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## **Carbon Nanotubes: A New Methodology for Enhanced Squeeze Lifetime CNTs**

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### **Abstract**

A new potential application of nanotechnology for mineral scale prevention in the oil and gas industry is presented. In current squeeze treatments, in which scale inhibitors are squeezed into wells to adsorb or precipitate onto rock surfaces for later release, a large proportion of the injected inhibitor does not adsorb and is therefore returned very quickly from the reservoir upon well re-start. Here it is demonstrated that nano-particles have the potential to enhance squeeze lifetime by greatly increasing the adsorption of inhibitors within the formation. An extensive literature review is presented, exploring the potential for using nano-scale materials in squeeze treatments. One of the observations from scale inhibitor squeezes into sandstone reservoirs is the apparent lack of suitable surfaces available for adsorption. The main constituent of sandstones, quartz, has a very low ability to adsorb inhibitor (1 mg/l). Given this, research using nanotechnology was targeted towards enhancing the available sites for scale inhibitor adsorption within the near wellbore. Specifically, research was undertaken to examine the potential benefits of using carbon nanotubes in a process called Nanotechnology Assisted Squeeze Treatment (NAST). The process involves carbon nanotubes adsorbing and permanently modifying the near wellbore with scale inhibitors subsequently adsorbing onto the nanotubes. This process was observed to be significantly higher than a non-modified near wellbore surface, with a maximum adsorption of more than 85 and 160mg/g onto the nanotubes in solution of distilled water (DW) and CaCl<sub>2</sub> in DW; respectively, compared to 1 mg/g directly onto the rock. Coreflood tests comparing the NAST procedure with a simplified standard coreflood show the potential for improvement of the squeeze lifetime.

### **Introduction**

Inorganic scale precipitation, including formation of CaCO<sub>3</sub>, MgCO<sub>3</sub>, FeCO<sub>3</sub>, BaSO<sub>4</sub>, CaSO<sub>4</sub>, SrSO<sub>4</sub>, etc. occurs when two incompatible brines are mixed or where the conditions (i.e. temperature and pressure) in a system are changed and there is a resulting change in the solubility of certain salts. This can cause blockage of the oil path and damage to the production system. A chemical squeeze treatment is used to pump scale inhibitor (SI) downhole to adsorb or precipitate onto the formation rock. The aim is to establish a downhole reserve of SI from which subsequent desorption or release maintains a concentration of SI within the reservoir sufficient to prevent scale formation. The lifetime of the squeeze treatment is defined as the time when the return Scale Inhibitor (SI) concentration falls below the Minimum Inhibitor Concentration (MIC), which is typically 1-20 ppm depending on the reservoir conditions and SI properties. At this point the well needs to be re-squeezed. Regardless of whether the SI adsorbs or precipitates, the squeeze treatment process is expensive due to the squeeze implementation, chemical inhibitor costs and most importantly because of production losses/deferred during the shut-in period of the squeeze. Hence, improvements to increase the lifetime of SI are highly desirable for the petroleum industry. Ideally, all the inhibitor injected into the well should be retained within the formation and liberated slowly to maintain the SI concentration above the MIC. However, in practice, a large fraction of the inhibitor, almost a third, flows back after a few days of performing the squeeze [1].

Reducing the cost of the squeeze process requires an increase in adsorption of the SI within the formation; therefore, improving the adsorption of inhibitors is one of the core issues. Recently, attempts to improve squeeze treatments and increase squeeze lifetime have been made by a number of means including using cross-linking the inhibitors [2], increasing the pH of the aqueous solution by adding additives [3, 4], employing inhibitor particles [5], boosting precipitation and adsorption by additives [6, 7], using calcium in precipitation squeeze treatment [8, 9] and more recent new ideas such as using fixing agents [10], altering the rock mineralogy [11] and employing nano-particles for further displacement [1].

Nanotechnology has become an important part of many fields of science and engineering (e.g. pharmaceuticals and electronics) as the functionality of nano-materials has increased. A key feature of nano-scale materials is that they usually show very distinct physical, chemical, biological and mechanical properties compared to their macroscopic size counterparts. Nano-materials have been employed in various applications, such as panel displays [12, 13], chemical sensors [14], hydrogen storage [15, 16], electronics devices [17-19], medical applications [20, 21], nano-scale materials [22, 23], and reinforcing composites [24]. One of these interesting nano-materials is carbon nanotubes (CNTs), which have been widely studied due to their remarkable physical and chemical properties. Their strength and flexibility along with electrical and chemical characteristics offer potential for exploitation in many applications. After the discovery of CNTs, a number of practical applications could be envisaged [25]. The helicity and diameter of CNTs can affect the electric conductivity of CNTs, which ranges from semi-conductive to metallic. This is potentially usable in a range of applications for electronic devices. Another fascinating aspect of CNTs is their topology: since individual layers are closed, their graphitic properties disappear [25]. In addition to the above mentioned characteristics, Stone-Wales defects of CNTs bring about various electronic structures along the tube, resulting in the cap of the CNTs being more metallic than the wall [26]. Simultaneously, these defects enhance the reactivity of the end of the CNTs, such as in making the caps of CNTs open [27] to enable filling of the CNTs by another substances [28-30] or functionalization by chemicals [31].

This work introduces a new application of nano-materials in the oil and gas industry, specifically to improve the squeeze lifetime using CNTs. The new methodology will be referred to as a Nanotechnology-Assisted Squeeze Treatment (NAST), and results from a programme of tests are reported to illustrate the potential feasibility of the NAST.

