



# APPLICATION OF SILICON OXIDE AND ALUMINIUM OXIDE NANOPARTICLES FOR HYDRATE PREVENTION AND CONTROL IN SUBSEA PIPELINES DURING HYDROCARBON PRODUCTION

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**Abstract:** Hydrate formation in subsea pipelines poses significant challenges to flow assurance and operational safety. This paper takes a look at gas hydrate inhibition in a simulated offshore environment using silicon oxide nanoparticles and aluminium oxide nanoparticles as inhibitors. The essence of this work is to compare the effectiveness of silicon oxide nanoparticles and aluminium oxide nanoparticles for hydrate inhibition. Experiments were conducted using a mini flow loop. It will involve mitigating hydrate formation using varying weight percentages of the inhibitors (0.01wt%, 0.02wt %) and then evaluate their effect on hydrate inhibition in the mini flow loop. Sensitivity charts for pressure, temperature and time both nanoparticles were made. From the analysis, 0.01 weight percentages of silicon oxide nanoparticles has close match with 0.01 weight percentage of aluminium oxide nanoparticles, and 0.02 weight percentage silicon oxide nanoparticles showed better inhibitory capacity than aluminium oxide nanoparticles of 0.02 weight percentage.

**Keywords:** Gas hydrate, silicon oxide nanoparticles, aluminium oxide nanoparticles, simulated offshore environment

## I. INTRODUCTION

The oil and gas industry is one of the most critical industries in the world, responsible for producing the majority of the energy that powers our daily life operations. Subsea pipelines play a critical role in this industry, facilitating the transportation of hydrocarbons from offshore fields to onshore facilities Rajaei et al., (2019). However, a persistent challenge in subsea pipeline operations is the formation of gas hydrates, which are ice-like crystalline structures that develop when natural gas or other hydrocarbons combine with water under specific high-pressure and low-temperature conditions Sloan Jr. et al.,(2003). These hydrates can accumulate and obstruct the pipeline, leading to significant production losses, expensive maintenance costs, and even catastrophic failures Kumar et al., (2019). For hydrate to form there has to be the presence of water, hydrate formers such as methane, ethane, propane, butane and also nitrogen, non-hydrocarbons like carbon dioxide (CO<sub>2</sub>) and hydrogen sulphide (H<sub>2</sub>S), low temperatures (0 to -40° C or 32 to 104<sup>0</sup>F) and high pressures (>200psig) Sloan, (2003). The formation of hydrates in subsea pipelines was first recognized as a challenge in the late 1960s. Initial reports from experimental studies highlighted the potential for hydrate formation and deposition in pipelines transporting deepwater hydrocarbons. Various investigators have worked on predicting hydrate formation conditions so as to avoid natural gas hydrate problems (NGH). They include but are not limited to Elgibaly et. al (1998) that presented a comprehensive neural network model for predicting hydrate formation conditions for various pure gases, gas mixtures and different inhibitors. The model was trained using 2387 input-output patterns collected from different reliable sources. The predictions were compared to existing correlations and real experimental data. Efforts to detect and monitor hydrate formation in subsea pipelines led to the development of various technologies. Acoustic monitoring, pipeline pigging with hydrate sensors, subsea temperature, and pressure monitoring systems were introduced to provide real-time data on hydrate formation risks. Yang, X., (2020). Oduola et.al (2017),

carried out design fabrication and validation of a 39.4- inch(12m) long laboratory flow loop made of 0.5inch 316 stainless steel pipe enclosed in a 4-inch PolyVinylChloride (PVC) skid mounted and fitted with temperature and pressure gauges, mixing vessels ( gas and inhibitor) and natural gas cylinder for hydrate studies. The loop was able to predict hydrate formation adequately and has been used in screening and selecting Kinetic Hydrate Inhibitors (KHIs). In all of these, synthetic chemicals in were used.

