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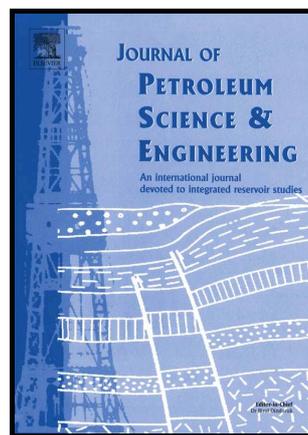


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## Author's Accepted Manuscript

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# Adsorption of polyphosphinocarboxylic acid (PPCA) scale inhibitor on carbon nanotubes (CNTs): A prospective method for enhanced oilfield scale prevention

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## Abstract

A scale inhibitor ‘squeeze’ treatment is used in the oil and gas industry as a control measure to reduce the risk of mineral scale precipitation and deposition in the near-wellbore rock formation and associated installations. One of the determining factors in a successful squeeze job is the potential of formation rock to adsorb scale inhibitor (SI); the higher the adsorption, the better the treatment. This paper investigates the potential of employing carbon nanotubes (CNTs) to increase the adsorption of a common SI (polyphosphinocarboxylic acid, PPCA) on formation rock as part of a new methodology forming a ‘Nanotechnology-Assisted Squeeze Treatment’ (NAST). The focus here is assessing the adsorption potential of PPCA on CNTs for the purpose of creating a longer-lasting squeeze treatment. Analyses using various techniques including Transmission Electron Microscopy (TEM), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Thermogravimetric Analysis (TGA) and Raman Spectroscopy are presented, and results indicate that up to 180 mg/g of PPCA adsorbed on CNTs, with strong bonding, which is significantly higher than the 1 mg/g adsorption of PPCA on crushed formation rock. Adsorption of PPCA decreases with increasing temperature of the solution, indicating an exothermic reaction. The impact of water salinity on adsorption is also considered, with calcium producing a positive effect on adsorption and sodium the opposite. It is also illustrated that a good dispersion of CNTs in the solution can dramatically increase the adsorption due to the exposure of higher surface area to PPCA in the solution. The influence of using CNTs on adsorption of SI onto internal surface of sandstone rock were evaluated using coreflood tests with simplified brines.

The results demonstrate the potential of employing CNTs to increase adsorption of SI in squeeze treatments and possibly to improve the squeeze treatment lifetime.

**Keywords:** Carbon Nanotubes (CNTs); Mineral Scale Inhibition; NAST; PPCA; Adsorption; Squeeze Treatment

## 1. Introduction

One of the common issues in the oil and gas industry is the formation of mineral scale such as calcium carbonate and barium sulfate which leads to a blocked oil path, damage to the production system, and consequently a reduction in hydrocarbon production. Mineral scale formation can occur on the surface of production systems from lower completion to topside process, as well as in the porous rock where the oil is trapped and in the near wellbore, resulting in a reduction in oil flow.

In order to prevent scale formation or reduce the risk of precipitation, scale inhibitors are pumped downhole to adsorb into the formation rock and then slowly desorb to inhibit mineral scale formation during production of hydrocarbon; this is called a 'squeeze treatment'. The squeeze 'lifetime' can be expressed as the volume of water produced by a well before which the SI concentration decreases under a critical concentration level required to avoid scale precipitation. The volume of water protected against scale formation is dependent on the quantity of scale inhibitor adsorbed in the near wellbore coupled with desorption rate. Inhibitors can be absorbed on the rock or precipitate on the formation rock with the assistance of calcium cations in a reservoir. Both mechanisms can simultaneously take place based on the formation water and the inhibitor's chemical characteristics.<sup>1</sup> The quantity of inhibitor reacting with or adsorbing on the rock surface in adsorption/desorption squeeze treatments is the key factor to estimating inhibitor retention<sup>2</sup>. Squeeze treatments are an expensive procedure due to production loss and chemical cost; hence, improvement in the squeeze lifetime is crucial for the oil and gas industry. Prolonging a squeeze treatment's lifetime has been attempted by cross-linking inhibitors<sup>3</sup> and changing pH solution, using calcium as a precipitation squeeze<sup>4-6</sup>, enhancing additive's precipitation and adsorption<sup>4,5</sup>, applying kaolinite to modify near-wellbore surface properties<sup>7</sup> and chemically modifying internal surface of formation rock<sup>8</sup>.

A typically 10% solution of SI is squeezed into the near wellbore area and pushed for example 2-4m further into the reservoir by an over-flush to increase the adsorption of SI by increasing the surface area of absorbent. In addition, the well is shut down for 12 to 24 hours to increase the adsorption of SI on formation; this is due to the fact that the wellbore area is heated up by the reservoir and the higher the temperature is, the more adsorption happens on rock surfaces. An ideal squeeze treatment includes high adsorption amount and rate of the inhibitors on rock surface and slow desorption, but sufficient to prevent scale formation, from the surface of rock. However, what happens in reality during the hydrocarbon production is that one third of the SI flows back from reservoir after a few days<sup>9</sup>; this is due to poor adsorption properties. Moreover, one third of the SI is usually lost in the formation and does not come back to the production due to pushing the SI far in the reservoir in order to increase the surface area of formation rock. Adsorption processes depend on three main factors including: i) characteristics of the adsorbate, ii) solution properties (conditions such as temperature, pH, composition, etc.) and iii) adsorbent characteristics. Scale inhibitor (adsorbate) properties are known before being employed in the oil field. Dependent on the reservoir conditions and the purpose (suitable for corrosion and/or scale inhibitor, be functional during nucleation and/or growth, etc.) of usage, appropriate scale inhibitors are selected to be squeezed in the well. In addition, new regulations compel the oil and gas industry to move towards more green inhibitors. This means firstly much research is involved in modifying the scale inhibitor (adsorbate) efficiency. Also companies are constrained due to new environmental regulations. Regarding solution properties, reservoir conditions and injected water vary among the wells; one squeeze modification may be suitable to an individual well, but inappropriate for another one. Although many investigations were performed to increase the squeeze lifetime, indeed successfully in particular cases, a wide-ranging solution suitable for most wells has not been established. Therefore, a good methodology should be applicable in most cases. One of the areas that has potential for improvement is the adsorption of SI on formation rock by increasing the amount and rate of adsorption.