Each well has distinctive properties such as different brine compositions, pressure, temperature and most importantly geological characteristics. Between adsorption and precipitation squeeze treatments, adsorption squeeze methods are more desirable as the probability of damaging the formation rock is lower [32]. Adsorption processes depend on three main factors including: i) characteristics of the adsorbate, ii) solution properties, including temperature, pH, composition, etc. and iii) adsorbent characteristics. Scale inhibitor (adsorbate) properties are known before deployment in the oil field, and appropriate scale inhibitors are selected depending on the reservoir conditions and the inhibitor requirements (e.g. being suitable for corrosion and/or scale prevention, being effective during nucleation and/or growth, etc.). New regulations compel the oil and gas industry to move towards more 'green' inhibitors, meaning that much research has focused on modifying the scale inhibitor (adsorbate) efficiency [33]. Although many investigations have explored ways to increase the squeeze lifetime, in most cases the reported results

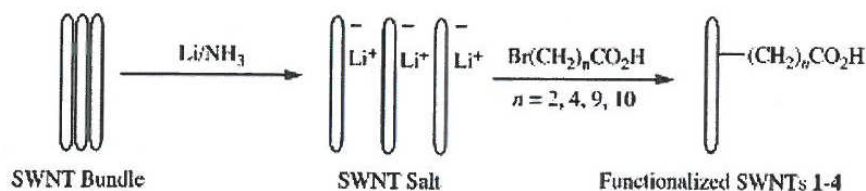


Figure 1—Schematic of functionalisation of CNTs by reductive alkylation [41]; the picture quoted from [41]

are well-specific; to date a wide-ranging solution suitable for most wells has not been established. A methodology that is applicable in most wells would of course be highly desirable.

An alternative (or complementary) approach to modifying the inhibitor is to modify the properties of the adsorbent, i.e. the formation rock. Therefore, the objective of this work is to show how the adsorption of scale inhibitors can be increased by changing the chemistry of the formation rock using nano-materials. Again, the modification ideally needs to be independent of the rock compositions of rock to enable wide application in the majority of reservoirs.

### Challenges

An extensive review of the literature on applications of nano-materials in various fields of science reveals a number of novel methodologies that could be translated into modified squeeze treatments. For example, nanowires on spherical substrates have been explored to enhance drug delivery [34] by improving adhesion to cell surfaces through tangling of the nanowires with the nano-scale surface features of the cells. Other promising nano-structures for enhancing scale inhibitor adsorption are carbon nanotubes (CNTs) and fullerenes. However, the focus has been concentrated on CNTs in this paper. For more information about potential applications of other nano-materials on enhancing squeeze lifetime see the references [35, 36].

Regardless of the type of nano-material, there are two main challenges: (i) how to employ these nano-materials (methodology development) — i.e. establishing the mechanisms of interaction with both scale inhibitors and rock surfaces, and (ii) how to deliver them downhole.

### Carbon nanotubes

CNTs have demonstrated extraordinary properties (e.g. electrical, optical, strength with flexibility, reactivity, etc.), and the effects of functionalized CNTs on scale crystal growth have been previously explored [37-39]. It has been demonstrated that carboxylic functionalised CNTs (COOH-CNTs) are able to prevent vaterite- which is not stable - to form calcite, which is a stable form of calcium carbonate [37]. The same work also illustrated that vaterite could be coated by CNTs.

Functionalisation of CNTs by carboxylic acid groups without using an ultrasonic bath via reductive alkylation has been studied [40-44]. The schematic representation of alkylation is illustrated in Figure 1. An interesting observation from that work is the tendency of CNTs to adsorb a chemical analogue to phosphinocarboxylic acid (PPCA), one of the common scale inhibitors, highlighting the potential for a beneficial interaction with scale inhibitors.

CNTs have several outstanding characteristics that make them attractive to well bore problems. They are stable at high temperatures and have a high Young's modulus, enabling them to withstand the high pressures and temperatures of reservoirs. Their abundance of carbon atoms provides many active sites for functionalization by scale inhibitors, and their high specific surface area means that extensive physical adsorption of inhibitors can be achieved. Therefore, two possible options for exploiting CNTs were proposed: i) SI functionalized CNTs and ii) calcium coated CNTs, but only the former was analysed in this study.

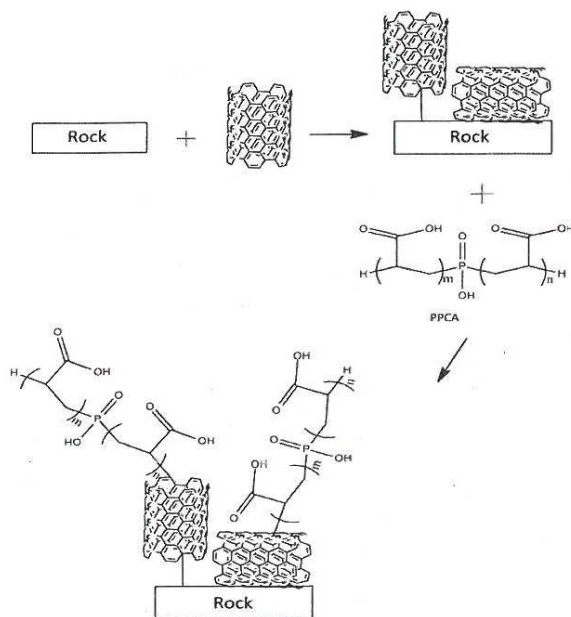


Figure 2-Schematic of proposed methodology using CNTs to react with SI

For the SI-CNTs interaction, the proposed methodology is to first pump CNTs to bond covalently to the rock surface followed by the injection SI downhole to react with the CNTs. Subsequently, the SI could desorb into the formation water during production and prevent scale formation. The major challenge is whether or not CNTs have a tendency to adsorb scale inhibitors. The idea of using SICNTs was mainly inspired by previous works [4044] on functionalising CNTs by polymers which are similar to polyphosphino carboxylic acid (PPCA) scale inhibitor. The schematic representation of Inhibitor-CNTs methodology is illustrated in Figure 2.

### Making quartz reactive with NPs

As mentioned earlier, two approaches are needed to be addressed in this work, which are:

- i. To prove the principle of using nano-particles.
- ii. To deliver the nano-particles downhole.

As the objective of this work is to increase the adsorption of SI on the rock surface by modifying the properties of the rock, how to attach CNTs onto the rock surface required to be investigated. Hence, the possibilities of bonding nano-materials to the surface, particularly quartz, were studied. Literature regarding how to attach nano-particles to the substrate and how to treat the rock surface in order to react with nano-particles are thoroughly reviewed.

The covalent attachment of individualized single walled carbon nanotubes (SWNTs) to the silicon surface via orthogonally functionalized oligo-(phrnylene ethylene)

(OPE) aryldiazonium salts has been illustrated by Flatt et al [45], the schematic is shown in Figure 3.

The same methodology as used by Flatt [45] can be employed in the proposed methodologies. The issue with Flatt's work is that to follow their procedures requires specific conditions (for example, the experiment needs to be conducted in nitrogen environment), which are not feasible in a reservoir.

