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Evaluation of the Effectiveness of Zinc Oxide and Calcium Oxide Nanoparticles with Nitrogen Gas for Enhanced Oil Recovery.

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ABSTRACT
This study examines the effectiveness of zinc (ZnO) and calcium (CaO) oxide nanoparticles when used in combination with nitrogen gas (N2) to drive enhanced oil recovery. After the physical and rheological parameters of the heavy crude were established, ten (10) liters of the heavy crude were added to a reservoir tank that contained thirty (30) liters of an enhanced oil recovery flooding system. After soaking for 24 hours and being pumped with 1 bar of N_2, the crude was then flooded with N_2 and afterwards treated with 5, 10, 15, 20, and 25 grams of ZnO, CaO, and both Nano particles in equal amounts with the single Nano particle mass concentration. At various nanoparticle mass percents, the density, viscosity, and crude oil recovered were measured. The density for ZnO nanoparticle, CaO, and the combination nanoparticle decreased from 0.90100/cc to 0.88680g/cc, 0.88760/cc, and 0.90580g/cc, respectively. Also, the result shows that as the mass percent concentration of both the single and the combination nanoparticles increased, the viscosity of the crude oil reduced from 0.8621cp to 0.6044cp for ZnO, 0.7404cp for CaO, and 0.7428cp for the combined nanoparticle. As the mass percent concentration of the nanoparticles increased, the quantity of oil recovered increased. Result reveals that the combined nano particle outperformed the single nano particle with the highest recover factor.

Keywords: Efficency, Nanoparticles, Nitrogen gas, Enhanced Oil Recovery.

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I. INTRODUCTION

The process of extracting oil from hydrocarbon reservoir leads to depletion in reservoir pressure, recovery efficiency reduction, as well as reduction in production rate, which varies over the lifecycle of a well. Therefore, the formation will need additional means of stimulation in ensuring that production volumes remain at sustainable levels for as long as possible. One of the means or method of improving production rate is the injection of Nitrogen which has been successfully in that regards (Bazargan *et al*, 2019).

Primary recovery is the first or initial stage in the oil production process. This involve placing increased pressure on the wells in order to move the oil to the surface in other words, primary recovery relies on the natural difference in pressure between the surface and the underground reservoir, which however, relatively small capital investment (Glover, 2001). As the oil is produced gradually from the well, the pressure underground will begin to decrease slowly, thereby causing the volume of oil production to reduce. To alleviate this, oil production industries can use artificial lifting systems such as rod pump electrical submersible pump to continue production. These approaches are usually being usually known as natural drive mechanism (Glover, 2001). The recovery factor from conventional oil production is above 30% but for heavy oil, it is within the range of 5-10% (Al-Nakhli *et al.*, 2016). However, when the pressure of the natural lift is not sufficient enough to drive or move the oil to the surface, then the primary recovery process has reached the maximum limit of extraction.

As the oil is produced gradually from the well, the pressure underground will begin to decrease slowly, thereby causing the volume of oil production to reduce. To alleviate this, oil production industries can use artificial lifting systems such as rod pump electrical submersible pump to continue production. At any moment the primary recovery methods stop to produce oil naturally the next stage which is the secondary stage comes into play, to push the oil from the reservoir to the surface. They rely on the supply of external energy into the reservoir. hence secondary reservoir methods increase the reservoirs pressure by water injection, natural gas injection and gas lift, which inject carbon dioxide (CO_2), Nitrogen (N_2), or some other gas into the well, reducing the total density of the fluid in the wellbore. On average, the recovery factor of primary and secondary oil recovery operations is between 35 and 40%, depending on the properties of the oil and the feature of the reservoir rock (Fleshman and Lekic, 1999) The most widely used method of secondary oil recovery is gas injection. As soon as gas, such as nitrogen or carbon dioxide, is introduced into the reservoir, it expands. This expansion moves oil through the formation and into the well. Gas injection is an enhanced oil recovery process that makes use of Nitrogen gas (N_2) or Carbon dioxide (CO_2) for the miscible displacement of crude oil reservoir (unconventional). The principle for oil recovery results from when the gas dissolves in the oil, thereby reducing the oil viscosity and improving oil mobility. The implementation of gas injection becomes successful when the gas is pumped at high downhole pressure, into the formation via injection well, the gas however, forms a miscible slug that mops up stranded oil and makes it move towards the production well through the production casing.