Nanotechnology is one of the stunning technologies applied to many fields of science, which shows a promising future. One of the extraordinary nano-materials is carbon nanotubes (CNTs), the potential of which has been explored in many applications such as composite reinforcement, electronic devices, energy storage, field emission devices, nanometer-sized electronic devices, medical applications, sensors and probes. The authors have recently

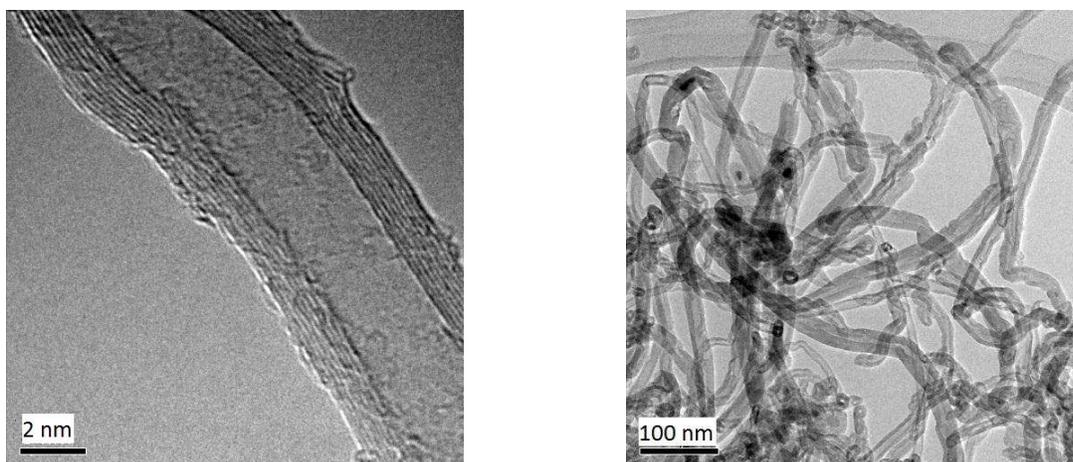
suggested<sup>10,11</sup> that squeeze treatments could be enhanced by using CNTs to improve the adsorption of SI on formation rock. The idea is first to pump CNTs downhole to bond strongly to the formation rock internal surfaces, followed by the injection of SI downhole to react with the CNTs. Subsequently, the SI could desorb into the formation water during production in order to prevent scale formation.

The purpose of this paper is to explore this idea more rigorously, focusing on the adsorption of SI on CNTs, and to extend the previous coreflood tests, which used only distilled water, to corefloods involving brine. The rest of the paper is organized as follows: section 2 provides details of the materials and experimental procedure used, section 3 presents the results of adsorption tests of PPCA on CNTs, section 4 characterizes the resulting PPCA-CNTs, section 5 presents new coreflood performance results, while section 6 briefly discusses the bonding of CNTs to rock surfaces. Potential health, safety and environmental risks are discussed in section 7, before conclusions are drawn in section 8.

## **2. Materials and Experimental procedure**

### **2.1. Materials**

PPCA was supplied in aqueous solution with commercial name of Bellasol S40 with 37.5-42.2% content from BWA Water Additives. CNTs were supplied in powder form and used as-received. The supplied CNTs were  $8 < \text{nm}$  diameter,  $0.5\text{-}2 \mu\text{m}$  length and  $500 \text{ m}^2\text{g}^{-1}$  surface area. The CNTs were provided from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, which were multiwalled carbon nanotubes. Figure 1 shows TEM images of as-received CNTs used in this work. Silica particles (as analogue to formation rock since the majority of rock formation is quartz) provided from Sigma-Aldrich were also used in this work in order to compare the results of CNTs with various types of sands. Silica particles were  $35\text{-}70 \mu\text{m}$  with  $100 \text{ \AA}$  pore size. The rock used in this research was crushed sandstone with grind size of  $108\text{-}180 \mu\text{m}$ .



**Figure 1. TEM images of as received CNTs used in this work**

## 2.2. Dispersion of CNTs

Effective dispersion of CNTs is essential for successful use in the field, as they would need to be delivered over long distances in appropriate solutions. Two different types of dispersants were initially used to disperse CNTs. **Error! Reference source not found.** shows dispersion of CNTs in Dimethyl-Formate (DMF) and Sodium Dodecyl Sulfate (SDS). DMF dispersed higher amounts of CNTs compared to SDS; however, SDS is more environmentally-friendly dispersant, see Refs. (11) for more detailed information.



**Figure 2. Dispersion of CNTs in SDS and DMF**

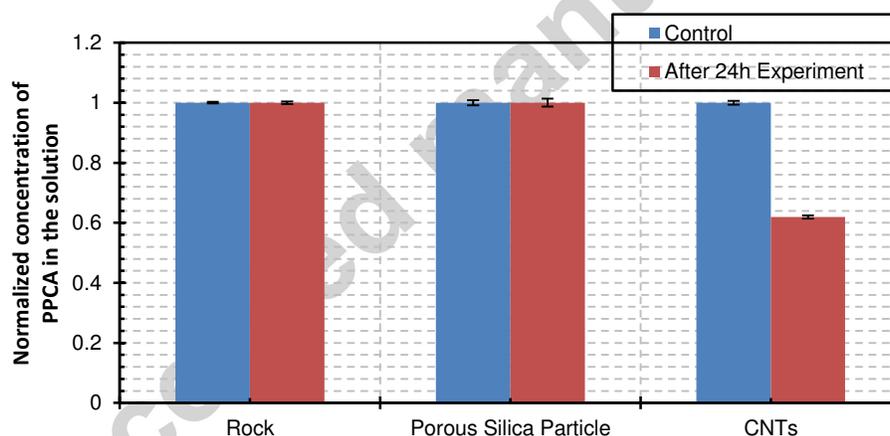
## 2.3. Experimental method

A 50 mL solution of various concentrations of PPCA and deionized water (DW) or brine was prepared every time for the experiments. Three samples were taken for Inductively Coupled Plasma mass spectrometry (ICP-MS) measurements (prior to adding CNTs/sands) to determine

the concentration of PPCA in the solution as a reference. After that, the desired amount of CNTs (in most experiment: ~300 mg) were added to the solution, which was magnetically stirred for a desired time (up to 24h). Then 3 mL of solution were filtered by a 0.45  $\mu\text{m}$  syringe filter (Millex-HV 0.45  $\mu\text{m}$  Millipore) and measured by ICP-MS followed by filtering the whole solution. Finally, CNTs were collected on the top of the membrane and dried before performing Thermogravimetric Analysis (TGA) and Raman Spectroscopy.