One of the common chemicals to treat quartz or glass surfaces for immobilising other chemicals such as proteins and DNA is organosilane. Organosilanes are able to have chemisorptions on various surfaces such as quartz, glass and metal oxide [46]. COOH-fullerenes onto the hydrophilic substrate have been studied by Wei et al [47], as shown in the schematic diagram in Figure 4.

Treatment of substrates by various organosilanes has been widely investigated in the literature [48-55] for different purposes. One organosilane was utilised in the oil field in order to increase the adsorption of SI as a fixing agent [10, 11]. In this work the key point is to pre-treat the rock surface to have a covalent bond with CNTs. Scale inhibitors can then be injected when needed, but NPs are pumped downhole just once and so offer prolonged attachment to the rock surface.

### **Nanotechnology-Assisted Squeeze Treatment (NAST)**

The NAST methodology focuses on increasing the adsorption of scale inhibitors on the rock surface in order to increase squeeze lifetime by modifying the rock; its procedures are illustrated in Figure 5. The NAST is divided to two sections: NAST1 and NAST2. The first part of the technology, NAST1, deals with how to treat the rock surface to be reactive to the NPs and how to deliver NPs to bond with the pre-treated surface. NAST2 challenges the feasibility of the NAST methodology in terms of the possibility of adsorption of SI on the NPs and the proof of the proposed methodology.

The schematic representation of the various NAST procedures is presented Figure 6.

#### **NAST1**

Three approaches are involved in the NAST1: i) pre-treatment of the rock surface by organosilanes, ii) dispersion of the CNTs in the solution and iii) attachment of the dispersed CNTs on the treated surface.

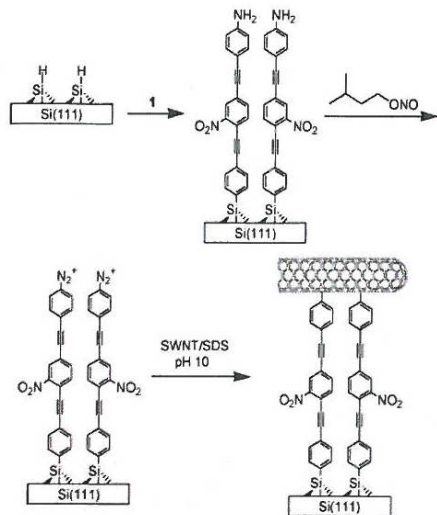


Figure 3—Schematic of attaching CNTs to silicon surface [45]; the picture quoted from [45]

### Stage i: Pre-treatment of the rock surface by organosilanes

The first step of the NAST is to treat the rock surface by chemicals, which can later react with CNTs. Quartz substrates were treated by different organosilanes by using various methodologies [4855]. 3-aminopropyltriethoxysilane is one of the common silanes that has the potential to be used in NAST. Also, 3-aminopropyltriethoxysilane has been used to bond to kaolinite and to increase adsorption of SI [10, 11].

### Stage ii: Dispersion of CNTs

The disaggregation of CNTs in a solution is one of the critical stages in investigating the applications of CNTs to avoid plugging of the wellbore during injection. Hence, surface chemistry of the CNTs becomes important to study dispersion of CNTs in solution [56]. CNTs are disaggregated by a) mechanical — ball milling and high shear mixing; and b) chemical methods — altering the surface energy physically (non-covalent treatment) and chemically (covalent treatment) [57]. The behaviour of CNTs in different dispersants has been demonstrated in the literature [56-59]. The dispersion process is simple and can be accomplished by adding CNTs in dispersants and sonicating the solution for a desired time. CNTs are un-wrapped from each other by means of sonicator by overcoming van der Waals interactions between CNTs. Moreover, dispersants simultaneously interact with the CNTs to be disaggregated by electrostatic interaction between dispersants and CNTs [60] and/or steric repulsion between adsorbed dispersants [61-63]. Concentration, the type of dispersants and the purity of CNTs are the main keys for dispersion of CNTs. CNTs are dispersed in both ionic and non-ionic solutions such as N, N-Dimethylformamide (DMF), sodium dodecylbenzene sulfonate (SDBS), chloroform, dodecyltrimethylammonium bromide (DTAB), acetone, toluene, benzene and Sodium Dodecyl Sulphate (SDS). Two of them are the most common ones — DMF and SDS. DMF and SDS were chosen for dispersion of CNTs in this work, since previously work is available. Although dispersing CNTs by using various surfactants and dispersants has been extensively investigated in the literature [56-66], the applications of previous work require extensive care to ensure that sufficient dispersal of CNTs is achieved.

### Stage iii: Attachment of the dispersed CNTs on the pre-treated surface

Attachment of CNTs on the different surfaces by various methodologies was demonstrated in the literature [45, 47, 67-77]. To bond CNTs to rock surface, CNTs are required to be functionalised by carboxylic groups to simplify the procedures. COOH-CNTs are produced by acidifying the CNTs in the solution of sulphuric and

nitric acids [69-73]. Carboxylic groups of CNTs react with amine groups of organosilane treated on the surface. To facilitate the reaction of carboxylic with amine groups, cross-linkages such as DCC (N, N' -Dicyclohexylcarbodiimide) and EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide) need to be utilised.

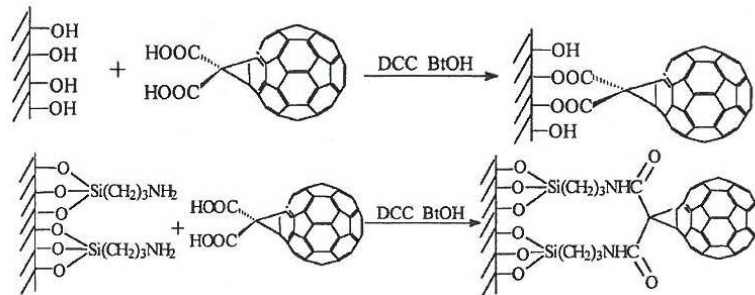


Figure 4—Schematic representation of attaching fullerene onto quartz surface [471; the picture quoted from [47]. DCC and BtOH stand for N, N'-Dicyclohexylcarbodiimide and (1H-benzotriazol-1-ol), respectively.