Gas injection is alternated often with water injection using water injection pump system in order to further improve sweep efficiency (Fleshman and Lekic, 1999).

Enhanced Oil Recovery (EOR) processes are executed to increase the ability oil to flow to a well by injecting water, chemicals or gases into hydrocarbon reservoir or by altering the physical properties of the oil. The main objectives are to produce additional amount of crude oil that could not be produced during primary and secondary production of oil (Siregar *et al.,* 2007). Primary and secondary oil recovery (including water flooding or re-injection of produced natural gas) produce on the average about one-third of the original oil in place (OOIP).

There are different production stages or processes encountered during the life of an oil producing field. Firstly, when an oil field is made to produce, naturally oil flows to the surface due to the reservoir pressure in the initial stage of oil production. However, as the pressure of the hydrocarbon reservoir reduces, water is injected to boost the pressure during the secondary stage of oil production. Finally, the oil remnant can be produced by a variety of processes such as CO_2 injection, natural gas miscible injection and steam recovery in enhanced (tertiary) oil recovery phase(EOR) (Siregar *et al.,* 2007). Nitrogen gas (N_2) injection is a hydrocarbon recovery (gas injection) process where nitrogen gas is injected into an oil reservoir to enhance the oil recovery factor (Alagorni *et al.,* 2015). When the injection is done below the Minimum Miscibility Pressure (MMP), it is an immiscible recovery process, in which recovery is increased by oil swelling, viscosity reduction and reduction in crude oil vaporization. On the other hand, above the MMP, nitrogen injection is a miscible vaporizing drive. Miscibility of nitrogen is only achievable with light oils that are at high pressures, and suitable only in deep reservoirs (Belhaj *et al.,* 2013). Globally, the use of Nitrogen (N_2) injection has been in existence since mid-1960s as a secondary or tertiary recovery method, which maintains reservoir pressure to enhance oil recovery in different lithological reservoirs (Wu *et al*., 2013).

Regarding various nanoparticles, Calcium oxide nanoparticles have gained favourable recognition. This is due to their properties (which however seem unusual) and application (potential) in different fields. Calcium oxide (CaO) is cheap, non-corrosive, has a high basicity, economical and easy to handle when compared to homogenous base catalysts. In comparison with fundamental catalysts, CaO can be recycled, as they require only mild reaction conditions to produce high yields of products in short reaction times. (Zhang *et al.,* 2010). There are several or numerous applications of CaO, however, the principal practical use of CaO is in catalysis, in the transesterification of fats or oils to produce biodiesels (Boro *et al.,* 2014). Calcium oxide is a gray-white granular powder that contains calcium and oxygen.

The use of Nitrogen gas (N_2) is a promising application for EOR. While the specifics of each reservoir dictate which EOR method has the greatest potential for oil recovery. Nitrogen gas has properties which make it the ideal gas for certain conditions. Nitrogen's low compressibility shows that les energy is needed or required to inject it into high pressure reservoir. Nitrogen is inert, non-corrosive and richly available at any location (Clancy, 1985). These properties make Nitrogen advantageous where field material cost, degradation and availability of alternative gases are a concern. As a non-toxic, non-greenhouse gas, nitrogen also is an environmentally favourable choice.

Apart from the above highlighted benefits of Nitrogen gas (N_2) injection, there are more benefits which include lowering production and operational costs by cryogenic air separation (Belhaj *et al.*, 2013).