### 3. Adsorption Results and Discussion

The ICP-MS results illustrate that CNTs are able to adsorb PPCA significantly more than silica particles and rock. Given that surface area is a key factor in quantifying adsorption, the amount of CNTs used for experiments was selected to give the same surface area as the silica and rock. The results of adsorption of PPCA in DW on rock, silica, and CNTs are illustrated in Figure 3.



**Figure 3. Adsorption of PPCA in DW on CNTs and two different types of sands**

The first column in Figure 3 shows the concentration of PPCA in solution before starting the experiments as a reference/control. The second one is the concentration of PPCA remaining in the solution after 24 hrs experiment. No adsorption of PPCA on silica sand and rock was observed; this is due to very low tendency of silica sand and rock to adsorb PPCA. It has previously been shown that the presence of  $\text{Ca}^{2+}$  in the solution plays an important role for adsorption of PPCA on rock<sup>2</sup>. In addition, the presence of clay mineral, particularly kaolinite, in the rock has been demonstrated to be necessary for adsorption of inhibitors onto the rock<sup>14</sup>. It is

seen that PPCA does not have a tendency to react with silica/rock in DW; on the other hand, it has a strong propensity to bond with CNTs.

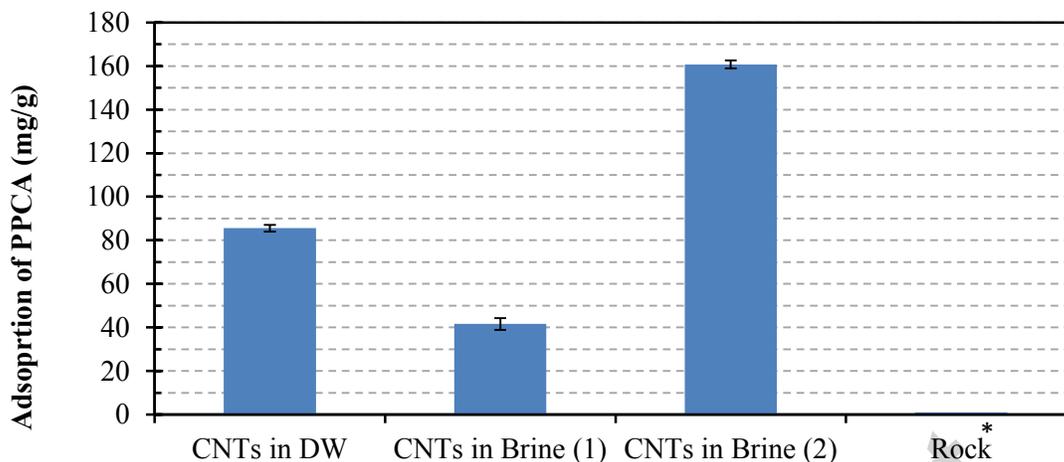
The adsorption tests were also performed in simple brine solutions with compositions given in Table 1 to study the effects of some common ions available in formation water on adsorption of PPCA on CNTs.

**Table 1. Brine compositions used in this work**

	NaCl (g/l)	NaHCO <sub>3</sub> (g/l)	CaCl <sub>2</sub> .6H <sub>2</sub> O (g/l)
<b>Brine (1)</b>	76.26	0.76	0
<b>Brine (2)</b>	0	0	3.826

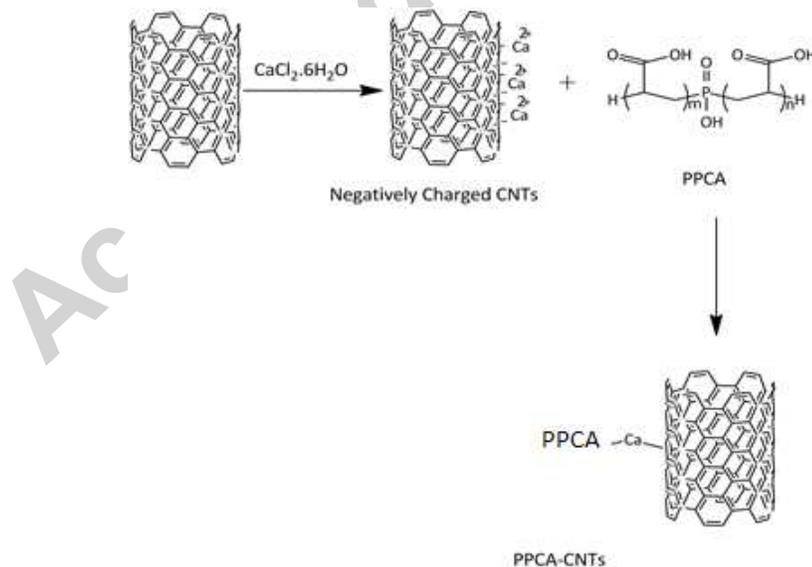
The results in Figure 4 illustrate adsorption of PPCA on CNTs in various brines compared with on the rock. Simple brine compositions were chosen to eliminate the complexity effects of actual formation water in this work; however, the result for rock in Figure 4 is in synthetic formation brine. Figure 4 shows that the adsorption of PPCA on the CNTs even in the high salinity solution (second column) without calcium is much higher than on rock. Adsorption of PPCA on the CNTs in the solution with calcium is more than 160 mg per gram of CNTs; compared to 1 mg/g on rock<sup>15</sup>.