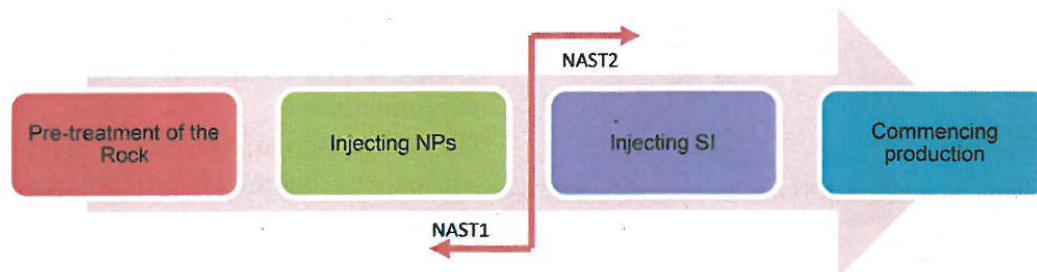


Figure 5—The NAST methodology for enhanced squeeze lifetime

## NAST2

The second part of the NAST deals with investigating on adsorption and desorption of SI on and from the CNTs. NAST2 is the main stage of the NAST methodology, since squeeze lifetime can be increased by increasing the adsorption of SI in the reservoir. PPCA was chosen for the preliminary experiments because it was similar to other works [40, 41]. In addition, PPCA is one of the common inhibitors used. Options for functionalizing CNTs were limited to using mechanical devices (i.e. ultrasonic bath and high-shear mixing) or normal reactions between CNTs and inhibitors (i.e. using chemicals as intermediate to increase the affinity of reaction).

## Materials and experimental methods

### Materials

Quartz crystals as the rock analogue were 10 X10 X5mm in size with both sides polished. The core plug used in this work was pink Doddington with 19.6% porosity and 2112 Kgrn-3 apparent density.

CNTs were supplied in powder form, used as-received. The supplied CNTs and f-CNTs (COOH and OH functionalised Multi-Walled Carbon Nanotubes (MWCNTs)) were <8nm diameter, 0.5-2,um length and 500 m2g-1 surface area (dispersed CNTs). The composition of the COOH-CNTs was 95% (wt.) purity and 1.5% (wt.) ash, and with 3.86% (wt.) COOH content for COOH-CNTs. Silica particles (weight of silica was chosen to have the same specific area with CNTs) were also used in this work in order to compare the results of CNTs with various types of sands. Silica particles were 35-70,um with 100A pore size.

## Experimental Methods

### NAST1 experimental procedures

As NAST1 is divided into 3 stages, the experimental procedure of each step is presented separately.

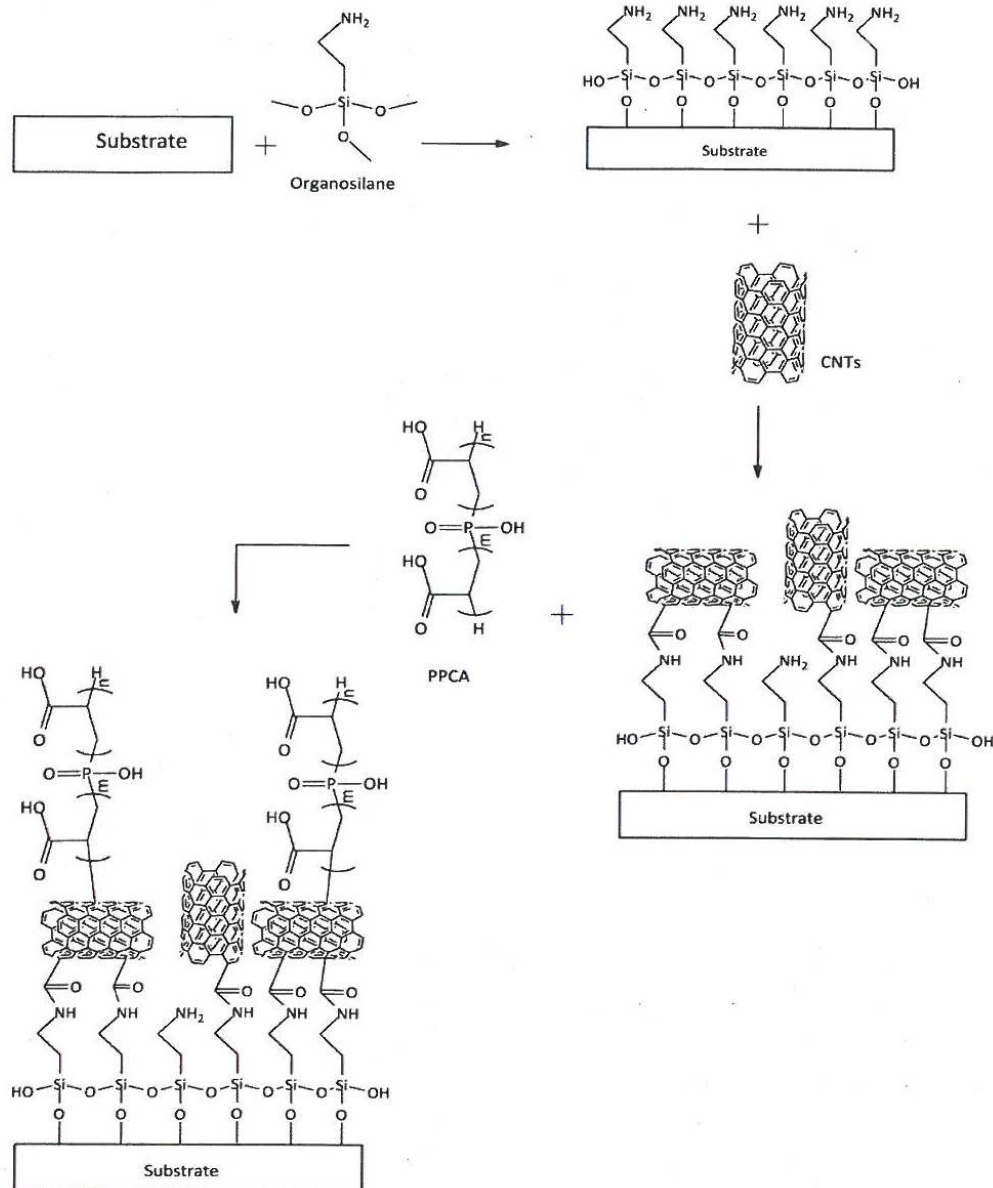


Figure 6—The schematic representation of the NAST methodology by employing CNTs

### Stage i: Experimental process of pre-treatment of rock surface. The experimental procedures are 149, 50, 551:

- The quartz coupon was cleaned by the plasma chamber with OH- bonds created on the surface.
- The substrate was immediately immersed in a 2% solution of the organosilane and ethanol/water (95/5, v/v) for the desired time (1hr).
- The quartz coupon was rinsed several times by ethanol followed by distilled water (DW).
- The treated surface was used in the experiments to deliver CNTs to react with

the surface (see stage iii below).