Traditional methods to prevent hydrate formation, such as chemical inhibitors and thermodynamic control, have their limitations. Therefore, there is a need for alternative methods to prevent hydrate formation in subsea pipelines. This work seeks to use silicon oxide nanoparticles and aluminium oxide nanoparticles as gas hydrate inhibitors.

The term nanoparticle refers to extremely small particles. Silicon oxide nanoparticles (SiO<sub>2</sub> NPs) have gained significant attention in recent years as a potential solution for hydrate prevention in various industries. SiO<sub>2</sub> NPs, also known as silica nanoparticles, are composed of silicon and oxygen atoms arranged in a regular lattice structure.

Firstly, their large surface area to volume ratio provides an enhanced adsorption capacity, allowing them to absorb and store large amounts of gas molecules. This adsorption capability helps in reducing the gas concentration in the surrounding environment, thus preventing the formation of hydrates.

Furthermore, silica nanoparticles exhibit excellent stability and dispersion in aqueous systems, making them suitable for various applications in hydrate prevention. They can be easily dispersed into fluids and added to pipeline systems, where they disperse evenly and create a barrier between gas molecules and water, hindering hydrate formation. Their stability ensures long-term efficiency and performance, making them a valuable solution for hydrate prevention.

Additionally, silica nanoparticles can act as flow assurance additives, improving the flow properties of fluids and reducing viscous effects. This property is particularly beneficial in preventing hydrate formation in pipelines and equipment, as it enhances the dispersion of gas molecules and minimizes their aggregation.

Zhang et al. (2017) explored the use of functionalized silica nanoparticles as a hydrate inhibitor. By modifying the surface of silica nanoparticles with hydrophobic moieties, they achieved improved adsorption capacity and stability, leading to a more effective prevention of hydrate formation. Aluminium oxide nanoparticles, also known as alumina have gained attention for their potential application in hydrate inhibition. These nanoparticles exhibit stability, high surface reactivity, and tunable surface properties through surface modification techniques (Yang et al 2021).

Nanoparticles are typically less toxic and have lower environmental impact compared to chemicals such methanol and glycols (Fattah et al 2020). The high surface area-to-volume ratio of aluminium oxide nanoparticles allows for increased contact with gas and water molecules, enhancing their adsorption and interaction at the gas-water interface (Fattah et al 2020). This increases interfacial interaction can disrupt the formation of hydrate crystals and hinder their growth, effectively inhibiting hydrate formation. The surface properties of aluminium oxide nanoparticles can be tailored through surface modification techniques, such as functionalization and coating, to improve their performance as hydrate inhibitors (Yang et al 2021). Fourier Transform Infrared Spectroscopy (FTIR) showed the presence of tannins, and alkaloids (with functional groups containing nitrogen, oxygen and carbon) with aromatic rings. The presence of flavonoids, tannins, saponins and alkaloids in silicon oxide and aluminium oxide nanoparticles contributes to its ability to inhibit hydrates just like conventional alcohols methanol and glycols.

## **II. MATERIALS AND METHOD**

The materials used include compressed natural gas (CNG) with specific gravity of 0.5, having 98.44 mole percent methane and 1.50 mole percent carbon dioxide, water, ice blocks, silicon oxide nanoparticles and aluminium oxide nanoparticles. The equipment used is a Mini Hydrate Flow Loop ( Odutola et. al, 2017).

The Mini flow loop is presented in plate one and plate two shows the hydrate flow loop process diagram. The loop is approximately 39.4 inches (12m) long, made of 316 stainless steel of 0.5-inch internal diameter encased in a skid mounted amaflex insulated 4 inch Polyvinylchloride (PVC) pipe. It has a control panel housing the three switches that control the whole process with a Refrigerating unit which is used to actually simulate the offshore environment. It has three pumps, five pressure gauges and three temperature gauges with two differential pressure gauges including a manual pump. It also has an inhibitor or mixing vessel, a CNG bottle that can withstand pressure up to 100 bar (1450 Pisa). It has a visual flow meter which indicates how the fluid flows (Odutola et.al, 2017).