CNTs have recently been studied<sup>16-20</sup> to desalinate brackish and sea water using various methods. It is shown that CNTs are capable of attracting sodium in the solution and enabling water to pass through the CNTs membrane<sup>17-19</sup>. So, lower affinity of CNTs to PPCA in Brine (1) solution could be due to the tendency of sodium to CNTs. The Point of Zero Charge (PZC) of the p-CNTs is at pH 5-6 which leads to negatively charged CNTs; above this pH value CNTs attract positive-charge ions. Since the pH of Brine (1) solution was >8, above the PZC of CNTs, the CNTs became negatively charged and react with sodium in the solution causing more aggregation and subsequently less active sites adsorption of PPCA.



**Figure 4. Comparison results of adsorption of PPCA on CNTs in different solutions. \*The adsorption of PPCA on rock was taken from Jordan et al.<sup>15</sup>. The adsorption of PPCA on Rock\* is 1 mg/g**

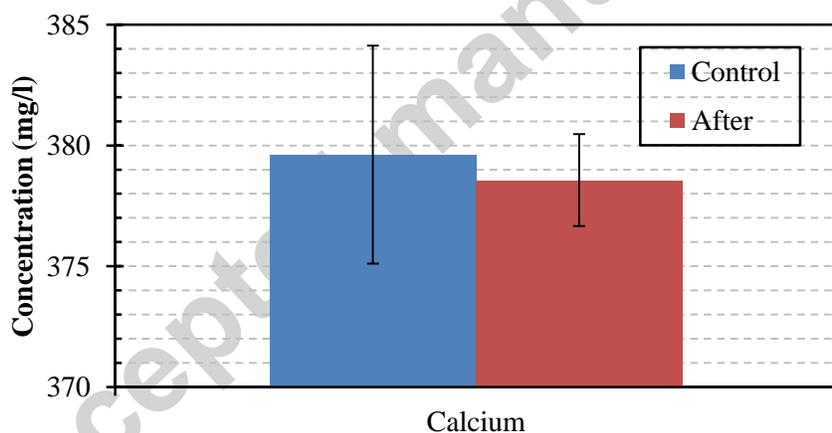
The same explanation can be used to interpret the results for the experiments with presence of calcium, note pH of Brine (2) was  $\sim 6.5$ . The assumption is that  $\text{Ca}^{2+}$  interacts with the CNTs in the solution like sodium in Brine (1). In contrast to sodium, calcium has two free electrons to react or to be paired with other chemicals. Therefore, one of the free electrons can interact/bond with CNTs and another one to PPCA. The schematic of this hypothesis is shown in Figure .



**Figure 5. Schematic of adsorption of PPCA on CNTs in Brine (2)**

The concentration of calcium in the solution before and after the experiment was also quantified by ICP-MS. Figure 6 illustrates the amount of calcium in the solution before (control)

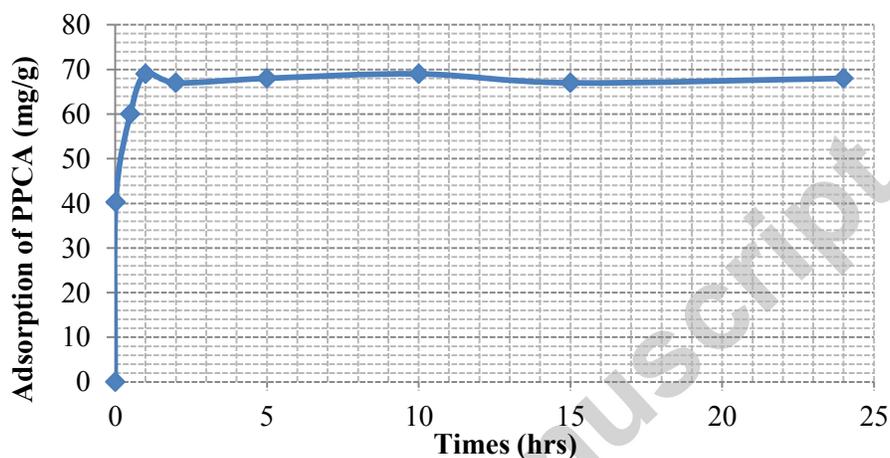
and after the experiment. It is observed that the amount of calcium difference in the solution is in the range of error bars based on ICP-MS resolution. Bearing in mind the ICP-MS error, it is not possible to state whether adsorption of calcium on CNTs has happened. Similarly, looking at the data in terms of mass (mg) or mass per volume (mg/l) loss, sufficient information cannot be given. As the molecular weight of PPCA is much greater than calcium and with consideration that each calcium element reacts with one PPCA, the amount of calcium required for 483.83 mg/l adsorbed PPCA (according to the ICP-MS for this experiment) cannot be measured by ICP-MS. Stoichiometrically speaking, 483.8 mg/l adsorption of PPCA in 50 ml solution equals to 6.37  $\mu\text{mol}$  of PPCA, when the molecular weight of PPCA is 3800 g/mol. Thus, with the assumption that each adsorbed PPCA reacts with one calcium atom, 5.1 mg/l is required to have 483.8 mg/l adsorption of PPCA on the CNTs. Then, a 5.1 mg/l calcium difference was expected to be quantified by ICP-MS. It is difficult for the ICP-MS to distinguish 5 mg/l change in 400 mg/l of calcium; Relative Standard Deviation of 1.25%.



