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A Study of pH and Zeta Potential of Nanoparticle Transport in Porous Media

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Abstract:- Fines migration is a serious problem facing the oil and gas industry. Migration of fines can be controlled through the use certain substances which have the capacity to trap fine particles.

In this paper, some nanoparticles and fluid dispersants which have the ability to control migrating fines were investigated. The nanoparticles were hydrophobic silicon oxide; the fluid dispersants were ethanol, potassium chloride and water, while the fines and the formation were kaolinite and glass beads respectively. An experiment was conducted to determine the best nano-fluid that could trap a relatively large amount of fine particles. Results show that hydrophobic silicon oxide dispersed in ethanol had the best performance. 0.5g of hydrophobic silicon oxide dispersed in ethanol trapped 17.58g of kaolinite. The primary mechanisms through which fines were trapped were electrostatic forces of adsorption between the molecules of the nano-fluids and fines and are affected by PH and zeta potentials. The pH values of the nano-fluids and the concentrations of the nanoparticles dispersed in fluids were measured, while the zeta potentials were calculated by a modified Smoluchowski's equation. Trapping of fines was mostly favoured by low PH values and concentrations and high zeta potential of silicon oxide nanoparticles dispersed in ethanol.

***Keywords*:-** *Nanoparticles; Fluid Dispersants; Nano-Fluids; Kaolinite; Fines Migration; Trapping; PH; Zeta Potential; Concentration; Smoluchowski's Equation.*

I. INTRODUCTION

Migration of formation fines is a very crucial issue to oil and gas producing companies in different parts of the worlds, including the Niger Delta. Fines migration in reservoirs leads to numerous problems which include destruction of subsurface and surface equipment, replacement costs, environmental issues, permeability impairment in formations and even blowouts can occur in extreme cases. If unattended to, this problem can ultimately result in production shutdown even when reservoirs still contain substantial quantity of recoverable hydrocarbon.

Fines are tiny grains of sand, silt and clay particles that disintegrate from the rock matrix. The major causes of fines migration are age of the rock and the degree of consolidation of rock formation. These fine particles can be trapped (prevented from migrating). From studies, three primary trapping mechanisms of fines that have been identified are pH values of nanofluids, zeta potential and electrostatic forces of adsorption that exist between the molecules involved. Other possible mechanisms might exist but will be negligible compared to these three mechanisms.

An investigation was done to find out if the presence of a new agent, negatively affects conductivity through proppants. The results from effluents collected showed that nano-agents captured migrating fines in the sand pack (Huang et al, 2008). These laboratory experiments demonstrate that some nanoparticles have the ability to prevent formation fines from migrating. A field case study to investigate how nano-treated proppants can control fines migration on an off shore fracpack was carried out in a well in the Gulf of Mexico and results were reported to be very good (Huang et al, 2010). Another reported nanoparticles laboratory experiment and field applications showed that nano particles can control migrating fines in formations (Belcher et al, 2010).

Since some nanoparticles can control migrating fines on sand, it is imperative then to find how the concentration and different types of nanoparticles will affect the trapping of fine sand grains. The flow rate is also very important during flooding of the system. It was discovered that silicon oxide and aluminium oxide have good performance in trapping fines (Ogolo et al, 2012). Release of clay fines in porous media has long been known to be triggered by the PH value of the surrounding fluid. Low pH values keep fines in place but high pH values can dissolve silicon cement to create fines (Essam et al, 2007). High pH values which change the existing lower pH of formation fluids are mostly initiated by water flooding. Since low pH values have been known to prevent detachment, hydrochloric acid has been used to prevent fines migration but has been detrimental to formation since it destroys other existing bonds of formation particles and is environmentally unfriendly.