Plate1-hydate mini flow loop ( Odutola et.al, 2017)

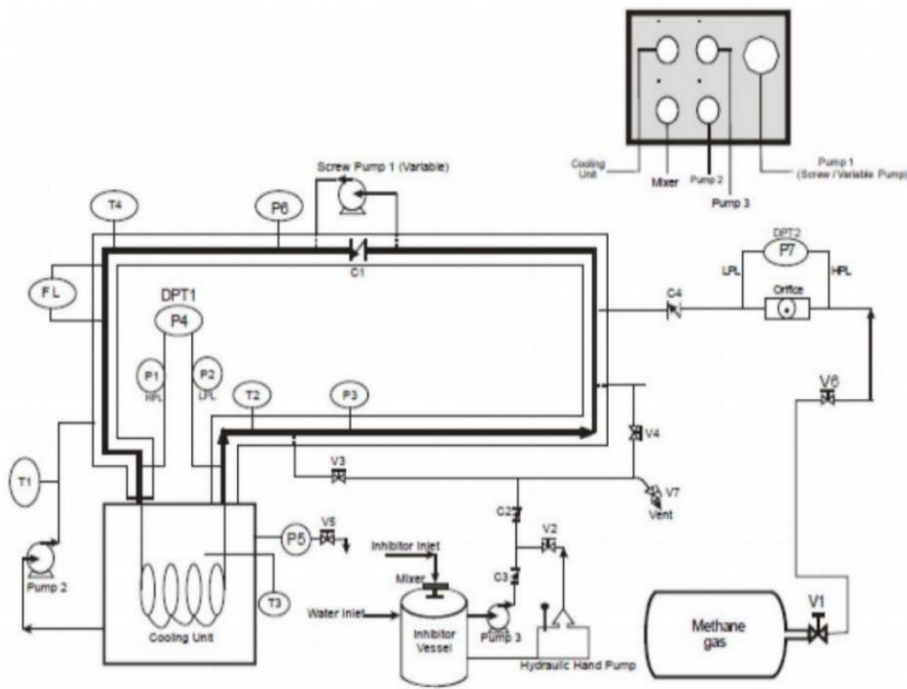


Plate 2- Schematic diagram of mini hydrate flow loop (Odutola et. al, 2017)

**III. EXPERIMENTAL PROCEDURES**

The control panel is connected to the power source and the system is flushed with ordinary water to ensure that the loop is free from debris and/or rust. Water is poured into the inhibitor vessel and Pump 3 is switched on from the control panel. Water is then drawn into the loop by opening Valve 4 until the pressure of 25 psi is attained. The valve is closed and Pump 3 switched off. The water is then vented out through Valve 6, 5 or 7. The process is repeated for three or four times. To begin the experiment, about 2900ml of water was measured and put into a mini transparent bucket, then 0.3g of silicon oxide nanoparticles and aluminium oxide nanoparticles was poured that was earlier mixed in 100ml of water and agitated, making sure that the nanoparticles were properly mixed and none settled at the bottom after doing this, the solution was poured into the mixing chambers which is also known as the inhibitor Vessel.

The CNG tank is turned on via Valve 1, then Orifice and Valve 6 is opened to build the pressure up to 150 Pisa, after which the valves and Orifice are closed. Pump 2 is turned on to draw water into the refrigerator and allow water to circulate in the PVC pipe. Pump 1 is turned on after pump 2 (that is after circulation is achieved via Pump 2 as earlier explained) and is set at 150V or 250ft<sup>3</sup>/hr. to cause agitations in the loop. The initial temperature and pressure are recorded. Ice blocks are added into the refrigerator (about 0.7m of the 0.5-inch pipe is a spiral loop immersed in cold water in the refrigerator) to facilitate the cooling process.