**Figure 6. ICP measurement of calcium before and after experiment**

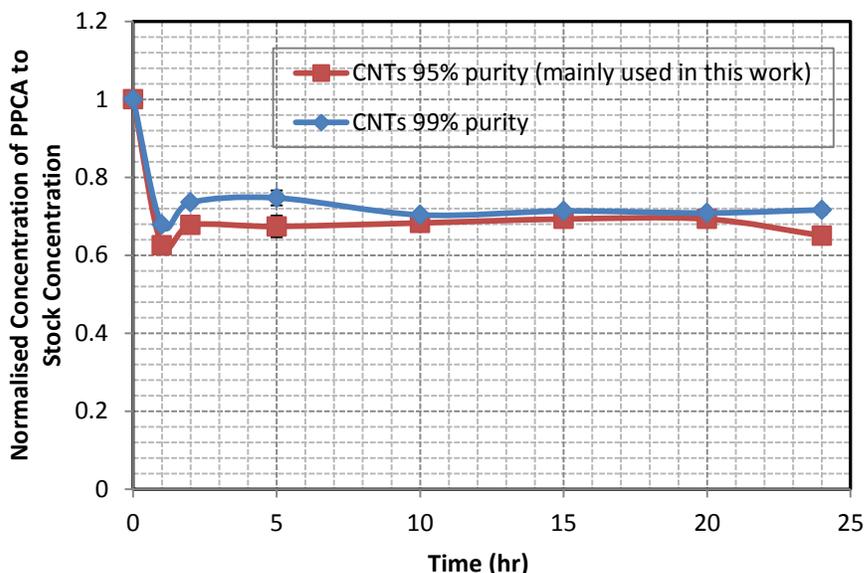
Figure 7 shows the amount of adsorption of PPCA on CNTs as a function of time. Samples were taken for ICP-MS measurements at different times; while the adsorption at zero shows the control (before adding CNTs to the solution). The first sample was taken immediately (less than 5 second) after adding CNTs to the solution of 1000 ppm PPCA and DW. Additional samples were taken after 0.5, 1, 2, 5, 10, 15, 24 hours. It is observed that a significant amount of PPCA was adsorbed by the CNTs in fewer than 5 second; this is more than 57% of maximum adsorption in this experiment (70 mg/g). This indicates a quick adsorption of PPCA on CNTs, which can be very useful for enhancing the squeeze treatment process and its lifetime. It is also

observed that more than 85% of maximum adsorption in this experiment was adsorbed after 0.5 hours. In addition, the adsorption amount reached a plateau after a one hour experiment; all available sites on CNTs might be occupied by PPCA in one hour. Quick adsorption could be beneficial for squeeze treatment since the well shut-in hours could be significantly reduced results in lower production loss during shut-in.



**Figure 7. Adsorption of PPCA on CNTs as a function of time with 1000 ppm of PPCA in DW and 300 mg of CNTs**

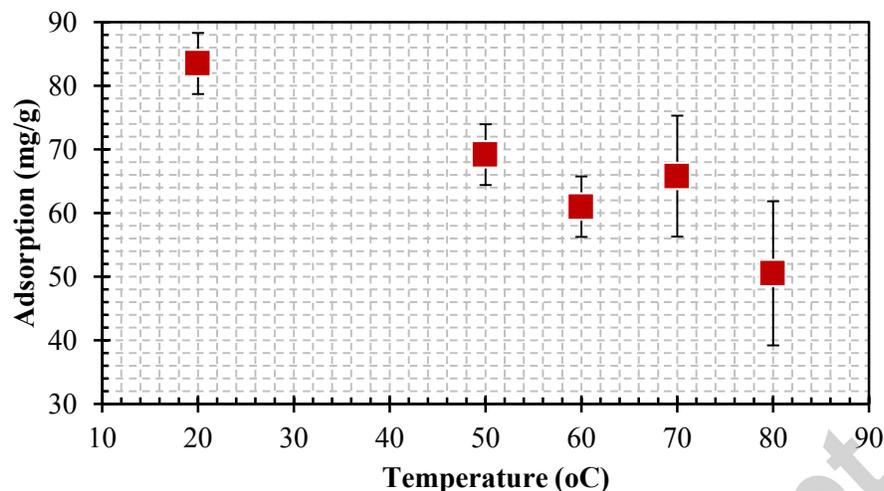
The CNTs used in this work were categorized 95% purity by the vendor. Higher quality CNTs (99%) were also sourced from a different vendor to understand the effects of impurities in the CNTs. Figure 8 illustrates the amounts of PPCA remaining in the solutions as a function of time when using two different types of CNTs. It is observed that the adsorption amount of PPCA on both CNTs are similar, which indicates that the effects of impurities in the CNTs are negligible. In addition, the high affinity of CNTs to adsorb PPCA is also demonstrated with both of these different types of CNTs.



**Figure 8. Adsorption of PPCA on two different CNTs qualities from two different vendors.**

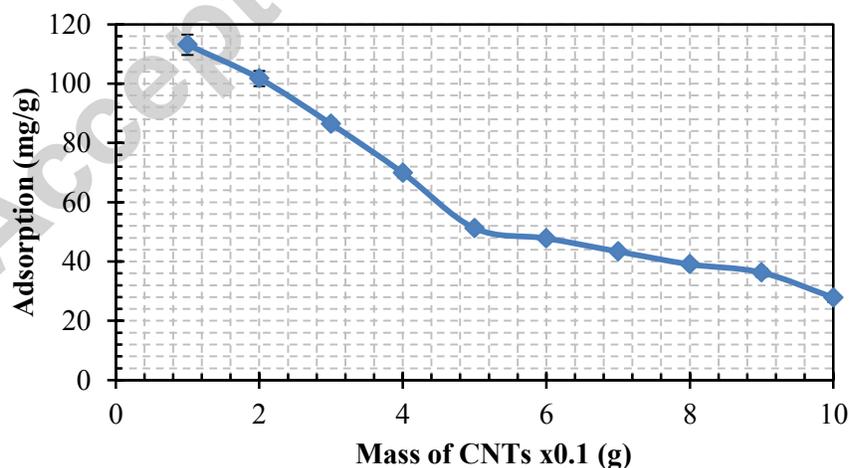
The effect of temperature on adsorption of SI on rock has been the subject of many studies<sup>1,6,15</sup> since this affects the shut-in hours in squeeze treatment designs. For this reason, adsorption of PPCA on CNTs at a range of temperatures was tested. Figure presents the adsorption (mg/g) of PPCA on CNTs at various temperatures, showing a decline in adsorption of SI when the temperature increases. In contrast to formation rock, adsorption of PPCA on CNTs decreases as the temperature increases, leading to a negative value of enthalpy ( $\Delta H < 0$ ). This implies an exothermic reaction between CNTs and PPCA; it was shown that adsorption of most chemicals on CNTs is exothermic<sup>21-24</sup>.