Cations are naturally attracted to anions. A system containing negatively charged particles of clay and metallic oxide nanoparticles (positively charged) will result in adsorption of the clayey particles on particles of metallic oxides through electrostatic attraction to maintain electrical neutrality. Adhesion process traps as much fines as possible until the positive charges of the oxide have been exhausted before the excess negatively charge fines start migrating through the sand pores. Some of the forces of attraction that exists between clays (fines) and positively charged particles include cation – anion interaction, cation – dipole interaction, hydrogen bonding and van der Waals forces. The attachment of nanoparticle to the rock grain surfaces is governed by electric double layer force, and the interaction energies between rock grain surfaces and nano particles are explained by using DLVO (Derjaguin-Landuaverwey-Overbeek) theory (Hock et al, Guzman et al,2006, Rodriguez et al, 2011). DLVO theory explains the aggregation of aqueous dispersion quantitatively and describes the forces between charged surfaces interacting through a liquid medium. It combines the effects of the Van der Waals attraction and the electrostatic repulsion due to the so-called double layer of counter ions. The electrostatic part of the DLVO interaction is computed in the mean field approximation in the limit of low surface potentials – that is, when the potentials energy of an elementary charge on the surface is much smaller than the thermal energy scale. Fluid velocity, salinity, particle size and water saturation are some of the factors affecting transport and retention of nanoparticles.

II. METHODOLOGY

A series of experiments were conducted to determine the concentration of hydrophobic silicon oxide nanoparticles, the mass of ethanol, density and PH of nanofluids (nanoparticle dispersed in ethanol and in KCL). Zeta potential of the nanofluid (nanoparticle dispersed in ethanol) was obtained from Smoluchowski's equation.

A. Materials and Experiments

The main materials used for this work were glass beads which represent the sand in the formation (sometimes sand instead of glass beads will be mentioned during the course of this project), kaolinite which serves as fines, different concentrations of nanoparticles - hydrophobic silicon oxide (it has no affinity for water), Potassium chloride, KCl, ethanol and water. Each of the last three substances was used as dispersing fluids to saturate the glass beads. The essence of using different dispersing fluid in the experiment was to find out which of them will most effectively enhance the performance of the nanoparticles in trapping migrating fines in glass beads and also to determine which fluid dispersant has the lowest PH. The nanoparticles were mainly selected based on literature reviews, geologic findings and previous studies of some of these compounds. Each concentration of nanoparticles used was dispersed in each dispersing fluid and the trapping capacity of the nanoparticles was evaluated.

B. Parameters and Calculations

➢ *Definition of Terms*

q = flow rate (cm^2/s)
p = pressure (psi) = **ρ**gh
μ = Viscosity (cp); a constant viscosity of 3centipoise was used
K = Permeability (cm^2)
A = area of the core (cm^2)
g = gravity of the fluid in the core (cm/s^2)
ξ = Zeta potential of the fluid (mv)
ρ = fluid density (g/cm^3)
ξ_0 = permittivity of free space = $6.94257 \times 10^{-12} C^2 N^{-1} m^{-2}$
ξ_r = relative dielectric constant = 80.1
r = radius of nanoparticles (cm) = 20×10^{-11}cm
k = Debye screening length (cm) = (9.6×10^{-11}cm) is a measure of the diffused ionic double layer thickness that surrounds charged surfaces in aqueous system. It can also be obtained mathematically with the equation below:

$$k = \sqrt{\frac{e^2 \Sigma n_i z^2}{\varepsilon_r \varepsilon_o k_B T}} \qquad (1)$$

K_B = Boltzmann's constant
e = charge on an electron = 1.6×10^{-19}C
z = valency of an ion
n = number of concentration of an ion
T = temperature (298K)

➢ *Equations, Data and Calculations*

The zeta potential is calculated by modified SMOLUCHOWSKI EQUATION.

