

Optimizing graphene nanoplatelets (GNPs) dispersion for improved scale inhibitor squeeze treatment

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Abstract. The formation of mineral scale has been a major nuisance in oil field operations as it leads to multifarious flow assurance issues. Conventional squeeze treatment commonly employed to inhibit detrimental scale formation lacks in various aspects to effectively mitigate it thereby making this treatment less effective and at times unviable as production operations are moving into deeper and tighter formations. Employing nanotechnology to improve the efficiency of squeeze treatment is presented in this paper by the formulation of high and stably dispersed of Graphene Nanoplatelets (GNPs) nanofluid that can render high active surface area for PPCA scale inhibitor chemical to effectively non-covalently adsorb to the highly dispersed GNPs platform. GNPs dispersion is characterized and measured using UV-Vis spectrophotometry analysis by the parameter of percentage extractability. The concentration of 40mg/L of GNPs corresponds to the highest value of 40% extractability that depicts optimum concentration of GNPs for its highest dispersion. The presence of benzene ring in Triton X-100 surfactant molecular scheme acting as a dispersing agent has proved to be the dominant factor that promotes strong bonding between the surfactants hydrophobic tail with GNPs surface creating sufficient steric hinderance thereby giving high and stable GNPs dispersion. Furthermore, sonication process is essential for effective GNPs dispersion process.

Introduction

Scale formation and deposition in the reservoir rock matrix is a common flow assurance predicament that leads to multiple problems during hydrocarbon production. Scale mineral is formed by precipitation due to chemical reactions as ions that are dissolved in produced water react with each other to form an insoluble solid [1]. The driving forces that are responsible for scale formation are changes in temperature, pressure, alkalinity and incompatible mixing of formation and sea water as oil and gas fields use sea water or brine injection for pressure maintenance and for primary/secondary oil recovery [1-2]. Brine is the primary cause of calcite and sulfate scales. The most common types of scales witnessed are sulfates and carbonates scales of calcium, barium and strontium [1-3]

Uninhibited scale formation and its subsequent deposition in the reservoir formation is problematic for oil and gas operations that adversely affecting its economy. Solid scale deposition in the producing reservoir matrix can lead to irrevocable permanent formation damage by building-



up in the near well-bore region plugging reservoir pore throat and perforations thereby eventually cutting-off production. If not remediated, continuous scale deposition can lead to permanent formation damage as shown in Figure 1.0. Scale build-up can narrow down or completely choke production tubing and flow lines. Pipeline plugging due to scale deposition can result in drastic hike in operational pressure drop thereby reducing well productivity which is economically unwarranted and pose acute safety hazard in oil field operations [4]. It may also lead to perilous scenarios by interfering with running and operation of downhole equipment which can cause equipment damage leading to operational failure [4-5]. Scale formation also gives impetus to corrosion phenomenon.

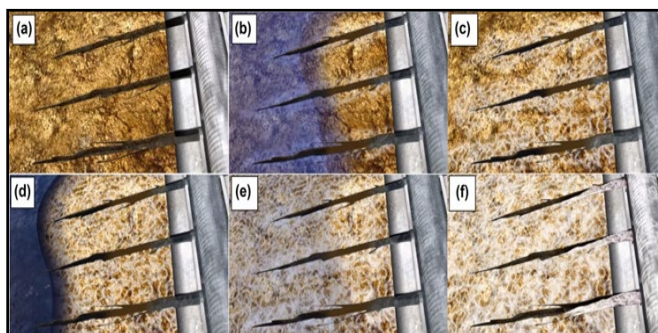


Fig 1 Scale deposition process (a-f) in the near wellbore region depicting formation damage [5]

Scale removal is a common well-intervention operation with a wide range of mechanical, chemical and scale inhibitor treatment options. There are various scale inhibitor delivery methods such as continuous injection of scale inhibitor chemical into the well bore via macroni string, injection into the gas lift system [6] and slow dissolution of the inhibitor chemical placed in rat hole [7-8], but the most commonly used and effective method for scale control is scale inhibitor squeeze treatment [9].