Note that the section (i) is performed in this work instead of using acid treatments on the surface to create OH bond on the surface and samples are normally dried in a nitrogen atmosphere [49, 50, 55], but it was not implemented in this work as an attempt was to optimise current methodologies which would be practical for use in the oil field.

**Stage ii: Experimental procedure of dispersing CNTs in a solution. DMF is used in this work. The experimental method for using DMF was followed by others [71, 72, 78]**

Carboxylic functionalized CNTs (COOH-CNTs) were added to the DMF solution with ratios of 1:5 (mg/ml), followed by putting the beaker in an ultrasonic bath for 2 hrs. The solution was then left static for 24 hrs to precipitate the un-functionalised CNTs to the bottom of the beaker. The upper suspension (top half) was used in experiments to assure that the dispersed CNTs are going to be employed in the NAST in order to remove the possibility of agglomerated CNTs on the substrate.

**Stage iii: Experimental methods of bonding CNTs to rock surface**

3mg DCC was added to the solution of CNTs in DMF, followed by immersing a functionalised quartz coupon into the solution for fixed duration (1 day). CNTs bonded to the surface were imaged by FEG-SEM (Field Emission Gun Scanning Electron Microscopy) after drying the surface.

**NAST2 experimental procedures**

**Adsorption experiment**

The adsorption experiments were carried out to create an adsorption isotherm. The methodology is: a 50mL solution of PPCA and DW/brine was prepared. Three samples (1000 mg/l) from the solution were sent for ICP measurement in order to determine the concentration of PPCA in the solution as a control. Subsequently, the desired amount of CNT or silica sand was added to the solution and was magnetically stirred with a magnetic bar for 24 hrs. Then 3ml of the solution was filtered by a 0.45µm syringe filter and measured by ICP.

**Desorption experiment**

Desorption experiments were performed in distilled water; DW was used to have analogue solution as in adsorption tests in order to understand/simplify adsorption/desorption process. The procedure involved pouring the solution (DW) into the vacuum pump with the PPCA functionalised CNTs embedded on the membrane. Figure 7 shows the schematic of the desorption set-up. In desorption experiments, the solution of CNTs in PPCA and DW was filtered through a vacuum pump filter after finishing static adsorption tests. After rinsing the CNTs on the top of the membrane several times followed by washing the bottom part of set-up, a 50ml solution of DW was poured to the vacuum filter to go through the f-CNTs (functionalised CNTs) and the membrane. Samples were taken from the bottom of the set-up for ICP measurement. The bottom part of the set-up was again disassembled and rinsed with DW. These procedures were repeated two times in order to measure the desorption of SI from the f-CNTs. The flow rate of fluid passing through CNTs and the membrane for the desorption test was 200 ml/min, which was the default of the pump used in this work.

**Coreflood experiment**

Doddington rock was used in the coreflood tests with porosity,  $\phi$ , of 19.65% and average permeability,  $K$ , 800mD. Doddington rock had 2112 Kg/m<sup>3</sup> apparent density and the compositions including 97% quartz, 2% feldspar, <0.5% clay and <1% others. Below is a preliminary coreflood procedure, which can be modified later in order to be employed in the well. The coreflood tests were performed at room temperature with the flow rate of 1 ml/min to follow adsorption/desorption experiments. The NAST coreflood follows the procedure below, which is developed by this group from the NAST1 and NAST2:

- i. 10 pore volume of injected fluid (PV) of 2% 3-aminopropyltriethoxy silane in a solution of ethanol/DW (95/5 v/v) was injected into the core followed by shutting the core for 1h.
- ii. The core was flushed with 5 PV ethanol to remove un-reacted organosilane from the core, followed by rinsing with 5 PV DW.
- iii. 10 PV of dispersed COOH-CNTs in DMF with DCC was subsequently injected into the core and the core was then shut for 24h.
- iv. The core was afterwards rinsed with 10 PV DW.
- v. The solution of PPCA and DW (10 PV) was then injected into the core and effluent samples were taken for ICP measurements.
- vi. The core was then shut-in for a further 24hrs.
- vii. Post-flush was finally begun using the background solution — DW - and effluent again sampled for ICP.

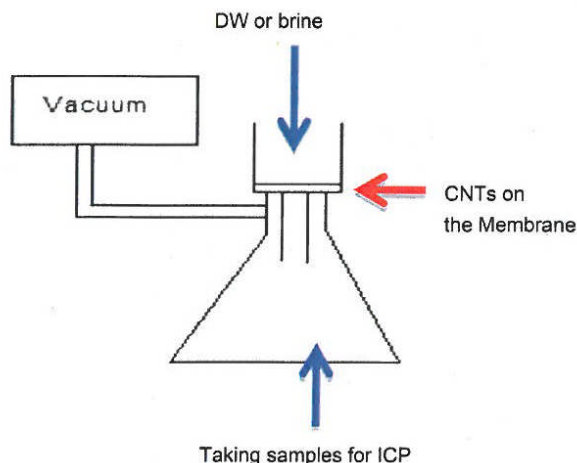


Figure 7-Schematic representation of desorption set-up

Simplified standard coreflood test without addition of CNTs was also performed to compare the results, which the procedure is as follow:

- i. 10 PV of PPCA and DW solution was injected into the core and samples were taken from the effluent for ICP to quantify the output concentrations.
- ii. The core was shut for 24h to enable PPCA to be adsorbed by the rock.
- ii. Background solution (DW here) was pumped into the core and samples were taken for ICP at desired times.

## Results

The main objective of this work is to develop the new methodology and demonstrate the potential feasibility of NAST for enhanced squeeze lifetime. Hence, the preliminary experiments for the attachment of CNTs on the crystal quartz surface and adsorption/desorption test of PPCA on/from the CNTs were conducted followed by simplified coreflood tests to show the feasibility of the NAST.