It has become necessary to classify nanomaterial due to the enormous diversity of these tiny particles, which makes impossible to place or put them under a single class. Diameter, size, surface area, morphology, dimensions, and manufacturing processes are all factors that could be used to categorize nanoparticles. Generally, however, nanomaterials are classified based on their morphology, composition, uniformity, aggregation as well as dimension. As pointed out earlier, are structural components with a size smaller than 1μm with an external dimension in the nanoscale (Mageswari *et al.*, 2016). They exist in spherical, tabular and irregular shape and can be found in a single fused, agglomerated form (Patel *et al.*, 2018).

II. MATERIALS AND METHODS

Materials

Table 1: Experimental Materials for Enhanced Oil Recovery Method

Equipment	Materials	Glass
Crude oil	Redwood viscometer	Beaker
Zinc Oxide (**Nano particle**) Calcium Oxide	Stopwatch	Crucible
Nitrogen (Gas)	Retort stand Measuring cylinder	Pyncnometer Thermometer
	Air cooler chamber	
	Weigh balance	
	Enhanced oil recovery laboratory setup Pemsky-Martens flash	

Methods

Determination of Density

The weight of the empty dry pycnometer was determined after which the pycnometer was filled with crude oil sample ensuring that there was no bubble inside the pycnometer and its weight was recorded using the weighing balance. The crude oil density was determined at every given temperature with the use of a thermometer. The procedure was repeated for crude oil at initial condition, the crude oil sample with Nitrogen gas (N_2 (control), and for the different mass percent concentrations of the nanoparticle.

$$\text{Density } (\rho) = \frac{\text{weight of filled pynometer} - \text{weight of empty pynometer}}{\text{volume of pynometer}} \quad (1)$$

Determination for Specific Gravity

The specific gravity was measured using hydrometer. The operation of the hydrometer is based on the Archimedes principle which that the solid suspended in a fluid will be buoyed up by a force to the weight of the fluid displaced. During this process the cylinder was filled with the crude oil and the temperature of the crude oil sample was measured by the use of thermometer and recorded. The hydrometer was dropped into the sample slowly and carefully, away from the wall of the cylinder until a steady floatation in the center of the cylinder was observed. A hydrometer is usually made of glass and consists of a cylinder stem. The procedure was repeated for crude oil at initial condition, the crude oil sample with carbon-dioxide (control), and for the different mass percent concentrations of the nanoparticle. The equation used in calculating the specific gravity of the crude oil is;

$$\text{API Gravity} \frac{141.5}{\text{SPECIFIC GRAVITY}} - 131.5 \quad (2)$$

Using a Redwood Viscometer to Determine Viscosity

Redwood viscometer was used to gauge the viscosity of each sample that was created.

The viscometer was thoroughly cleaned and dried, water was added, and a thermometer was used to measure the water's temperature. Crude oil was then added to the oil cup to the required level indicated by the marker point, and the water was heated to a uniform temperature using a thermometer. When the temperature was reached, the ball was raised above the orifice hole at the same time that the stopwatch was started, and the oil was then measured.

$$\left(At - \frac{B}{t}\right)\rho \quad (3)$$

Where;
A=0.026
B=0.188
t=time
ρ = density

Enhanced Oil Recovery Experiment

After the properties test was done the enhanced oil recovery test was done using: The set up used for this is a laboratory set up for enhanced oil recovery, this set up can be used for various type of enhanced recovery method which includes water, air etc but in this case silicon oxide is used to enhanced the recovery of the crude. The setup is made up of series of equipment that represents the setup of a well head, the set up makes use of a Nitrogen gas cylinder (N_2) that acts as the reservoir pressure, this cylinder is connected to a 10litre metal tank which stands as the reservoir, a pipe is connected to this tank which along it's line comprises of a tap handles (stands as the well head valve) and a pressure gauge used to read the tank outlet pressure (reservoir outlet pressure), a condenser to condense any gas if present then a second tap handle which stands as a valve which leads to the collection container (storage tank). The tap handles were opened and the stopwatch set for 10 seconds at the same time, the inlet pressure and the outlet pressure were recorded as the fluid flowed, as the 10 seconds elapses, the Nitrogen gas cylinder was closed, the tap handles was also returned to a closed position. The volume of the crude oil and water recovered were recorded.

