂)	Brine (with 0.4% SiO ₂)	Crude Oil
Density (g/cm ³)	1.0167	1.0171	1.0191	1.0146	0.9996	1.0189	1.0183	0.9110
S. G	1.0202	1.0203	1.0224	1.0178	1.0028	1.0221	1.0215	0.9138
°API @ 15°C	-	-	-	-	-	-	-	22.46
Dynamic Viscosity (cP)	0.95	0.97	0.86	0.96	0.91	1.04	0.94	60.2

Table 4. Fluid properties at 45°C (113°F).

Properties	Brine (30g/l NaCl)	Brine (with 0.2% Al ₂ O ₃)	Brine (with 0.4% Al ₂ O ₃)	Brine (with 0.2% MgO)	Brine (with 0.4% MgO)	Brine (with 0.2% SiO ₂)	Brine (with 0.4% SiO ₂)	Crude Oil
Density (g/cm ³)	1.0063	1.0111	1.0131	1.0066	0.9678	1.0129	1.0123	0.8991
S. G @ 15°C	1.0142	1.0203	1.0204	1.0138	0.9749	1.0221	1.0204	0.9078
Dynamic Viscosity in cp	0.66	0.66	0.66	0.68	0.61	0.68	0.66	19.2

Table 5. Rock Properties.

Composition	Sample ID	Dry Weight (g)	Wet Weight (g)	Length (cm)	Diameter (cm)	Cross Sectional Area (cm ²)	Pore Volume (cm ³)	Bulk Volume (cm ³)	Porosity (%)	OOIP (ml)	Oil Recovered (ml)
CONTROL	C1	128.8	156.0	7.0	3.8	11.346	26.75	79.42	33.68	15.0	11.0
	C2	127.3	153.2	7.0	3.9	11.951	25.48	83.66	30.46	13.0	9.0
SILICON OXIDE	D1	134.4	161.1	7.5	3.5	9.625	26.26	72.19	36.38	12.5	10.0
ALUMINIUM OXIDE	D2	120.2	147.4	7.0	3.9	11.951	26.75	83.66	31.98	12.0	11.0
MAGNESIUM OXIDE	E1	127.0	154.2	7.0	3.9	11.951	26.75	83.66	31.98	12.8	12.0
	E2	126.8	154.0	6.9	3.9	11.951	26.75	82.46	32.44	12.0	11.7
CONTROL	F1	125.7	151.2	7.0	3.9	11.951	25.08	83.66	29.98	13.0	10.0
	F2	128.5	154.2	7.0	3.9	11.951	25.28	83.66	30.22	12.0	10.0

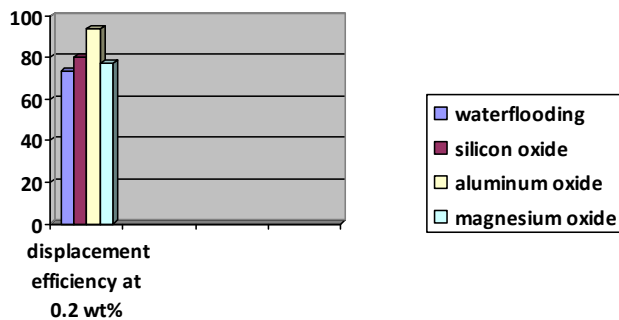


Figure 5. Displacement efficiency at a nanoparticle concentration of 0.2%.



Figure 6. Displacement efficiency at a nanoparticle concentration of 0.4%.

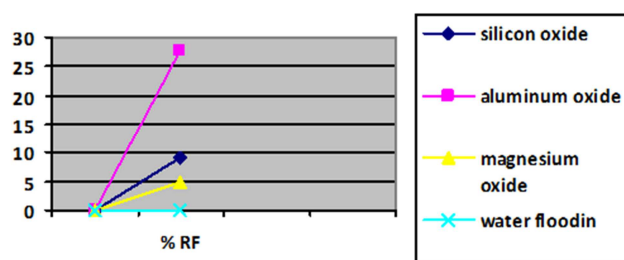


Figure 7. Recovery factor for some metallic oxide nanoparticles at 0.2 wt%.

4. Discussion

From the result we can see that aluminium oxide nanoparticles have the highest recovery, followed by silicon oxide with magnesium oxide having the lowest recovery. Analysis of the particles and the observations noticed will give us more insight on their different behaviours.

From figure 7, we can clearly see that aluminum oxide has a higher RF followed by silicon and lastly magnesium oxide.

The recovery factor is subject to the recovery from secondary recovery which is the benchmark for ascertaining the additional recovery by 0.2 wt% of the following nanoparticles.

During the analysis it was noticed that aluminum oxide nanoparticles reduced the adhesive force between the crude oil and solids. That is an indication that it reduces the wettability of oil in an oil wet rock, making it more water wet. Furthermore, it tremendously reduced the oil-water interfacial tension more than any other nanoparticle used in the analysis as was seen in the ease of oil separation from water during the efflux period.