Downhole conventional squeeze treatment employed in many reservoirs use acid phosphonate inhibitors and various types of polymers [10]. In this technique, commercial scale inhibitor chemical solution such as Phosphino polycarboxylic acid (PPCA) [11] is pumped downhole (squeezed) at high injection pressures in order to partially adsorb by temperature activated precipitation onto the reservoir rock followed by 12 to 24 hours well shut-off. The adsorbed and retained chemical on the reservoir rock acts as a scale inhibitor chemical storage as shown in Figure 2.0.

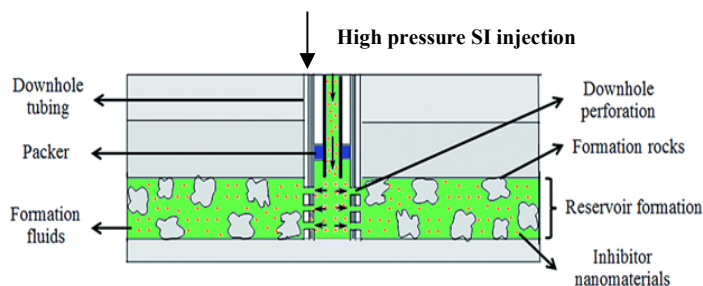


Fig 2 Scale inhibitor (SI) injection in downhole region [12]

During production, flow of reservoir formation water desorbs and dissolves this adsorbed inhibitor chemical which flows into the production and distribution system to inhibit scale formation process. Scale inhibitor chemical adsorption and retention onto the producing formation rock is of paramount importance which determines the effectiveness (success) of the employed squeeze treatment. Squeeze treatment 'lifetime' can be defined as the volume of water produced by a well before the adsorbed scale inhibitor concentration dwindles below the critical threshold

concentration value referred as minimum inhibitor concentration (MIC) or minimum effective dose (MED) [13-14]. Scale inhibitor concentration below MIC/MED makes it incapable to prevent or mitigate scale formation phenomenon.

Squeeze treatment is an exorbitant process that requires large volumes of chemical with powerful pumping requirements for its injection into the reservoir. Well must be shut-off for about 12-24 hours which causes production loss and consequently translates into lesser revenue generation. In addition, due to high injection pressures, a significant quantity of scale inhibitor chemical is lost due to vaporization into the permeable reservoir formation matrix. The efficiency of squeeze treatment needs to be improved by enhancing the adsorption and retention of the chemical onto the producing reservoir rock [4-15].

In light of recent interest in nanotechnology application in oil and gas industry, research efforts are being oriented towards exploring the role of nanomaterials to improve and enhance conventional squeeze treatment process widely applied for scale control [16]. By analysing the adsorption potential of conventional squeeze treatment, it can be deduced that lack of availability of active surface for scale inhibitor chemical adsorption is one of the primary reasons for lower efficiency with short squeeze lifetimes. Furthermore, weak interactive bonding between the scale inhibitor chemical molecules and reservoir rock surface is also mainly responsible for premature inhibitor flush-out when water starts to leach out of the reservoir matrix at certain flow rates. In order to effectively inject nanomaterial into the reservoir to mitigate the negative outcomes and improve conventional squeeze treatment, formulation of highly stabilized GNPs nanofluid is proposed. GNPs nanofluid should be resistant to agglomeration and flocculation which can be achieved by adopting an effective dispersion strategy by optimally dispersing GNPs into the solvent solution.

Graphene Nanoplatelets (GNPs)

GNPs are nanoparticles with an average thickness of 3-10 nm that are comprised of short stacks of platelet-shaped graphene sheets in a planar form shown in Figure 3.0. They are good conductors of heat and electricity. Hydrogen or covalent bonding capability can be added through functionalization at sites on the edges of the platelets. Due to their unique nanoscale size, shape and composition material, they can be used to improve properties of a wide range of polymeric materials and composites. They are emerging as a multi-dynamic coating material rendering high surface area for various applications [17].