The reservoir was emptied totally. After the mixture settled, the water cut was recorded and the amount of water and crude recovered calculated. A sample of the recovered crude was taken and tested for its properties again.10litres of crude oil sample was mixed with 2 grams of silicon oxide and allowed to mix properly for 24hours. After 24hours the samples were made to undergo the same procedures used for the recovery of the previous sample, the reservoir and flow lines were emptied properly, after getting the cut, the crude oil recovered was used to carry out the properties test again, The 10litres of crude oil samples was mixed with Zinc and calcium oxide nano-particles in different mass percent concentrations (5g, 10g, 15g, 20g, 25g) , it was allowed for 24 hours which is also known as soaking period to mix before flooding with Nitrogen (N_2). The procedure was repeated, equally recorded and calculated the quantity of oil recovered, and also testing for the crude properties of the crude recovered respectively for the different samples, the reservoir set up was emptied and its environment properly cleaned.

III. RESULTS AND DISCUSSIONS

Effects of Nitrogen Gas and Nanoparticles on Density

The effect of the mass percent concentrations of nanoparticles and carbon-dioxide on the density of the crude oil is presented in Fig 1

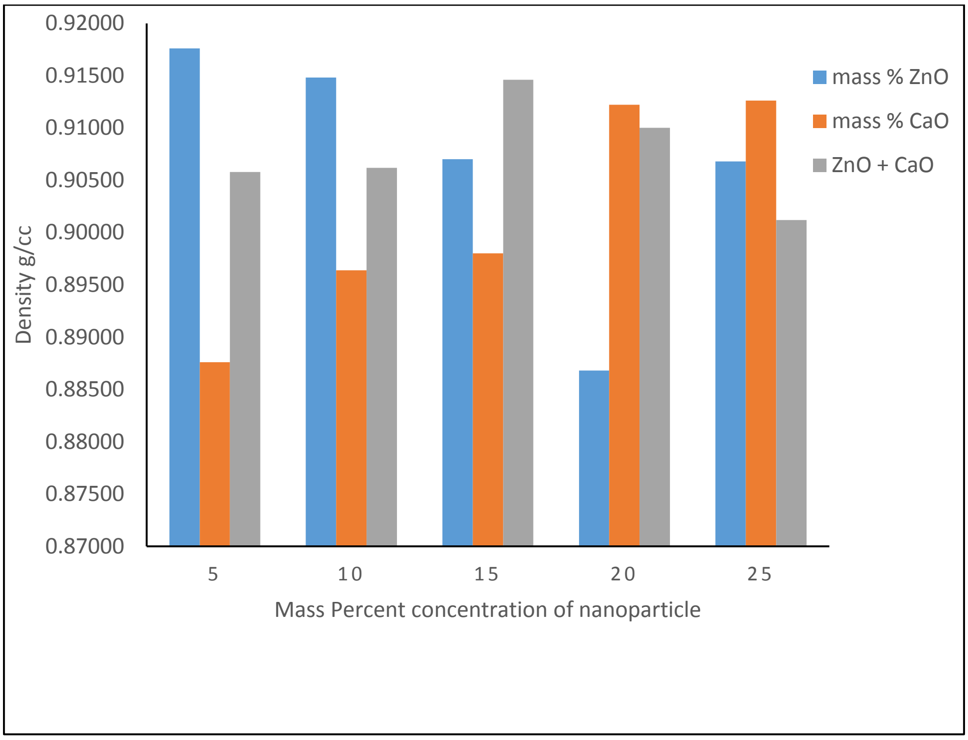

Fig 1: Effects of Nitrogen and Nanoparticles on Density at different Mass Percent Concentrations.