Considering the lowest amount of adsorption (~50 mg/g) from Figure at 80°C and comparing this with adsorption of PPCA on the rock with 1 mg/g, the adsorption of PPCA on the CNTs is still much higher than on rock. The injection temperature in squeeze treatments is 5-15°C in the North Sea, which causes a big issue for squeeze treatments, as adsorption of SI on rock significantly decreases at low temperatures. On the other hand, high adsorption of SI on the CNTs at low temperatures is observed. This potentially leads to having high adsorption during the injection of SI and reducing the shut-in period to one hour.



**Figure 9. Adsorption of PPCA on CNTs in different temperatures**

The data in Figure show the adsorption (mg/g) of PPCA as a function of mass of CNTs (g). Figure indicates that the adsorption of PPCA per mass of CNTs decreased when the mass of CNTs increases. The trend in Figure is unusual since a constant line was expected. This can be due to the effect of agglomeration of CNTs in the solution; CNTs were just stirred in the solution in this work. The greater the mass of CNTs in an identical volume of solution, the lower the chance of CNTs being disaggregated in the solution. This is supported by another experiment, which is shown later in this paper.



**Figure 2. Adsorption of PPCA on various mass of CNTs**

In order to understand the behavior in Figure - effects of agglomeration of CNTs in the solution – adsorption tests were carried out in various volumes of the solution (DW) with the

same amount (mg) of PPCA. Figure shows that the adsorbed amount (mg/g) increased with the volume of the solution to 180 (mg/g) from 100 (mg/g); this supports the results from Figure . Therefore, the capacity of CNTs to adsorb SI can be higher if CNTs are suitably dispersed in the solution due to creating higher surface area available in the system.

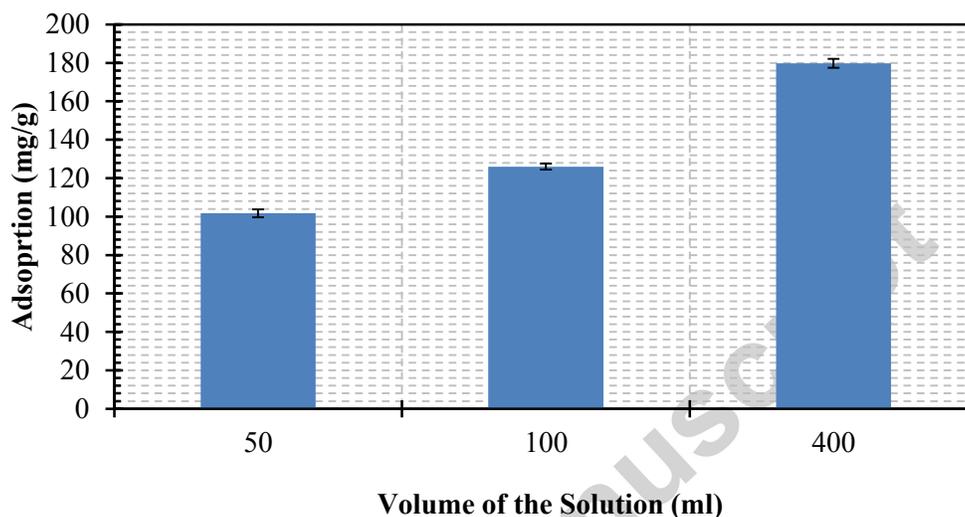


Figure 3. Adsorption of PPCA on CNTs in various volume of DW solution

#### 4. Characterization of PPCA-CNTs

**4.1 TGA Results:** Firstly TGA was run in ambient air on CNTs to characterize the purity of pristine CNTs (p-CNTs). It was found that the CNTs used in this work had < 5% impurities (95% purity as described by vendor) since the sample in TGA lost 95% of the weight before the temperature reached 600 °C. Figure illustrates the weight loss of PPCA-CNTs and pristine p-CNTs as a function of temperature. The weight loss was measured from a temperature of 200°C as it was assumed that all moisture absorbed by p-CNTs and PPCA-CNTs would be evaporated by 200°C. It is noticeable that the trend of weight loss between PPCA-CNTs and p-CNTs is different; more weight loss has been obtained by PPCA-CNT. The maximum weight loss difference was at ~500°C. The estimated adsorption of PPCA on CNTs by TGA for this experiment is 0.445 mg which is in reasonable agreement with 0.684 mg by ICP-MS; the difference could be due to the fact that the measurement used in TGA is from 200°C and some PPCA may be evaporated before reaching this temperature. However, TGA cannot be as accurate as ICP-MS in terms of measurement.