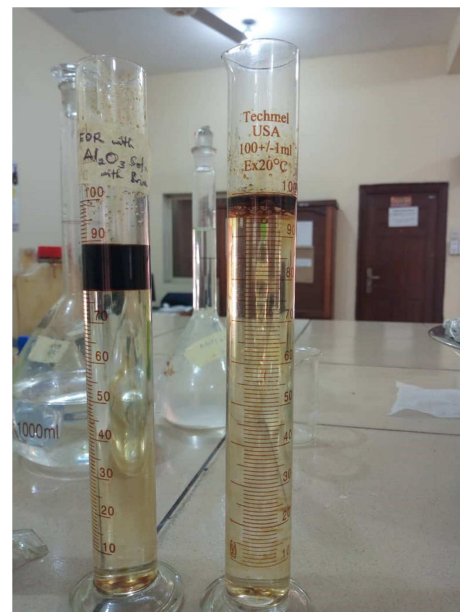


Figure 8. Oil recovered (efflux) from aluminum oxide nanoparticle.

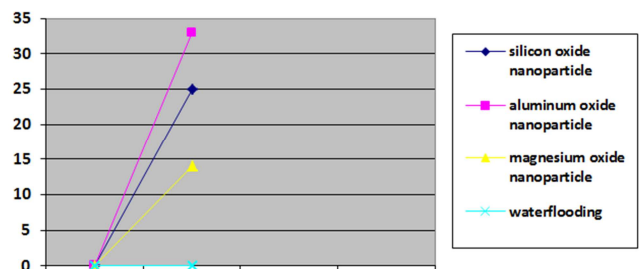


Figure 9. Recovery factor for 0.4 wt% nanoparticle.

From figure 9, it is seen that there is a slight increase in the recovery factor by aluminum oxide nanoparticle from the

previous 0.2 wt%. Silicon and magnesium oxide nanoparticles appreciated greatly in their RF as concentration increases therefore, silicon and magnesium nanoparticles performs well at relatively high concentrations.

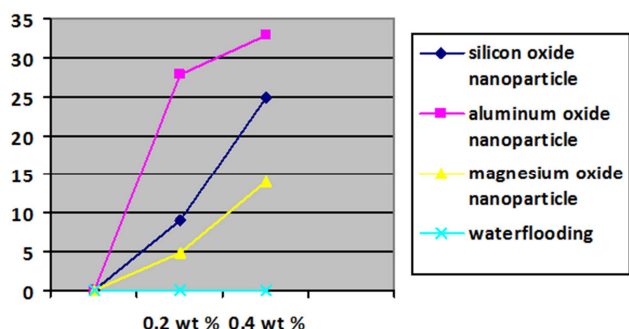


Figure 10. Comparison of 0.2 and 0.4 wt% recovery factor for some metallic oxide nanoparticles.

5. Conclusion and Recommendation

From table 5 we see that aluminum oxide nanoparticle has the highest recovery compared to silicon and magnesium oxide nanoparticle, although as the concentration increases, its recovery factor increases at a lower rate compared to silicon and magnesium oxide nanoparticles (see figure 10). So at high concentration, aluminum oxide nanoparticles may not have a linear recovery factor with lower concentration, it however has a relatively high permeability alteration. It reduces permeability more than silicon and magnesium oxide nanoparticles but recovers more than them. So aluminum oxide nanoparticle is best used at lower concentrations to achieve higher recovery with little alteration to the permeability. Furthermore, it has a shorter water breakthrough time (8 minutes) compared to the rest, which implies that it is cost effective and fast.

From figures 10 and 9 silicon oxide nanoparticles perform better at higher concentrations than the rest experimented. It had a breakthrough time of 10 minutes, very effective in wettability alteration and also cost effective.

Magnesium oxide nanoparticle is the least preferred, although it has an increased recover factor at higher concentration (see figures 10 and 9), it has a lower permeability alteration, however it agglomerates faster at lower flow rates and it is not as cost effective like aluminum and silicon oxide nanoparticles.

Aluminum oxide nanoparticle is the best compared to the other metallic oxide nanoparticles experimented on. It has the highest recovery factor, displacement efficiency, and interfacial tension reduction etc. but also alters permeability greatly at high concentrations. It is recommended to be used as;

- a) Demulsifier
- b) EOR agent

Whenever high concentration is needed, it is preferable to go for silicon oxide nanoparticle. It can be used together with aluminum oxide, with silicon having the higher concentration in the solution. Nanoparticle EOR is cost effective and

environmentally friendly but the concentration when not properly checked or controlled will hamper permeability.

I will continue with the research soonest to test more nanoparticles. I hope to consider more concentration values like 0.1 wt%, 0.3 wt%, 0.5 wt% and 1 wt% to have a proper view of the actual sequence of metallic oxide nanoparticles on permeability alteration and their overall effect as EOR agents.

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