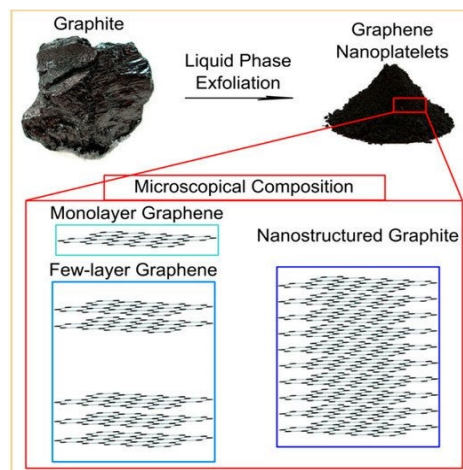


Fig 3 Schematic of the manufacture of GNPs starting from natural graphite [17]

Materials and Methods

Materials

GNPs were procured in powder form from Sigma Aldrich. Triton X-100 and PPCA were supplied by Merck. Probe Sonicator (model: Q-Sonica 500 with 12mm probe diameter) was used to mechanically disperse the GNPs nanofluid solution. Ultra-visible (UV-vis) spectrophotometer (model: Shimadzu UV-1900) was used to determine concentrations of the prepared solutions.

Preparation of dispersed GNPs nanofluid

Highly dispersed GNPs enable to formulate stabilized nanofluid that offer high active surface area to chemically bind scale inhibitor chemical for enhanced squeeze treatment along with superior rheological characteristics for its injection into the reservoir. GNPs are not readily soluble and flocculate in PPCA scale inhibitor solution as shown in Figure 4.0

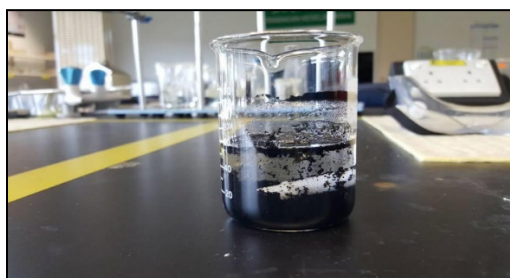


Fig 4 GNPs flocculation in PPCA solution

In order to determine optimum GNPs concentration for maximum dispersion, three concentrations of at 30, 40 and 50 mg/L GNPs labelled as sample A, B and C respectively were prepared in 18 MΩ cm deionized water while the concentration of Triton X-100 was kept constant at 5ml/L. These prepared solutions were sonicated for 10 mins for homogenous mixture of the components and was left static under the influence of gravity for 24 hours for any unfunctionalized and undispersed GNPs to precipitate and settle at the bottom of the beaker. Table 1 shows concentrations of A, B and C prepared samples.

Table 1 Concentration of GNPs prepared solutions

Sample	GNPs	Triton X-100
A	30mg/L	5ml/L
B	40mg/L	5ml/L
C	50mg/L	5ml/L

Characterization of GNPs dispersion

UV-Vis Spectroscopy

The dispersions of GNPs by Triton X-100 surfactant were characterized using UV-Vis spectrophotometry operating between the range of 200 to 800nm. To characterize the dispersion and measure the concentration of GNPs in a dispersed format, UV-Vis spectroscopy absorbance values were recorded at 650nm wavelength at which Beer-Lambert law is well obeyed as reported in previous studies [18-19].

Probe Sonication

Mechanical technique of sonication is applied to the prepared solutions for 10 mins to homogeneously dispersed GNPs into the solvent solution. High shear force created by ultrasonic cavitation breaks-up molecular agglomeration by overcoming Van der Waals forces of attraction.

Results and Discussion

Percentage (%) Extractability

Bundled GNPs are not active in the UV-Vis region and only individual GNPs absorb in this region. The degree of GNPs dispersion in a solution can be evaluated by the parameter of percentage extractability [20] which can be calculated as:

$$\% \text{ extractability} = c_1/c \times 100 \quad (1)$$

Where c_1 = concentration of GNPs recovered in solution (after dispersion) and c = original concentration of GNPs initially added in the solution to be dispersed.