$$\text{Mobility} = \frac{4\pi\varepsilon_0\varepsilon_r\,\xi(1+kr)}{6\pi\mu} \qquad (2)$$

$$\text{From Darcy's law } q = \frac{KAP}{\mu h} \qquad (3)$$

Since k/μ = mobility of the fluid, then we equate it with equation (1). The modified equation is then given as

$$\xi = \frac{6\mu q}{A\rho g 4\varepsilon_o\varepsilon_r(1+kr)} \qquad (4)$$

h = thickness of the core (cm)
Diameter of the core = 2.632cm
Length of the core = 19cm

$$\text{Bulk volume} = \frac{\pi d^2}{4} l$$

$$= \frac{3.142 \text{ x } 2.632^2 \text{ x } 19}{4}$$

$$= 97.95 cm^3$$

$$Permeability = \frac{Porosiity \times radius^2}{8}$$

$$= \frac{0.1882 \times 1.3365^2}{8} = 0.042 cm^2$$

$$Area\ of\ the\ core = \frac{\pi d^2}{4}$$

$$Area\ of\ the\ core = 5.4414 cm^2$$

$$\xi = \frac{6\times3\times7}{5.4414\times60\times8.126\times980\times4\times6.94257\times10^{-12}\times80.1(1+9.6\times10^{11}\times20\times10^{-11})}$$

$$\text{Zeta potential at 0.5gram} = 1.128 mv$$

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III. RESULTS AND DISCUSSIONS

Amongst the three fluid experimented, ethanol gave the best result. It has been observed that ethanol improves permeability in sand and probably, the improved permeability allowed relatively large quantities of fines to flow through the sand pores and get trapped along the way by the atomic sizes of hydrophobic silicon oxide nanoparticles distributed through the sand pores.

Worthy of note is the fact that very small amount of nanoparticles could trap relatively large amount of fines. The pore volume used during the experiment was 19.0ml. With hydrophobic silicon dispersed in ethanol, 0.5g of nanoparticles trapped about 17.58g of fines. Actual results can be better since pore blockage did not allow the full capacity of fines trapping to be explored. This emphasizes how effective hydrophobic silicon oxide nanoparticles can be in trapping migrating fines in sand.

The pH values of hydrophobic silicon oxide dispersed in distilled water could not be ascertained because hydrophobic silicon oxide lacks affinity for water. From this result, distilled water was able to trap a relatively small amount of fines. Permeability was a serious encounter when water was injected into the porous media. When 30g/L of KCl was used, it was discovered that the pH values of the fluid dispersant was relatively high compared to when ethanol was dispersed in nanoparticles. Since the pH value is relatively high, the zeta potential will definitely be quite low. Permeability problem was not encountered during flooding but the mass of fines trapped was relatively low compared to when ethanol was used as a dispersing fluid

Conc. of nanoparticles (g)	Mass of nanofluid (g)	Density of nanofluid (g/cm^3)	pH of nanofluid	Zeta potential of nanofluid (mv)
0.5	568.823	0.8126	6.10	1.128
1.0	569.323	0.8133	6.40	1.125
1.5	569.823	0.8140	6.65	1.122
2.0	570.323	0.8148	6.68	1.120
2.5	570.823	0.8155	7.10	1.118

Table 1:- Properties of Hydrophobic Silicon Oxide Nanoparticles and Nanofluid (Nanoparticles Dispersed in Ethanol)

pH of nanoparticle dispersed in water	pH of nanoparticles dispersed in KCL
X	7.12
X	7.30
X	7.56
X	7.70
X	7.90

Table 2:- PH Values of Nanofluid (Using Distilled Water and 30g/L of KCl)