The density of the crude oil decreased rapidly from 1.29g/cc to 0.91g/cc after 5grams of Zinc Oxide nanoparticle was introduced into the system. The density then decreased by 0.0028g/cc when 5grams of the constitute (Zinc Oxide) was added. A further decrease of about 0.0078g/cc was recorded at 15gram of the same nanoparticle, however at 20g, a further decreased of 0.0202 g/cc was observed. The density increased to 0.90680g/cc from 0.88680g/cc for 25 grams. For calcium oxide nanoparticle, it shows that the density of the crude oil decreased rapidly from 1.29g/cc to 0.90580g/cc after 5 grams of the stated nanoparticle was introduced into the system. The density remained steady when another 5 grams of the constitute was added. A decrease of 0.91460g/cc was recorded at 15 gram of the same nanoparticle, however at 20 grams, the density decreased by 0.0046 and further decreased for 25 grams. For 1:1 mass percent concentration of Zinc and Calcium oxide nanoparticles on the density shows that the density of the crude decreased from 1.29g/cc to 0.88760g/cc after 5grams of the stated nanoparticle was introduced into the system, signifying the nanoparticles had high effect on the oil. However, for 10grams of the mass percent concentration of the nanoparticles shows that the density increased to 0.89800 from 0.88760. Similarly, for 15g, the density increased to 0.91220 from 0.88760. An increase of 0.91260 was recorded for 20g and 0.91260 for 25grams.

Effect of Nitrogen Gas and Nanoparticles on Viscosity

The impact of mass percent concentration of nanoparticles and carbon-dioxide on the viscosity of the crude is presented in Fig 2

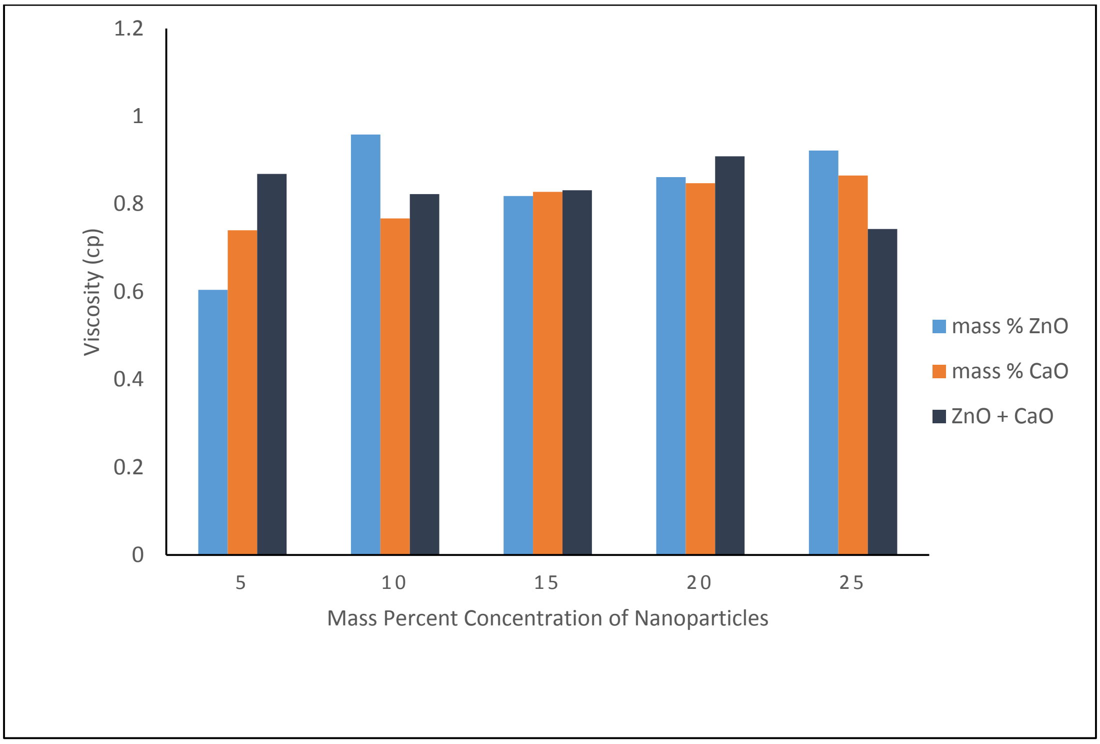

Fig 2: Effect of Nitrogen Gas and Nanoparticles on Viscosity at Different Mass Percent Concentrations.