Nanomaterial dispersion depends on the dispersing power of the dispersing agent such as surfactant, solution, sonication process and concentration of nanomaterial. Characterization of GNPs in Triton X-100 surfactant solution using UV-Vis spectroscopy is performed by recording the absorbance value for each dispersed GNPs solution at wavelength of 650nm as shown in Figure 5.0. Absorbance in the wavelength range till 380nm is deliberately ignored due to the presence of turbulence in the dispersed GNPs solution [21-22]. Therefore, it is cogent to take the absorbance at the wavelength of 650nm as the solution is at relative stability and the Beer-Lambert law is well obeyed by GNPs as absorbance is minimally affected by the ambient conditions of GNPs. The absorbance value for each GNPs is shown in Table 2.0.

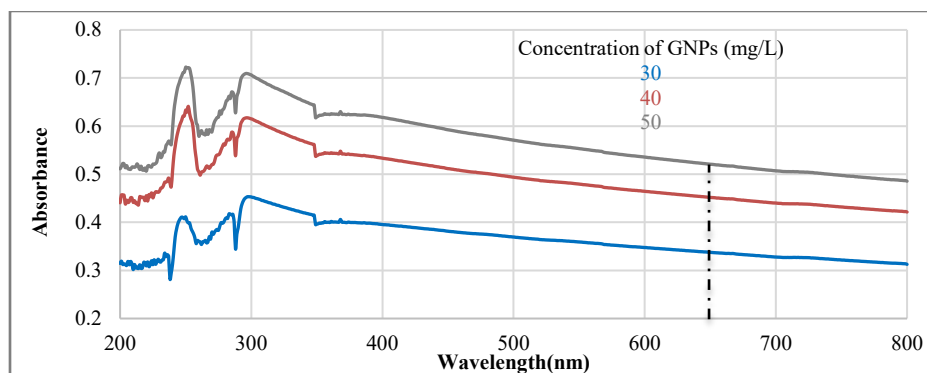


Fig 5 depicts UV-Vis spectra of GNPs with varying concentrations of GNPs in Triton X-100 surfactant solution

Table 2 Absorbance value for each graphene nanoplatelets concentration

Concentration (mg/L)	Absorbance
30	0.33
40	0.45
50	0.52

The correlation between absorbance and GNPs solution can be developed by plotting straight line graph validating assumption of Beer-Lambert law as shown in Figure 6.0.

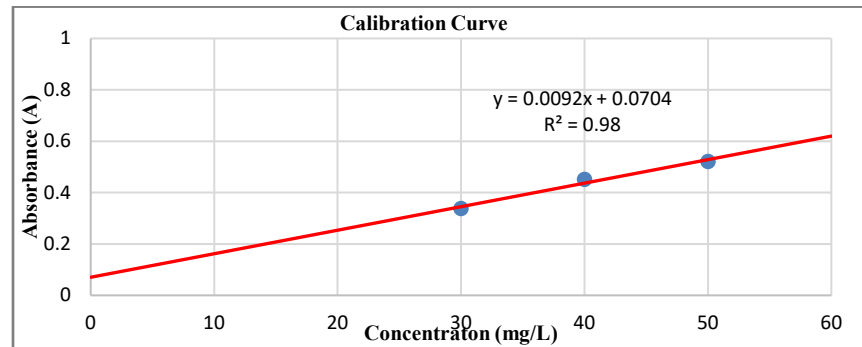


Fig 6 Absorbance vs Concentration correlation based on Beer-Lambert law

From this above graph, the concentration of a sample can be determined from its absorbance value by simple interpolation method. This is done by drawing a horizontal line from the y-axis (sample's absorbance) until it intersects the best fit line. Then a vertical line is drawn from that point to the x-axis. The x-axis value is the concentration of the sample. Absorbance using Beer-Lambert law can be defined by equation (2)

$$A = \epsilon l c_1 \quad (2)$$

where **A** = absorbance value of GNPs, ϵ = specific extinction coefficient of GNPs at 650nm, **l** = cuvette path length (constant value of 1.0) and **c₁** = concentration of GNPs after dispersion.