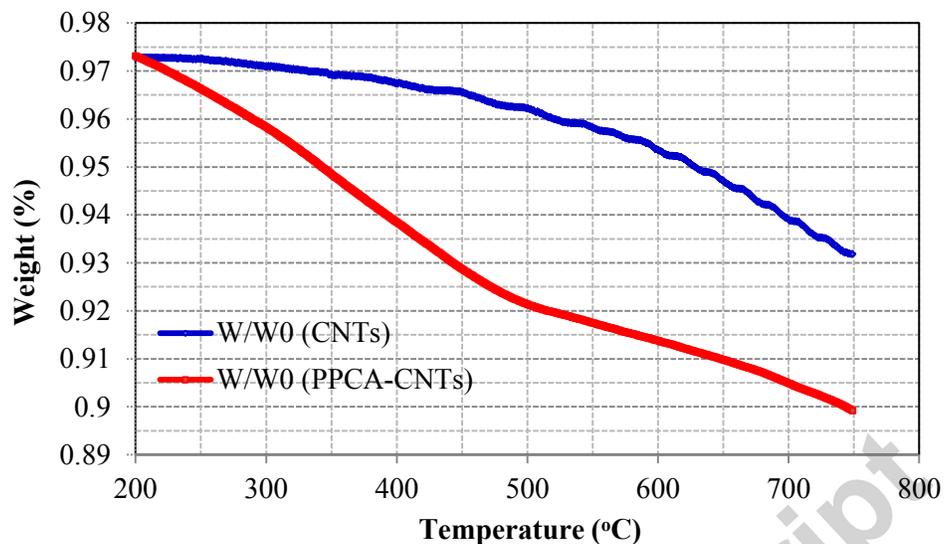


Figure 4. TGA of functionalized CNTs and p-CNTs

**4.2 Raman spectroscopy:** Figure shows Raman spectroscopy results of PPCA functionalized CNTs compared with p-CNTs. The values of 2600, 1590, 1310, 266, and 160  $\text{cm}^{-1}$  in Figure correspond to G', G, D-band and radial breathing mode (RBM), respectively. The ratio of D-band intensity to G-band ( $I_D/I_G$ ) has changed from 0.62 to 0.96 for p-CNTs to PPCA-CNTs; as such a 1.55 times greater ratio of D-band to G-band exists. This illustrates that PPCA-CNTs underwent a covalent bond functionalization process.

Interaction between scale inhibitor and rock is by electrostatic and van der Waals interactions<sup>1,25-28</sup>. This can explain the low adsorption of scale inhibitors on the rock surface, as the van der Waals and electrostatic interactions are weak and they can easily be broken. Since the adsorption of PPCA on the CNTs is via covalent bonds, it is presumed that the adsorption of SI on the CNTs can be increased by the NAST methodology.

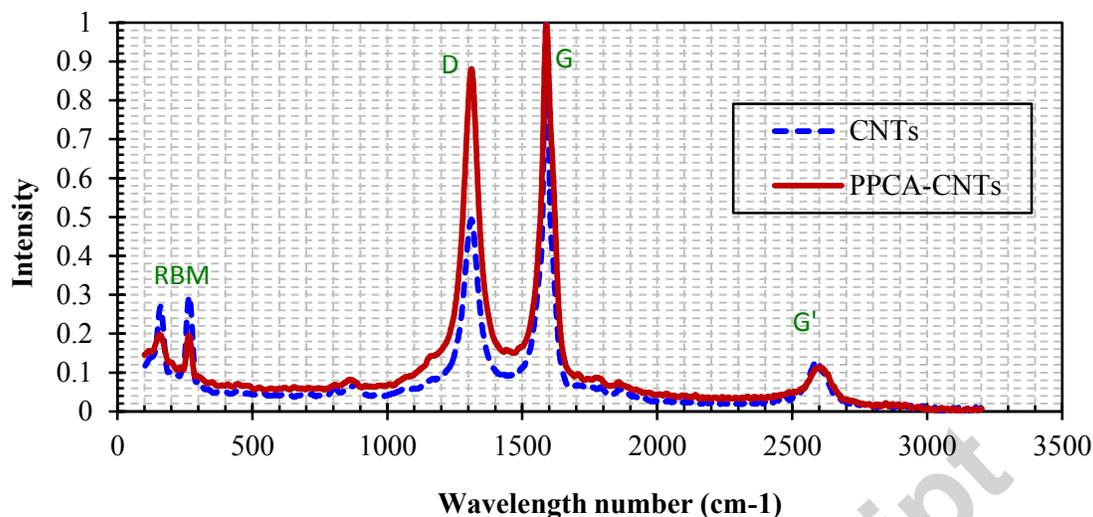


Figure 5. Raman spectroscopy of CNTs and PPCA functionalized CNTs

## 5. Coreflood tests

Since coreflood tests are a common practice in the oil and gas industry for assessing the performance of scale inhibitors before treating wells with the chemical, dispersed CNTs were pumped into a sandstone core plug followed by injecting PPCA to evaluate the performance of CNTs employing the NAST methodology. PPCA concentrations in the effluent of the coreflood was measured by ICP-MS to calculate the amount of PPCA adsorbed at every pore volume (PV). **Error! Reference source not found.** illustrates the coreflood results using CNTs comparing to the conventional coreflood test. A simple brine consisting of 3.812 g/l NaCl and 3.826 g/L  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$  was used in these experiments. As seen from **Error! Reference source not found.**, the amount of PPCA adsorbed onto the internal surface of the core was higher using CNTs compared to the conventional coreflood test. In addition, the core plug was saturated with PPCA after 3 PV in the conventional coreflood; on contrary, the core plug treated with CNTs was not fully saturated after 10 PV.

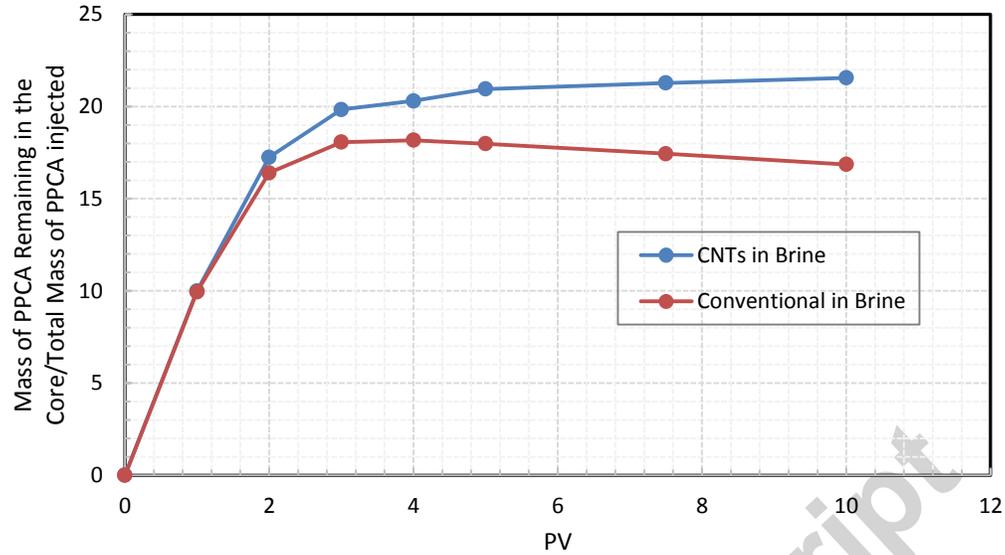


Figure 6. Ratio of PPCA mass remaining in the core to the total mass of PPCA injected in the core