when zinc oxide (ZnO) nanoparticle was added, the viscosity decreased from 1.6cp to 0.6045 cp when 5grams was added. The viscosity increased by 0.054cp when 10 grams of ZnO was added. The viscosity decreased from 0.65808 to 0.63836 when 15 grams was added. A further decrease of 0.62134 was observed for 20grams and 0.60199 for 25 grams.
when 5-gram of calcium oxide nanoparticle was introduced, viscosity decreased from 1.6cp to 0.54047. For 10 grams, the viscosity increased from 0.54047 to 0.541729, the viscosity decreased from 0.541729 to 0.53762 for 15 grams of CaO. The viscosity further decreased to 5.21494 for 25grams.

For equal mass percent concentration of zinc and calcium oxide, the viscosity increased from 1.6 cp to 0.76891cp when 5grams was added, when 10-gram the viscosity decreased from 0.76891 to 0.72262. For 15 and 25 grams of nanoparticles, the viscosity increased to 0.73168 and later decreased to 0.70884. An increase of 0.03301 was recorded for 25 grams.

Effects of Nitrogen Gas and Nanoparticles on Recovery Factor

The impact of mass percent concentration of nanoparticles and carbondioxide on the recovery factor of the crude is presented in Fig 3

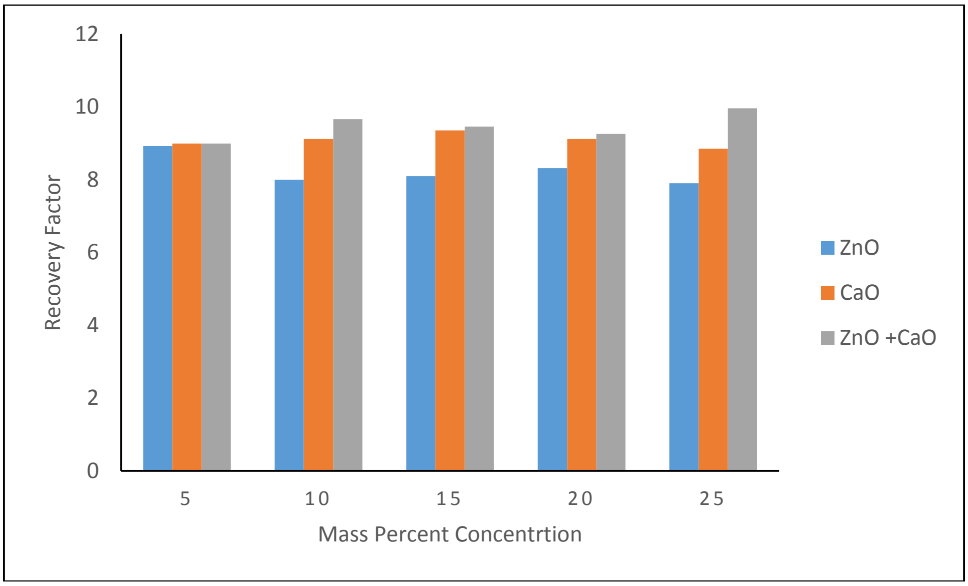

Fig 3: Effect of Nanoparticles and Nitrogen Gas on Recovery Factor at different Mass Percent Concentrations. Result reveals that the combined nano particle outperformed the single nano particle with the highest recover factor while the zinc oxide had the lowest recovery.

IV. CONCLUSION

In this work, the effects of Nitrogen (N_2) Calcuim oxide nanoparticles, and Zinc oxide nanoparticles on heavy crude oil recovery were assessed.

The findings were as follows:

1. The density of the crude oil decreased with increased in mass percent concentration of calcium and zin oxide.
2. The viscosity of the crude oil decreased with an increase in mass percent concentration of calcium and zin oxide.
3. Zin Oxide had the lowest Recovery Factor while the conbined nanoparticles had the highest recovery factor.

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