Adding ice blocks to the refrigerator serves as a means to maintain a consistently low temperature in the loop, specifically to simulate and sustain conditions where hydrate formation is most likely to occur. In the experimental setup, hydrate formation is highly dependent on temperature.

By lowering the temperature, we created an environment where the water in the pipeline is more prone to forming hydrates. This is because hydrates are crystalline structures that form when water molecules bind together in a lattice-like pattern at low temperature.

This step is crucial because;

**Mimicking Subsea Conditions:** Subsea pipelines are often exposed to very cold temperatures, especially at great depths. By adding ice blocks, you're creating an environment that replicates the extreme cold conditions that pipelines might experience in the deep sea.

**Enhancing Hydrate Formation Potential:** The low temperature encourages water molecules to come together and form hydrate crystals. This is crucial for the experiment, as we want to observe how effective the SiO<sub>2</sub>-NPs and AL<sub>2</sub>O<sub>3</sub> NPs can inhibit the formation of hydrates.

**Controlled Experimental Conditions:** By using ice blocks, we are able to control and maintain a specific low temperature throughout the experiment. This ensures consistency and allows for accurate measurements and observations.

**Retention Time in the Coldest Part:** The spiral loop immersed in cold water in the refrigerator serves to increase the retention time of the fluid in the coldest part of the loop. This is important because hydrates are more likely to form in the coldest areas.

The different readings for temperature, differential pressure, and pressures are noted down at an interval of two minutes for two hours throughout the duration of the experiment, which is 120 minutes. Recall that the loop has three temperature meters, five pressures Meter including the differential pressure meter.

The above step was repeated for 0.6g and 0.9g of silicon oxide nanoparticles and aluminium oxide nanoparticles respectively. The experiments were conducted using a mini hydrate flow loop, with a total of two analyses using different concentrations of silicon oxide nanoparticles (0.01wt%, 0.02wt%), and two analyses using different concentrations of aluminium oxide nanoparticles (0.01wt%, 0.02wt%). The presence of hydrates was indicated by a rapid decrease in loop pressure at a low temperature, sudden rise in differential pressure, and signs such as a plugged ¼ inch pipe at the sample test point and changes in effluent colour.

#### **IV. RESULTS AND DISCUSSIONS**

The various plots used for the analysis are: plot of pressure and temperature versus time for 0.01wt%, 0.02 wt% of silicon oxide nanoparticles and aluminium oxide nanoparticles (figure 1,figure 2, figure 3 and figure 4 ). These plots help to ascertain the formation of hydrate and how hydrates are inhibited in the laboratory mini flow loop.

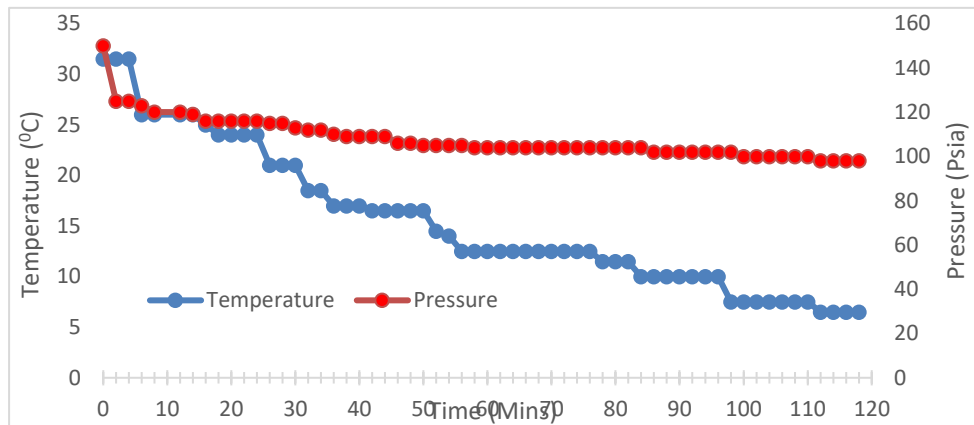


Figure1: Temperature and Pressure versus Time for 0.01wt% silicon oxide.