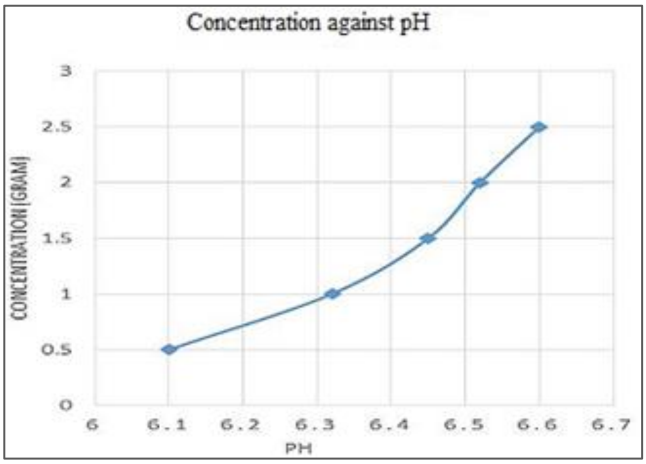

Fig 1:- A Graph of Concentration Against pH

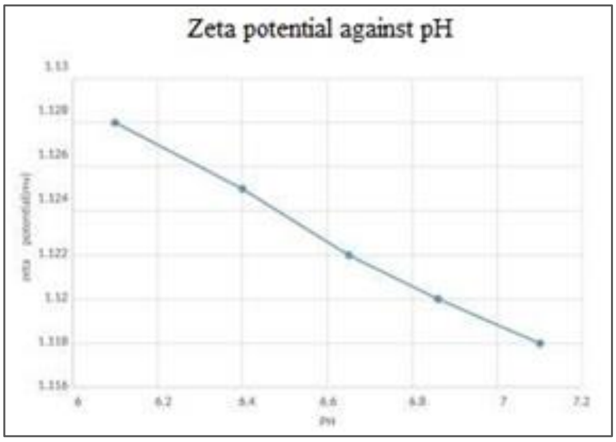

Fig 2:- A Graph of Zeta Potential Against pH

From the graph above (fig 1), it can be seen that even small concentration of nanoparticles can trap a relatively large amount fines. The concentration of nanoparticles also affects the pH of the nanofluid and subsequently affects the zeta potential of the nanofluid. The smaller the concentration of hydrophobic silicon oxide nanoparticles, the more effective it helps in trapping fines. The dependence of nanoparticles retention on pH is not only due to the electrostatic forces between nanoparticles and rock grain surfaces but also due to the nanoparticle size and other characteristics of the particle.

There is a common relationship between pH values and zeta potential. It has been observed that zeta potential increases with a decrease in pH values. High pH values give relatively low zeta potential, while low pH values give high zeta potentials. It can be seen from figure 2 below that a pH value of 6.1 will give very high zeta potential, implying that the stable colloidal particles will repel each other strongly thereby giving no traces of agglomeration.

IV. CONCLUSION

From the experimental results, ethanol containing silicon oxide was able to trap a relatively large quantity of fines compared to other fluids like distilled water. Nevertheless, the reference experiment where only ethanol was used did not trap a significant quantity of fines. This implies that the presence of silicon oxide in ethanol enhanced the capacity of the fluid to trap clayey fines. Cation-dipole interaction between the clays, ethanol and nanoparticles oxides is speculated to have contributed significantly to the enhancement of fines trapping in addition to cation-anion interaction. Since ethanol has a functional group O-H with a negative charge, the presence of other forces like cation-anion interaction, hydrogen bonding must have contributed to trapping of fines.

In trapping migrating fines in sand and preventing further migration, two or more electrostatic forces of adsorption must be operative. Even though one particular force might dominate in a system, it does not rule out the existence of other forces. Using KCl as nanoparticles dispersant for silicon oxide, the dominating force of adsorption in the system trapping and holding down the clays or fines will probably be the cation-pi interaction. This does not mean other forces are not in operation during aggregation. This means that the total strength that trap and prevents fines from further migration using nanoparticles dispersed in various fluids could be the contribution of the various intermolecular forces of attraction. The conclusions that have been made from this study are as follows: three primary fines trapping mechanism in the use of nanofluid to control migrating fines in sand are pH values of the nanofluid, zeta potential and electrostatic forces of adsorption. The electrostatic forces of adsorption that adhere fines to sand grains are cation-anion interaction, cation-dipole interaction, Van der Waals forces etc. Two or more electrostatic forces could be in operation in a system to trap and hold down fines from migrating even though a particular force could be dominating. The likely dominant interacting forces for the use of high concentration potassium chloride, ethanol is cation-anion interaction, cation-dipole interaction and also Van der Waals forces. Hydrophobic silicon oxide nanoparticles of small concentration tend to be effective in trapping large amount of migrating fines in sand because of its relatively low pH values in aqueous dispersants.

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