## Result of NAST1

Figure 8 shows by FEG-SEM the attachment of CNTs on the crystal quartz surface. CNTs uniformly attached on the quartz surface. It can be seen that CNTs were attached on the quartz surface and covered most of the surface. Figure 8 also shows that even with good dispersion of CNTs in solution there can still exist some agglomerated CNTs on the surface. It is not possible to get perfect coverage, but it can be accepted that most of the surface area of the quartz is covered by a single layer of CNTs. This preliminary result demonstrates that the first stage of the NAST (NAST1) is practical to achieve.

## Results of NAST2

A basic adsorption test was performed and the results were compared with experiments in sand. A solution of PPCA in DW (1000 ppm PPCA in 50 ml DW) was prepared for adsorption of PPCA on CNTs and sand. DW was used to eliminate the effects of ions existing in formation water on adsorption process to be able to interpret the adsorption of SI on CNTs without interference of any ions. Solutions were stirred for 24 hrs. The ICP results illustrate that CNTs are able to absorb significantly more PPCA compared to silica and North Sea sand. Silica has been used, as it is the main component of the reservoir rock. Given that surface area is a key factor in quantifying adsorption, the amount of CNTs used for the experiments was chosen to have the same surface area as the silica, which is 300 mg of CNTs. The comparison results are presented in Figure 9.

Concentrations of PPCA were normalized to the concentration of SI before starting the experiment (control). The first column in Figure 9 is named 'control' as it shows the concentration of PPCA in the solution before starting the experiment. In addition, the second column is the concentration of PPCA left in the solution after the experiments were stirred for 24 hrs. The concentration of PPCA in the solution after 24hrs for the silica sand and rock did not change after finishing the experiment. The lack of adsorption of PPCA on silica sand is due to low affinity of silica/rock to PPCA and less adsorption site on silica/rock. No clay minerals and cations were present in these experiments. However, it was demonstrated that presence of  $Ca^{2+}$  plays an important role in adsorption of SI on rock [79]. In addition, kaolinite has been shown to facilitate adsorption of inhibitors onto the rock [80]. It is concluded that PPCA does not have a tendency to react with silica in DW, but on the other hand it has a propensity to bond with CNTs. This was encouraging, since strong adsorption of PPCA on CNTs is one of the core requirements for the NAST process to be feasible. These preliminary results therefore showed the potential for CNTs to be employed in squeeze implementation. The adsorption tests were also performed in the basic brine solutions to study the behaviour of the PPCA on the CNTs in the brine. The brine compositions are shown in Table 1.

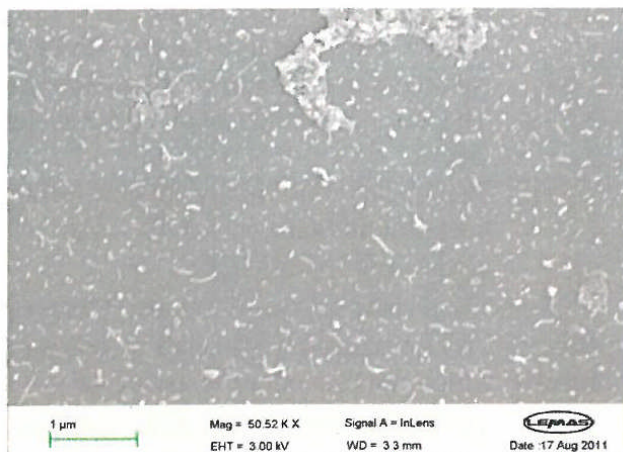


Figure 8-Sticking CNTs on the crystal quartz surface

The results are shown in Figure 10. Adsorption of PPCA on CNTs in various brines was compared with on the rock. Simple brine compositions were chosen to remove the influence of other ions in the real brine in order to make the results easier to interpret in the early stages of NAST. Figure 10 shows that the adsorption of PPCA on the CNTs is much higher than on rock even in the high salinity solution (second column) without calcium. On the other hand, adsorption of PPCA on the CNTs in the solution with calcium is more than 160 mg per gram of CNTs, which is much higher than 1 mg/g for rock in a brine solution [81]. Adsorption tests will be carried out in more complex brine solution close to a representative formation water composition in order to understand the effects of ions together on adsorption; this is the subject of future work as the second phase of NAST development.

### **Results of desorption**

Adsorption of scale inhibitors on CNTs has been demonstrated. The desorption of PPCA from the CNTs was as crucial as adsorption, since the SIs needed to be released to inhibit scale formation. Therefore desorption tests were carried out to determine the desorption behaviour of scale inhibitor (PPCA). Figure 11 illustrates the amount of PPCA which was desorbed from the CNTs after the second and third time of pouring the background solution into the vacuum filter. Prior to that, CNTs were rinsed once with DW in order to remove the loose or non-functionalised PPCA on the surface of CNTs. The '1st pouring' and '2nd pouring' in the Figure 11 represents the first and second time adding background solution into the vacuum after rinsing once, respectively.

Although Figure 11 does not show a large amount of desorption, it indicates that the desorption rate of PPCA from the surface of CNTs was significant with respect to the flow rate (higher flow rate compared with designed in coreflood tests). Moreover, the tests were performed at room temperature and higher desorption rates would be achieved at elevated temperature. This behaviour suggested that adsorption of PPCA on CNTs may be covalent but further investigation such as Raman spectroscopy was required to support this hypothesis, which can be a subject of future work.

### **Coreflood results**

In terms of assessing the feasibility of the entire NAST process to enhance squeeze lifetime in a real reservoir, it is important to try to represent flow in the reservoir in a much more realistic way using a coreflood test. The entire NAST procedure was applied step by step, and results are compared with baseline corefloods using a current standard procedure [80] in which no CNTs were used. Figure 12 illustrates the SI concentration at outlet of cores for standard and NAST coreflood tests. It is observed from Figure 12 that the effluent concentration of the standard coreflood without applying CNTs is higher at the beginning of the post-flush, which indicates losing SI quicker compared with the NAST.