The lower pressure levels observed indicate delayed hydrate formation, corroborating the inhibitory effect of the nanoparticles. Figure 1 and figure 3 further shows a noticeable delay in the onset of hydrate formation for both nanoparticles. This indicates that even at a relatively low concentration, both nanoparticles have an inhibitory effect on hydrate formation.

The differential pressure ( $P_4$ ) was relatively constant till the end of the experiment. The pressure ( $P_1$ ) reduced from 150psia to 98psia in two hours. While ( $P_2$ ) reduced from 150psia to 95psia .

For the various weight percentages compared, 0.01wt% of silicon oxide nanoparticles and aluminium oxide nanoparticles has a close match. At 0.02wt%, silicon oxide nanoparticles had better inhibitory capacity than aluminium oxide nanoparticles.

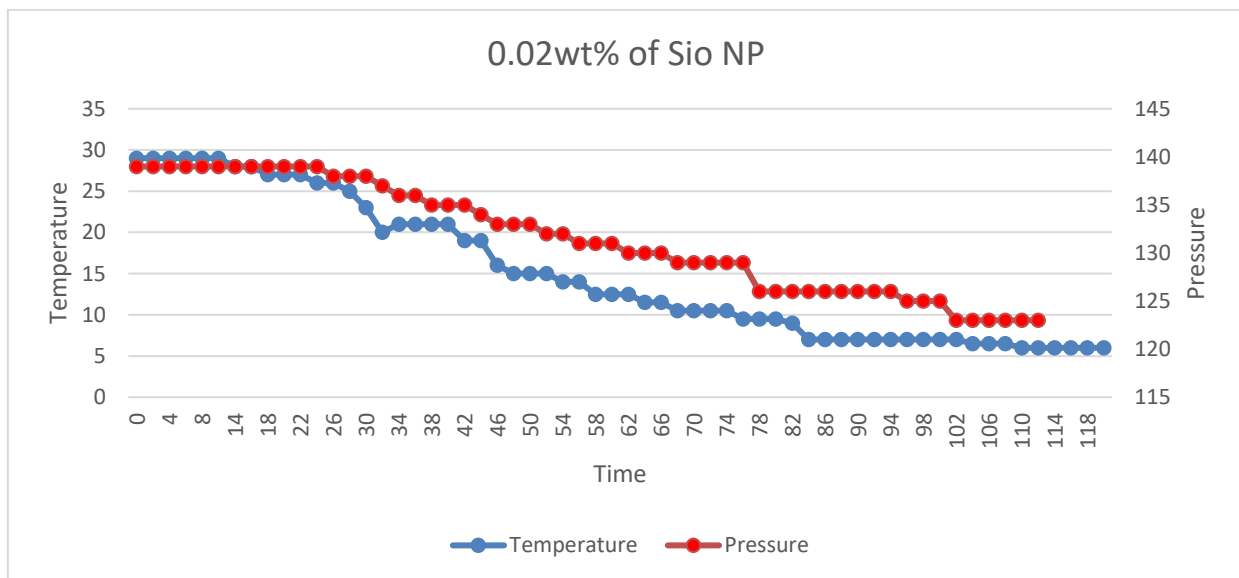


Figure 2- Pressure and Temperature versus Time for 0.02% silicon nanoparticles

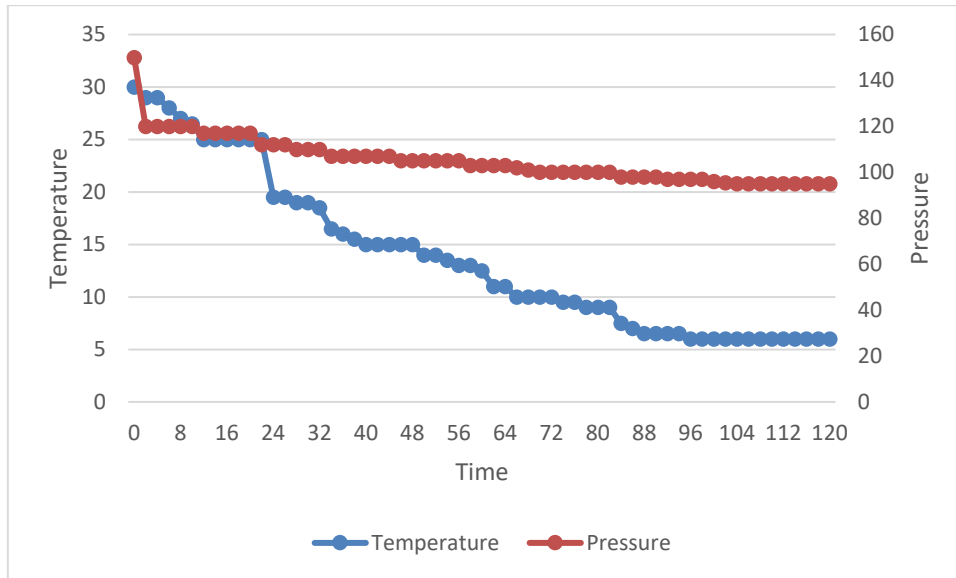


Figure 3- Pressure and Temperature versus Time for 0.01% aluminium oxide nanoparticles

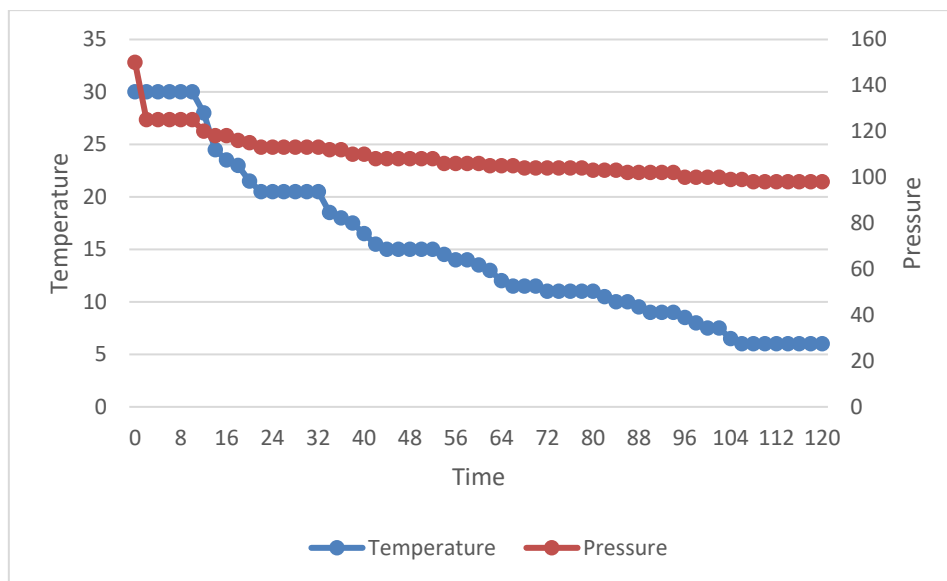


Figure 4- Pressure and Temperature versus Time for 0.02% aluminium oxide nanoparticles

## V. CONCLUSION

From the analysis of the experiment, 0.02wt% of silicon oxide nanoparticles showed better inhibitory capacity than same weight of aluminium oxide nanoparticles while 0.01 weight percentages of silicon oxide nanoparticles and aluminium oxide nanoparticles had a close match. From the results gotten, silicon oxide nanoparticles could be recommended for field trial.

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