## 6. Bonding of CNTs to rock

Bonding of CNTs onto rock is not the focus of this paper, however **Error! Reference source not found.** illustrates bonding of CNTs to quartz crystal and sandstone rock surface. Uniform attachments of CNTs mainly smaller than 100 nm are observed on quartz crystal surface; however, the attachment on porous rock surface occurred with some agglomerated CNTs. Since the experiments were performed in static conditions, the surface modification before sticking CNTs on the internal rock surface was not as successful as using a flat quartz crystal surface; however, in a dynamic condition the attachments of CNTs were more successful as shown by the coreflooding tests.

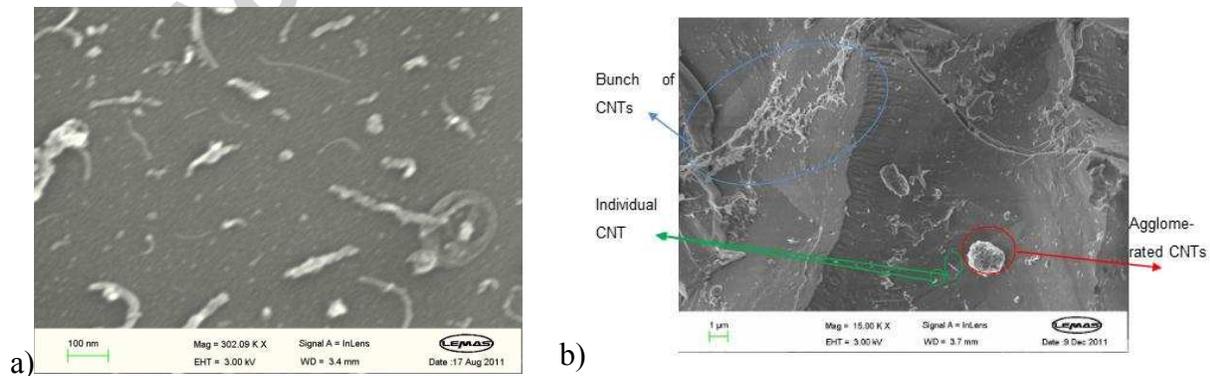


Figure 15. Bonding CNTs to a) quartz crystal coupon and b) sandstone rock surface

For more information regarding the ‘Nanotechnology-Assisted Squeeze Treatment’ (NAST) concept and attachment of CNTs to rock surface, see Refs. (12) and (13).

### **7. Potential HSE-related risks of using CNTs in the oil and gas industry**

One of the main concerns in applying CNTs in industries is HSE-related risks. The main issues of using CNTs arise where handled as powders. However, the CNTs in the NAST methodology are utilized in solutions, so this will eliminate most of the HSE-related issues of using CNTs in the oil and gas industry. In addition, potential HSE-related issues of using CNTs were reviewed in Statoil before starting the second stage of NAST development. CNTs under the current OSPAR convention and PLONOR lists are mostly categorized red or black chemicals in Statoil. Since using CNTs in the NAST methodology would be a one-time treatment in a well lifetime, only low amounts of CNTs are required for every well to increase adsorption of scale inhibitor in the formation rock. Understanding how much CNTs are exactly required is currently under investigation. Moreover, the bonding between CNTs and rock surfaces is strong<sup>9-12</sup>, so only little amounts of CNTs are anticipated to be back-produced from the near wellbore; this is under investigation in the second stage of development. Therefore, it was concluded that using a small amount of red or black chemicals to reduce a massive amount of yellow or red chemicals would be beneficial for both the industry and the environment. In addition, in case of using produced water in squeeze treatment HSE-related risks of using CNTs decreases since there will be little to no produced water discharging to environment. Development of the NAST and potential use of CNTs were not concluded as showstoppers under current legislation in Statoil.

### **8. Conclusion**

In this paper, adsorption of PPCA on CNTs in DW and simple brine was studied; this is the second part of the NAST technology. The first part of the NAST involves methodologies for CNT delivery to the near-wellbore area and the potential reaction of CNTs on the rock<sup>11-13</sup>. The objective of this paper was to introduce the potential of CNTs to increase adsorption of SI for the purpose of enhancing the squeeze treatment lifetime. Although the research is in the beginning of its development, the preliminary results are promising to go forward with the technology development. To summarize, the potential benefits of this work are the following:

- a) Adsorption of PPCA on CNTs is significantly higher (up to 180 mg/g) than on any of various types of sands.
- b) Adsorption of PPCA occurs very quickly within one hour. This can be beneficial for modifying current squeeze treatments in order to reduce the shut-in period.
- c) The influence of temperature on adsorption of PPCA on CNTs may also result in shortening the shut-in period.
- d) Agglomeration of CNTs in the solution plays a significant role in the amount of adsorption of SI on CNTs.
- e) PPCA strongly reacted with/adsorbed on CNTs; this strengthens the adsorption of PPCA on CNTs which may result in retaining PPCA in the near wellbore area for a longer period.

In addition to a high adsorption amount and rate, in order to have a successful squeeze treatment, slow desorption, but above the Minimum Inhibitor Concentration, is required during production from the near wellbore to prevent scale formation. Preliminary results from desorption experiments showed a low desorption amount of PPCA released from CNTs<sup>10-13</sup>. Improvement on desorption of SI from CNT is under development.

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## Highlights

Application of CNTs to be used in scale inhibitor squeeze treatment to increase adsorption of scale inhibitor on formation rock.

Faster and higher adsorption of scale inhibitor on CNTs were achieved compared with formation rock, which could results in longer squeeze treatment lifetime and shorter shut-in during the treatment.

Strong adsorption of PPCA on CNTs could retain PPCA in the near wellbore area for a longer period.

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