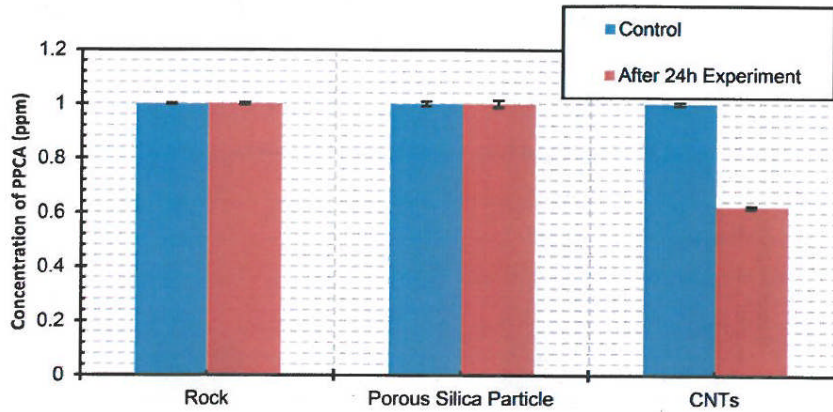


Figure 9-Adsorption of PPCA on CNTs and two different sands

Table 1-Brines compositions

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

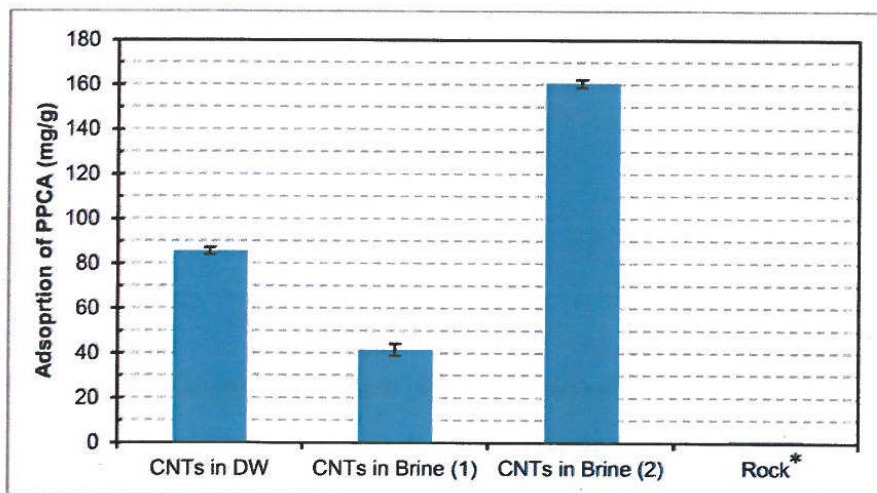


Figure 10-Comparison results of adsorption of PPCA on CNTs in different solutions. \*The adsorption of PPCA on rock was taken from Jordan et al [81]

In order to understand the behaviour of PPCA in the NAST coreflood, the amount of PPCA remaining in the core at every PV as a function of PV was plotted. A schematic representation of coreflood results represented in the return curve is shown in Figure 13. The graph shows the effluent concentration of SI as a function of pore volume (PV) fluid injected. The red and blue curves represent the concentration of SI during main injection of SI into the core and post-flush, respectively, at every PV. The vertical green line is the line separation which indicates where post-flush was started and the horizontal one shows the concentration of SI during main treatment. Squeeze treatment or a coreflood test is run until the effluent concentration reaches MIC. Interesting results can be extracted from the return curve; mass of SI remaining in the core can be evaluated. Hence, the area below the green line represents the total mass of SI injected in the core and the area below the red and blue curves indicates the mass ejected during the main treatment and mass ejected during post-flush, respectively. Therefore, the mass of SI remaining in core

at each PV can be obtained by subtracting the mass ejected from mass injected.

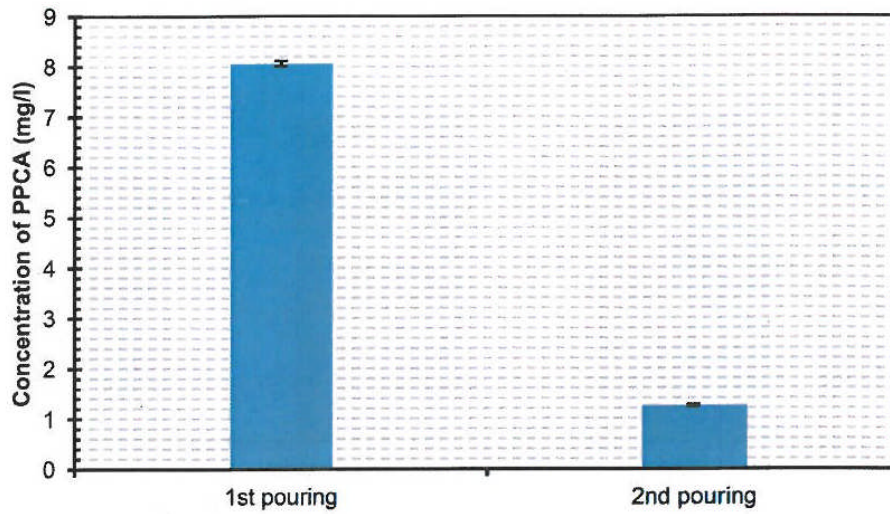


Figure 11-Desorption of PPCA from PPCA-CNTs by desorption test

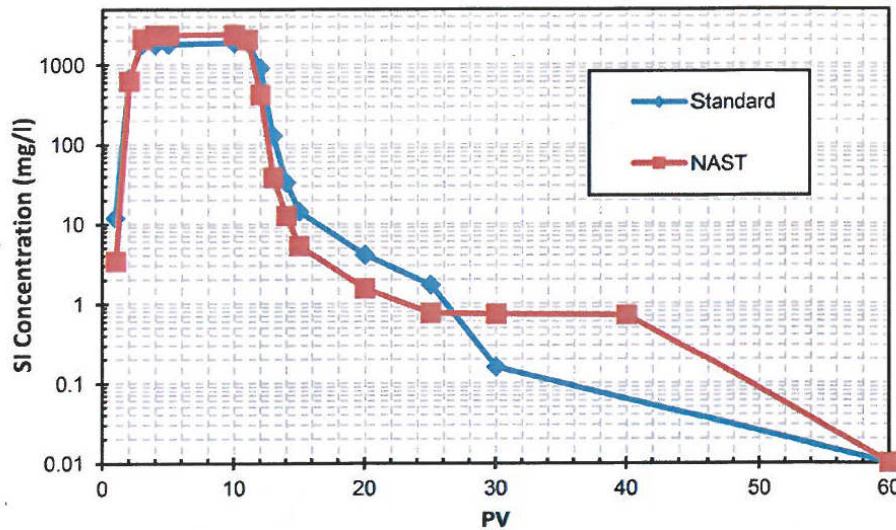


Figure 12 – Effluent SI Concentration return curve, comparison results of standard and NAST coreflows as a function of PV