From equation, concentration of GNPs after dispersion (**c₁**) is calculated which is used to evaluate % extractability values for each GNPs nanofluid solution as shown in table 3.0. The calculated % extractability concentration vs concentration follows a Gaussian trend as shown in Figure 7.0 that depicts a linear increase with increase in GNPs concentration until a maximum extractability limit is achieved. This limit is presumably the optimum amount of Triton X-100 surfactant to sufficiently coat the GNPs surface in a homogenous manner thereby rendering its highest dispersion. Decrease in % extractability at higher GNPs concentration indicates presence of insufficient Triton X-100 surfactant to effectively disperse GNPs. Also, this decrease indicates agglomeration of GNPs as higher GNPs concentration giving rise to the presence intrinsic Van Der Waals forces of attraction. The highest dispersion of GNPs solution was shown to be at 40mg/L followed by a sharp decline at 50 mg/L as shown in Figure 7.0. Figure 8.0 shows homogeneously dispersed stable GNPs solutions left under the influence of gravity for 48 hours.

Table 3 %Extractability and Absorbance values of GNPs concentrations

Concentration (mg/L)	Absorbance	%Extractability
30	0.33	39
40	0.45	40
50	0.52	36

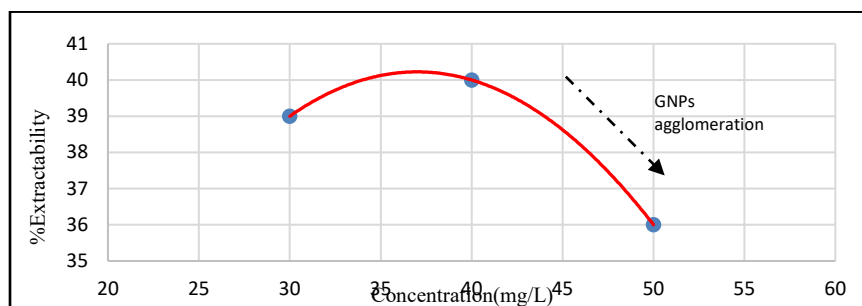


Fig 7 % extractability vs concentration trend of GNPs

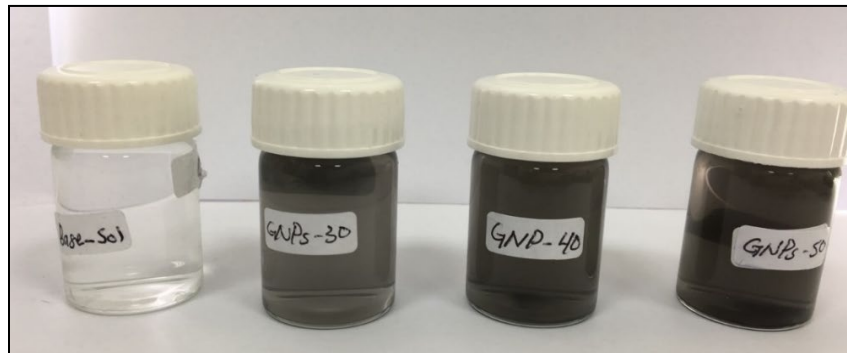


Fig 8 Different concentrations of GNPs dispersed stable solutions

Conclusion

These preliminary results demonstrate that surfactant molecules generally orient themselves in such a manner that their hydrophobic tail attaches with the GNPs surface while their hydrophilic tail bonds with the aqueous phase thereby reducing GNPs/water interfacial tension. The parameter of % extractability is a reliable measure that depicts the degree of dispersion of a solution. The concentration of 40mg/L GNPs gives the highest % extractability value of 40 depicting the best and stable dispersion of GNPs solution. Further increase in GNPs concentration leads to its agglomeration. The dispersing power of the surfactant depends on its bonding strength with the GNPs surface and thus creating sufficient steric hinderance [20] that can overcome the agglomeration potential of GNPs due to the presence of Van Dar Waals forces of attraction therefore rendering high degree of stable nanomaterial dispersion. The presence of benzene ring structure in Triton X-100 surfactant is a dominant factor that adsorb more firmly to the graphitic surface of GNPs due to $\pi - \pi$ stacking type interaction. In conclusion, the dispersing power of surfactant is inherent that mainly depends on its chemical structure organization.

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