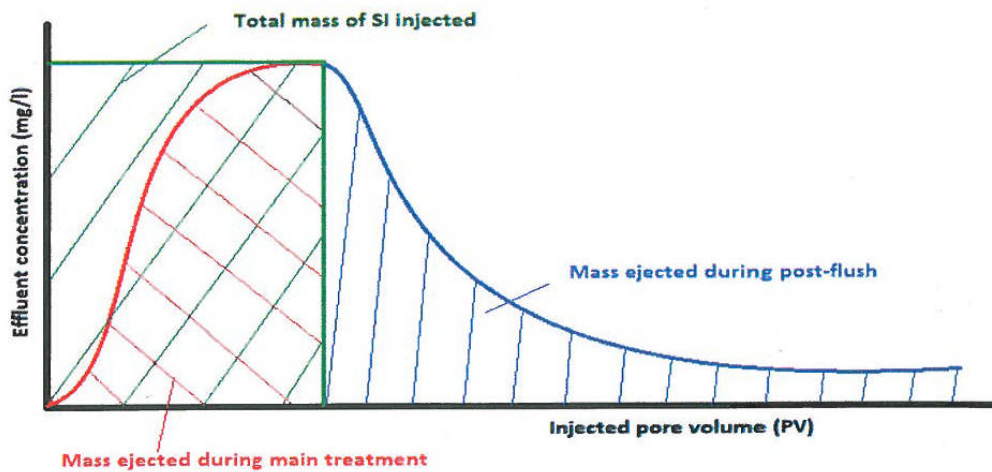


Figure 13-Schematic of return curve of effluent concentration of coreflood tests

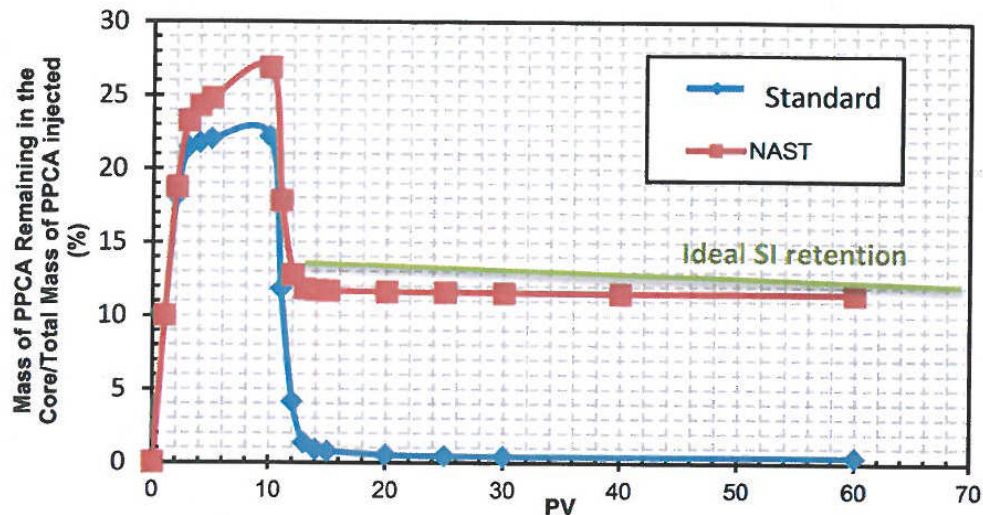


Figure 14-Mass of PPCA remaining in the standard and NAST corefloods as a function of PV; green line shows the ideal retention

The data presented in Figure 13 enabled the mass of PPCA remaining in the core to be calculated. Figure 14 plots the mass of PPCA remaining in the standard and the NAST corefloods over the total mass of PPCA injected as a function of PV. Higher retention and adsorption rate and slower release by the NAST from Figure 14 can be observed for PPCA injection and post-flush, respectively. However, very low desorption - below MIC - is an issue for the NAST in these experiments, but it may be solved by experimenting with more reservoir-like conditions (coreflood tests were carried out at room temperature). This can be the subject of future work. The ideal retention from the NAST and generally squeeze treatment would be to have SI desorbed just above MIC (The ideal retention is shown in Figure 14 by the green line).

It was shown above in the adsorption tests, that CNTs dramatically increased the adsorption of PPCA which indicated the main controlling factor was CNTs in the NAST coreflood tests. In addition, the objective was to compare the NAST coreflood results with a representative standard coreflood test. However, effects of ethanol, DMF and DCC can be easily neglected due to washing process at different stages in the NAST coreflood experiments. The only remaining chemical that could affect the results was aminosilane of which the influence was previously studied [10, 11]. However these studies cannot be compared due to different experimental conditions. This is the subject of future work to investigate the effect on aminosilane on NAST coreflood results.

### Conclusion and summary

A new methodology was introduced and developed in this work. An extensive literature was presented in which the properties of nano-materials for enhanced squeeze treatment were assessed. A detailed methodology was introduced in this work in order to apply CNTs to the current squeeze treatment to increase squeeze lifetime. Attachment of CNTs on the quartz was achieved by dispersing CNTs in DMF and with help of DCC as a cross-linker. Simple static adsorption tests were performed to evaluate the adsorption of PPCA (SI) on the CNTs. The preliminary results of NAST1 and NAST2 are promising. Although these results were achieved in simplified conditions, the potential benefits of the NAST methodology are the following:

- i. Scale inhibitor adsorption and retention is dramatically increased at the experiment conditions of this work (in DW solution at ambient temperature).
- ii. Slower desorption with the NAST would result in longer squeeze lifetime.
- iii. The modification of the near wellbore with CNTs is a one-off treatment. However, the CNTs should still be available for re-treatment with SI due to strong covalent reaction between CNTs and aminosilane.

The feasibility of a nanotechnology-assisted squeeze treatment has been demonstrated in this work. Preliminary results are encouraging, but there are several areas where the methodology needs to be optimised for the industrial use such as desorption process, dispersion of CNTs and effect of temperature on amount and rate of adsorption/desorption of SI.

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